

NOTE TO USERS

This reproduction is the best copy available.

UMI[®]

**EFFECT OF COMBINED PRESSURE AND
CONCENTRATION GRADIENTS ON GASEOUS FLOW
THROUGH SOILS**

by

Daniel Donald Evans

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

Major Subject: Soil Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

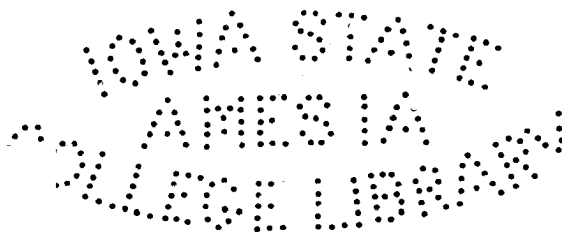
Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1952



UMI Number: DP13204

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform DP13204

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

TABLE OF CONTENTS

INTRODUCTION	1
REVIEW OF THE LITERATURE	3
Types of Gaseous Flow	3
Mass flow.	3
Mass flow through capillaries	3
Normal gas-dynamic flow.	4
Viscous slip flow.	4
Free molecular flow.	5
Transition zone flow	5
Mass flow through porous media.	6
Diffusion.	10
Diffusion coefficient	10
Diffusion through porous media.	13
Contributing Factors in Soil Air Renewal.	16
THE PROBLEM.	18
EXPERIMENTAL AND THEORETICAL RESULTS	20
Validity of Darcy's Law at Low Pressure Differentials	20
Differential and Functional Equations	27
Derivation of differential equation of flow.	27
Functional relationship between pressure and concentration.	28
Auxiliary differential equation.	30
Flow Through a Tube	33
Absorber at one end of tube.	35
Volatile liquid at one end of tube	39
Variable viscosity along tube.	41
Experimental Verification of Flow Equation.	46
Flow Rates of Carbon Dioxide and Oxygen, and Pressure Increase in a Soil Respiration Problem.	52

Effect of Changes in Barometric Pressure on the Flow Rate of Carbon Dioxide in Soil	60
DISCUSSION.	68
SUMMARY AND CONCLUSIONS	74
LITERATURE CITED.	77
ACKNOWLEDGMENTS	80

INTRODUCTION

Soil aeration is a principal factor influencing the growth of plants in soil. Oxygen movement into the soil and the removal of carbon dioxide from the soil take place as long as aerobic respiration occurs. The rate of consumption or liberation and the rates of movement of these two gases have a large effect upon the activity of microorganisms and consequently upon the availability of nutrients essential for plant growth. The uptake of nutrients by plants is also influenced by the aeration status of the soil because root respiration depends on aeration conditions. But the biological aspects of soil aeration will not be dealt with here. Only the purely physical aspect of soil aeration will be considered.

The principal gases of concern in soil aeration are air, oxygen, nitrogen and carbon dioxide. Diffusion is thought to be the most important process moving these gases through the soil. But in certain cases mass flow may be important. For example, because of the slower diffusion rate of carbon dioxide compared to oxygen, one should expect a slight build-up of pressure in the soil when, in the steady state, one molecule of carbon dioxide is liberated for every molecule of oxygen used. Anaerobic respiration would tend to accentuate this pressure difference.

The barometric pressure is always changing about some mean value. Since the soil offers resistance to the flow of gases, the pressure below the surface will lag behind the pressure at the surface. There will thus be set up a pressure differential, with attendant mass flow into or out of the soil, depending upon which way the barometric pressure is changing.

The diffusion coefficient of a soil is sometimes obtained by allowing the vapor of some liquid to diffuse through the soil. In another method an absorber is utilized which removes one component of the air. In both of these cases a total pressure gradient is established and the diffusion coefficient obtained is in error because mass flow has not been taken into account. Since these methods employ rather simple techniques, ways of computing the true diffusion coefficient by these techniques would be desirable. Errors introduced by neglecting mass flow should be studied and evaluated.

REVIEW OF THE LITERATURE

There have been several recent treatises on the effect of soil aeration on plant growth (26, 29, 33, 35). The subject is covered thoroughly in these treatises and need not be included here. In the present review of the literature types of gaseous movement in porous media will be considered independently of biological effects.

Types of Gaseous Flow

For present purposes, gas flow may be considered of two types. One of these, generally called mass flow, occurs when there is a difference in total pressure between points in the medium. The other, generally called diffusion, occurs when there is a partial pressure gradient of one component of a gaseous mixture and when there is uniform total pressure throughout. These two types of flow will be considered separately.

Mass flow

Mass flow through capillaries. Since the pores in a porous medium are sometimes considered as a bundle of capillaries with some effective radius, it is well to start with flow through a single capillary. When the kinetic theory of gases is used, flow through capillaries can be treated theoretically and checked experimentally with not too much difficulty.

There has been extensive work done during the past century on the flow of fluids through capillaries. Much has been written on the subject and reference can be made to several treatises (1, 2, 22) for a review of the subject. Wilson et al. (38), in a recent article, reviewed the

four distinct types of flow due to a total pressure gradient. They are: (a) normal gas-dynamic flow, (b) viscous slip flow, (c) free molecular flow, and (d) transition zone flow. These four types of flow will now be discussed. It will appear that the determining factor for a type of flow is the ratio of the mean free path λ of the molecules of gas to the diameter d of the capillary.

Normal gas-dynamic flow. When λ/d is small, that is, when the diameter of the capillary is large compared to the mean free path, normal gas-dynamic flow will occur. This type of flow obeys Poiseuille's law. Here the volumetric rate of flow \dot{V} (using Wilson's notation) in terms of the radius of the tube r , the length of the tube L , the viscosity of the gas u , and the pressure p , is given by

$$\dot{V} = \pi r^4 (p_1 - p_2) / 8Lu . \quad [1]$$

In the derivation of equation [1] it is assumed that the velocity at the wall of the tube is zero, also, that the velocity profile is the same at any point along the tube, and that u is a constant. This type of flow is also known as viscous flow or laminar flow. Note that in equation [1] the symbol u is used instead of the conventional symbols. Throughout this thesis u will be used for ease in typing.

Viscous slip flow. It is observed in flow through tubes at relatively low pressures (compared to one atmosphere) that u is no longer constant but depends on the pressure. This type of flow is called viscous slip flow and the phenomenon is believed to be due to the fact that the velocity at the wall is not zero but some finite value. Millikan (23) showed that when very small droplets of oil fall through air a certain correction must be made for the "mean free path effect". He explained

this effect in terms of the thermal agitation of the molecules at the surface of the drop. The surface of zero velocity becomes effectively one mean free path within the droplet. This is the same effect that occurs for the flow of gas through a stationary tube. Thus the effective radius of the tube is $r + \lambda$ instead of the actual r , and tends to increase the amount of flow taking place over the expected amount calculated by equation [1].

Free molecular flow. If conditions are such that collisions of the molecules with each other are rare compared to collisions of the molecules against the wall of the tube, the flow becomes independent of the viscosity of the gas and is called free molecular flow. This type of flow is inversely proportional to the pressure and occurs at low pressures where λ is large, or where the diameter of the tube is very small. Free molecular flow obeys the same laws as diffusion since it depends on the concentration gradient of the molecules and is independent of the viscosity. Each gaseous component flows independently of all others and at a rate determined by its molecular weight and partial pressures. This type of flow is also known as molecular streaming or Knudsen flow because Knudsen was the first to study it in 1909 (see Carmen (8)).

Transition zone flow. There is obviously a transition zone between free molecular flow and normal gas-dynamic flow. No theoretical treatment which is completely satisfactory has been given for this type of flow but progress has been made by Brown et al. (6) and Carmen (8). Wilson et al. (38) stated as a rough approximation, that for flow through tubes, if $\lambda/r < 1/100$, then normal viscous flow predominates; while if $\lambda/r > 1$, then free molecular flow is predominant.

Mass flow through porous media. The study of flow through porous media is much more recent than that for capillaries. But since some of the soil voids are capillaries, ideas developed with regard to capillary flow will apply in a certain sense to soils. Nevertheless, the capillary attack has been generally disregarded in the flow problem for porous media. D'Arcy is generally given credit for the first important work. On a purely empirical basis he found in the study of water flowing through filter beds, that the quantity of water passing through the bed was directly proportional to the cross sectional area of the bed and to the driving head of water and inversely proportional to the length of flow through the bed. The law implied by D'Arcy's work is commonly called Darcy's law. It is commonly expressed in differential form for one dimensional flow by

$$v = - Kgh/dx . \quad [2]$$

In this expression, v is the volume of water per unit of time passing unit cross-section taken perpendicular to the x direction, K is the permeability of the medium, and dh/dx is the space rate of change of hydraulic head. The validity of the law breaks down at high velocities because of turbulence (24). The minus sign is used in equation [2] because the flow occurs in the direction of decreasing hydraulic head.

Darcy's law has been found to be valid for gaseous flow through porous media provided h in equation [2] is replaced by the pressure p and K is replaced by k/u where k is the gas permeability and u its viscosity (25). In the case of gas flow v can no longer be taken as constant along a tube of flow because of the compressibility property of gases. Instead, v will vary inversely with the pressure. But equation [2] can be

integrated if (after h has been replaced by p) both sides of the equation are multiplied by p . The integration is then simple because the resulting equation has pv on the left hand side; and pv is a constant for an ideal gas. Kirkham (20) goes further and derives Laplace's equation for pressures near atmospheric and when gage pressures are used. The derivation is of great usefulness in that solutions for heat, electricity, and liquid flow problems that have been solved, and of which there are many, can now be used for any similar problems arising in gaseous flow. The error involved will be less than 2.5 per cent if a gage pressure of less than 50 cm of water is used and if the absolute pressure is about one standard atmosphere.

Darcy's law is valid also over a greater pressure range than zero to 50 cm of water on either side of 1 atmosphere pressure. But mathematical difficulties enter into the problem if one considers the extended range. The upper range of validity is discussed by Muskat and Botset (25). It is a function of the size of the pores and the magnitude of dp/dx . Muskat and Botset found in all cases for the flow of gases through sand, that the gradient of the square of the pressure ∇p^2 is proportional to a power of the mass velocity. They gave the general law for the flow of a gas through a porous sand in the form

$$\nabla p^2 = k(\rho v)^n$$

where ρ is the density of the gas, and v is velocity of the gas; k is the permeability constant of the sand, and n is a constant depending on the type of flow. The value of n was found to be between 1 and 2 corresponding respectively to completely viscous and completely turbulent flow.

Even for small pressure differentials from atmospheric pressure Darcy's law may break down for gas flow. If the law is strictly valid, the permeability coefficient k should be the same regardless of what gas or fluid is employed since k is presumably a parameter of the porous medium only. Muskat (24) presents a table of permeabilities for coarse sand as obtained by use of water and air as fluids. The values compare favorably. However, Muskat (24) also gives a table of values of the water and air permeability of a number of oil sands as measured by Fancher, Lewis, and Barnes. The table shows large discrepancies. Most values found for water were lower than for air. Klinkenberg (21) has presented an explanation for the discrepancies. He has attributed the effect to slip, the same phenomenon which has been discussed in this review. He has proposed a relationship to resolve difficulties. It is

$$k_a = k_1(1 + b/P_m) .$$

Here k_a is the apparent permeability as ordinarily determined from Darcy's law at any mean pressure P_m , k_1 is the true permeability, and b is a constant. To obtain k_1 , Klinkenberg measured k_a for several values of P_m , then plotted k_a against $1/P_m$ and extrapolated the curve to $P_m = \infty$ to yield the true permeability from the intercept. The permeabilities obtained in this manner checked the ones obtained by the use of water.

The lower the true permeability k_1 , the more important is the effect of slip. Klinkenberg gives the following errors based on experimental data for the case that $P_m = 1$ atmosphere. For $k_a = 10$ millidarcys, error = 25 per cent; $k_a = 25$ md, error = 17 per cent; $k_a = 100$ md, error = 11 per cent; and for $k_a = 1000$ md, error = 5 per cent. Due to the large sampling error and variability in natural porous material this error can be

neglected in many studies, especially when the permeability is larger than one darcy. In soils the permeability is generally greater than 1 darcy.

Wilson et al. (38) found through experimental work that viscous flow will exist in a porous medium if the ratio of the mean free path to pore diameter is less than 0.025. Free molecular flow will take place if the ratio is greater than 1.6. Between these two, transition flow occurs where slip is important.

To account for this slip factor, a correction term, derived by Ridgen (32) is generally applied to equation [2].

There has been some discussion as to whether the permeability of a porous medium depends upon the pressure differential. Grunberg and Nissan (15) reported, contrary to Klinkenberg's results, that air permeability is a function of the ratios P_m^2/Q_a^2 and $P_m \Delta P/Q_a^2$, where ΔP is the pressure difference across the tube, Q_a is the volumetric rate of air flow measured at atmospheric pressure, and P_m is the mean pressure along the tube. Yuster (39) reported results which verify Klinkenberg's findings. Yuster stated that Grunberg and Nissan's data was very limited as to the number of readings and also their technique required P_m to change with ΔP which throws doubt upon their analysis.

Evans and Kirkham (13) misquoted Klinkenberg on the subject of the validity of Darcy's law at small pressure differentials. It was reported that Klinkenberg found that Darcy's law is not valid at low pressure differentials when these are referred to atmospheric pressure. It was thought that Klinkenberg was referring to gage pressures when he meant absolute pressure. He was correct in the conclusion that the permeability

is a function of the absolute pressure. There are several references (13, 20, 21, 39) which show that the permeability is independent of the pressure differential over a wide range.

Diffusion

Diffusion coefficient. In an article on diffusion processes, Jacobs (17) credits Fick with the present theoretical treatment of diffusion. Fick found that the rate of diffusion across any plane at right angles to the direction of diffusion is directly proportional to the concentration gradient across the plane in question. This relationship has become known as Fick's law. Expressed in mathematical terms it may be written

$$\partial Q/\partial t = - DA\partial v/\partial x$$

where $\partial Q/\partial t$ is the rate of change of quantity of gas with time, $\partial v/\partial x$ is the concentration gradient, A is the cross-sectional area perpendicular to flow, and K is a proportionality constant generally called the diffusion coefficient. The coefficient D represents the amount of material that in unit time and with unit concentration gradient would cross a plane of unit cross-section at right angles to the direction of flow. The minus sign is used because the flow occurs in the direction of decreasing concentration.

Much work has been done on the theoretical aspects of the diffusion coefficient. It is a function of certain properties of the diffusing molecules and is measurable. It is a useful tool in obtaining various properties of the molecules.

Diffusion, along with viscosity and thermal conductivity, is transport phenomenon. Diffusion is associated with the transfer of mass,

viscosity with the transfer of momentum, and thermal conductivity with the transfer of kinetic energy. The elementary theories of these three phenomena are all similar for gases. The theories are all based on mean free paths and mean velocity; and it should be expected therefore, which is true, that they would not check experimental results closely. The simple theory fails to agree with experimental results especially in the case of diffusion (18).

An expression for the diffusion coefficient can be obtained from the simple theory for the case that the molecules of the gases involved are of about the same molecular weight. Such an expression was obtained by Meyer in 1899 whose work is discussed by Jeans (18). Meyer's result for the diffusion coefficient D_{12} of gas 1 diffusing into gas 2, according to Jeans, is

$$D_{12} = (v_1 \lambda_2 c_2 + v_2 \lambda_1 c_1) / 3(v_1 + v_2) \quad [3]$$

where v is the concentration, λ is the mean free path, and c is the mean velocity. Equation [3] shows a strong dependence of D_{12} upon the ratio of the concentration both because the concentration itself appears and also because λ is a function of the ratio of the concentrations.

Experimental results show a much weaker dependence of D_{12} upon the ratio of the concentrations than predicted by equation [3]. But several refinements have been made in the theory and the theoretical results have been brought thereby in close agreement with the experimental. For example, when Meyer's theory is corrected for persistence of velocity, a much closer agreement with observed values is obtained. The Stefan-Maxwell theory (18), which considers only the collisions of unlike molecules as important (since collisions of like molecules do not change the

momentum of the two molecules in the forward direction), shows no dependence whatsoever upon the ratio of the concentration. But at best, all theories mentioned so far are approximate since they consider the molecules as elastic spheres.

When molecules are treated as point centers of force which repel each other, then theoretical results developed by Chapman and Enskog give good agreement with observed values (18). Table 1 taken from Jeans (18)

Table 1

Observed and Theoretical Value of D_{12}
for Two Pairs of Gases.^a

Pair of Gases 1, 2 respectively	$\frac{v_1}{v_2}$	D_{12} (observed)	Observer	D_{12} (calculated) (Chapman)
$H_2 - CO_2$	3	0.21351	Deutsch	0.212
	1	0.21774	Deutsch	0.222
	1/3	0.22772	Deutsch	0.226
He - A	2.65	0.24418	Lonius	0.248
	2.26	0.24965	Lonius	0.250
	1.66	0.25040	Schmidt	0.251
	1	0.25405	Schmidt	0.254
	0.477	0.25626	Lonius	0.257
	0.311	0.26312	Lonius	0.259

^aSource, Jeans (18, p 213)

shows the variation with concentration D_{12} for hydrogen into carbon dioxide and helium into argon. Both the experimental values and values calculated using the theory of Chapman and Enskog are given.

From equation [3], D_{12} is seen to be a function of the mean free path and the mean velocity of the molecules. These in turn are functions of the temperature and pressure (22). The mean free path of the molecules is proportional to the absolute temperature and inversely proportional to the pressure. The mean velocity is, however, proportional to the square root of the temperature and independent of the pressure. Therefore, theory predicts that the diffusion coefficient varies as the $3/2$ power of the absolute temperature and inversely as the pressure because λ and c appear as products in both terms of the numerator.

Loeb (22) states that at pressures near atmospheric and temperatures near room temperature, experimental results show that D_{12} varies inversely with the pressure and as a power of the absolute temperature between 1.75 and 2. Loeb's discussion thus points out clearly wherein Meyer's theory has failed.

Diffusion through porous media. Fick's law also applies to diffusion through a porous medium (7). The diffusion coefficient will depend upon the temperature, pressure, concentration, and type of gaseous mixture through which diffusion is taking place. Also it will depend upon the size and distribution of the open spaces in the porous medium. Diffusion through porous media is of interest in many fields of study and the diffusion coefficient has been measured for a number of porous materials and several gases.

Buckingham (7) carried on experiments where he measured the diffusion coefficient of carbon dioxide for a thin layer of soil. He took great care to control the total pressure so that it would be uniform throughout his system but it is still doubtful whether he achieved his purpose as has been shown by Van Bavel (37). The calculations of Van Bavel show that even if the total pressure difference is less than that measurable by Buckingham, the error is sizeable. Diffusion is a relatively slow process and therefore only a very small total pressure difference across a porous sample causes a comparatively large flow of gas to occur.

Hagen (16) was interested in the movement of carbon disulfide, a soil fumigant, through soil. He sealed a source of carbon disulfide to one end of a column of soil and employed an air sweep at the other end to carry any vapor that diffused through the soil to an analyzer. There are two possible sources of error in this technique. Besides the chance of a nonuniform total pressure arising as a consequence of the air sweeping, it is theoretically not correct to assume a uniform pressure throughout a column of porous material when there is a volatile liquid source at one end. There will be inherently a pressure differential existing. This point will become clear in a later part of this thesis.

Penman (27, 28) used both carbon dioxide and carbon disulfide to measure the diffusion coefficient for soil. In the case of the carbon dioxide, he employed an air stream with a known partial pressure of the carbon dioxide at one end of the column of soil; and, another air stream, free of carbon dioxide, at the other end of the column. It is obvious that this technique may give erroneous results due to total pressure

differences. In the case of carbon disulfide he sealed a container of the carbon disulfide liquid to one end of a column of soil and allowed diffusion to occur. After a given time he weighed the container to find the amount of carbon disulfide lost. His technique here appears free of criticism except for the pressure gradient discussed above for a volatile liquid.

Blake and Page (14) conducted experiments in the field with buried sources of carbon disulfide. They did not attempt to solve the problem to determine the diffusion coefficient of the soil but merely made comparative measurements.

Taylor (36) and Raney (30) have developed methods of measuring the diffusion coefficient of soil that seem theoretically sound. Their techniques require the interdiffusion of nitrogen and oxygen. Since these two gases have nearly the same rates of diffusion, one would expect a fairly uniform total pressure throughout. Their methods also have the advantage that gases are used which are of interest in soil aeration studies. It is felt that Raney's field method requires improvement in regard to the manner of preparing the soil for measurement. With the present procedure there is doubt as to the existence of an undisturbed condition of the soil in the region of measurement.

Van Bavel (37), in a recent article, applied a correction in a special case for the mass flow attendant with diffusion. He did not consider the general problem of mass and diffusion flow nor did he take into account the differences in diffusion coefficients between the gaseous components.

Contributing Factors in Soil Air Renewal

Several factors aside from diffusion have been considered as of possible importance in renewing the soil atmosphere with atmospheric air. Temperature, barometric pressure, rainfall and wind will be briefly discussed.

Changes in the soil temperature cause an increase or decrease in the density of the gaseous phase of the soil. Therefore, if the temperature of the soil increases there results a decrease in the density; and, consequently, mass flow will occur out of the soil. Conversely, decreases in soil temperature will cause mass flow to take place into the soil. Rommel, as quoted by Keen (19), investigated this effect of temperature on gaseous interchange and found it to be insignificant. Rommel's calculations showed that temperature fluctuations could be responsible for less than one per cent of the gaseous interchange for normal plant growth.

Buckingham (7) discussed the importance of barometric pressure changes as a factor influencing the flow of air into and out of the soil and found the flushing effect of such changes to be of little significance. The mean amplitude of the diurnal fluctuations in barometric pressure is about 0.1 cm of mercury. Using this value in application to a uniform soil of 4 feet depth, Buckingham computed that the resulting compression of the soil atmosphere would be such as to allow air from the atmosphere to penetrate to a depth in the soil of only 0.6 inches. Obviously, this effect is small.

Russell (34) discussed the effect of blowing of wind over the surface of the soil as it might influence gaseous interchange. He concluded

that with the type of rough soil surface usually found, and in the presence of vegetation, the effect would be negligible.

Russell discussed also the importance of rainfall in its effect upon gaseous interchange and concluded that its effect is small.

It has been concluded (4, 7, 27, 30, 34, 35) that mass flow of gases is of little importance in the renewal of soil air. The main process has been stated to be diffusion.

THE PROBLEM

It is generally believed, as has been indicated, that diffusion is the major process which renews the gaseous phase of soils with gas from the atmosphere; flow due to a total pressure gradient has been considered unimportant. But difficulties which are encountered when a measurement of the diffusion coefficient is attempted lead one to believe that the diffusion coefficient may be influenced appreciably by a total pressure nonuniformity in the flow medium. Furthermore, such a nonuniformity seems impossible of elimination when studying diffusion processes in the steady state; and it is the steady state with which one deals primarily. It appears, therefore, that what investigators have designated as diffusion flow might really have been in many cases partly mass flow. Measured diffusion coefficients may have been in error.

Total pressure gradients which may interact with diffusion processes in soils may arise from several causes. One cause which should be examined, since it is always present, has been noted to be a changing barometric pressure. Changes in barometric pressure may amount to only a few millimeters of mercury; but, since diffusion transport is small, pressure changes of even a small magnitude may have an appreciable effect on diffusion flow in the soil. Also problems associated with the use of gases, which do not occur in the soil, for measuring diffusion coefficients should be examined. In fact it seems that the whole problem of combined flow due to total and partial pressure gradients of gases in soil deserves attention. The first problem which should be attacked should be the differential equation of flow. The differential equation (s) should be

set up and then integrated -- and that is the main problem of this thesis.

Although the principal emphasis here has been intended to be on the theoretical side, some experimental work has been done. In particular the validity of Darcy's law at low pressure differentials was examined experimentally. This law, together with Fick's law which has been well established, is basic in the theory.

EXPERIMENTAL AND THEORETICAL RESULTS

Validity of Darcy's Law at Low Pressure Differentials

Darcy's law has been shown to be applicable to gas flow through porous media for pressure differentials ranging from a few millimeters of water to about 50 cm of water (13, 20, 39). The test samples have been of length up to about 30 cm and the reference pressure has been 1 atmosphere. At pressure differentials lower than a few millimeters of water "the proportionality constant" could not be measured because of experimental error inherent in the equipment used.

Since in the diffusion problem pressure differentials of much less than one millimeter of water are important, it was decided to test Darcy's law at smaller pressure differentials than those heretofore considered. Quite different apparatus than that previously used was designed. The experimental arrangement finally used is shown in Figure 1. Nitrogen was allowed to escape from a nitrogen tank at a slow uniform rate into a length of glass tubing, 16 mm outside diameter and 14 mm inside diameter, filled with sized sand to a length of 10 cm. Sand was used as porous medium since sand can be sized and packed more uniformly than soil in general. After passing through the sand the gas entered a calibrated glass capillary tube of 3 mm inside diameter. There was a bubble of water in the capillary tube and, as flow took place, this bubble moved along the tube against atmospheric pressure. The amount of displacement of the bubble per unit time was a measure of the flow rate.

Sticking of the water bubble in the capillary tube was prevented by coating the tube with a commercial product called Dessicote. This

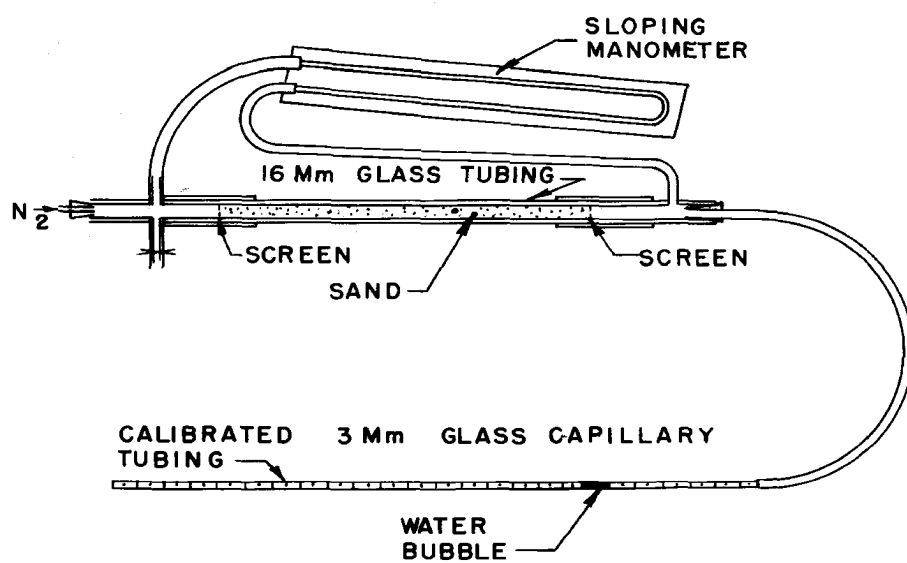


Figure 1. Apparatus for measuring air permeability at low pressure differentials.

product, a silicone (14), was supplied by the Beckman Instrument Corporation. Use of Dessicote not only prevented sticking of the bubble but also water-proofed the glass. Loss of water droplets was prevented and a film of water did not form on the glass behind the bubble. The accuracy of measurements was thus increased. Dessicote was not used for the manometer, nor is such use recommended by the supplier of the product.

The pressure differential across the porous medium was measured with a sloping manometer in which ethyl alcohol was used as fluid. The slope of the manometer was approximately 1/43. Pressure differences as low as 0.018 mm of water could be measured across the sample. A pressure difference of 0.018 mm across the sample corresponded to a gradient of 0.00018 mm of water per mm of sand.

The permeability k was calculated from observed values using the formula

$$k = Ql\mu / At\Delta P, \quad [4]$$

where Q is the quantity of nitrogen passing through the porous medium in time t , l and A are the length and cross-sectional area of the tube respectively, μ is the viscosity of the gas and ΔP is the pressure differential across the porous material. If, in equation [4], Q is expressed in cm^3 , l in cm , A in cm^2 , μ in centipoise, ΔP in atmospheres, and t in seconds, then k will be in units of darcys. If all quantities are in cgs units, then k has units of cm^2 . Use of cgs units has recently been recommended (31), but the darcy will be employed here since the latter unit was in common use when this study was started.

Figure 2 shows typical curves obtained in checking Darcy's law at low pressure differentials. The reciprocal of the time for the bubble to move along the calibrated tube through a volume of 0.85 cm^3 , corresponding to about 12 cm of capillary tubing was taken as a measure of Q . This reciprocal time is plotted in the figure against the differential pressure which operates across the ends of the porous medium. Curves for three different grades of sand are shown. In each case it appears that the linear relationship exists which is required for the validation of Darcy's law. In addition, the extrapolated curves pass through the origin; they thus indicate that the law holds down to zero pressure differentials.

The curves of Figure 2 are all for pressure differences of less than 0.4 mm of water and are for nitrogen. In order to see whether the same results would be obtained for the higher pressure differences used by Evans and Kirkham (13) additional tests were run. These tests were made with nitrogen and air as the gas, and covered two pressure ranges, 1.0 to 0.1 mm of water when nitrogen was used as the gas, and 40 to 20 cm of water when air was used as the gas. For the lower range the apparatus of Figure 1 was used. For the upper range different equipment was necessary. The apparatus shown in Figure 3 was then employed.

The apparatus of Figure 3, and the theory associated with it, have been described in detail elsewhere (13). Compressed air from a tank is conducted to the sample of porous material. The tank is compressed to a pressure of about 40 cm of water and then permitted to discharge through the porous medium. There is a water manometer on the tank. The time for the water manometer to fall between two levels in the 40 to 20 cm range

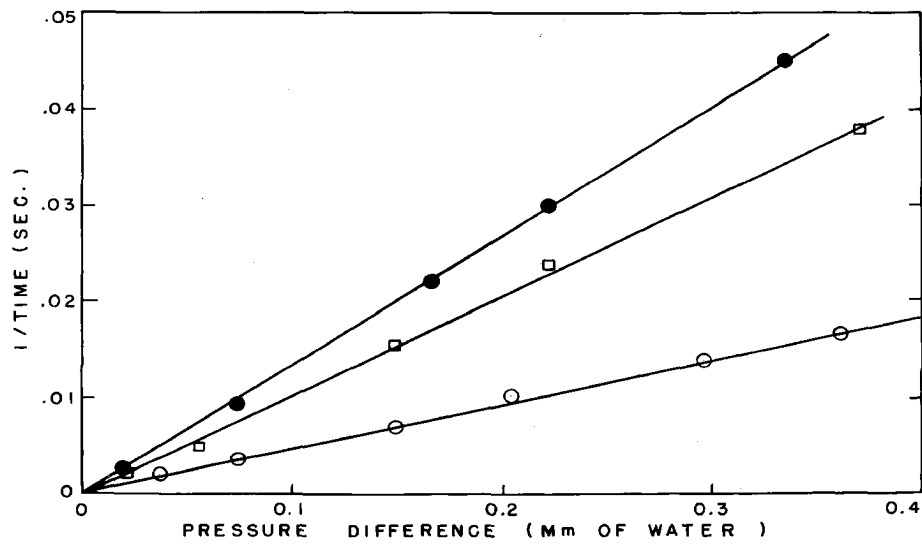


Figure 2. Plot showing the validity of Darcy's law at low pressure differentials.

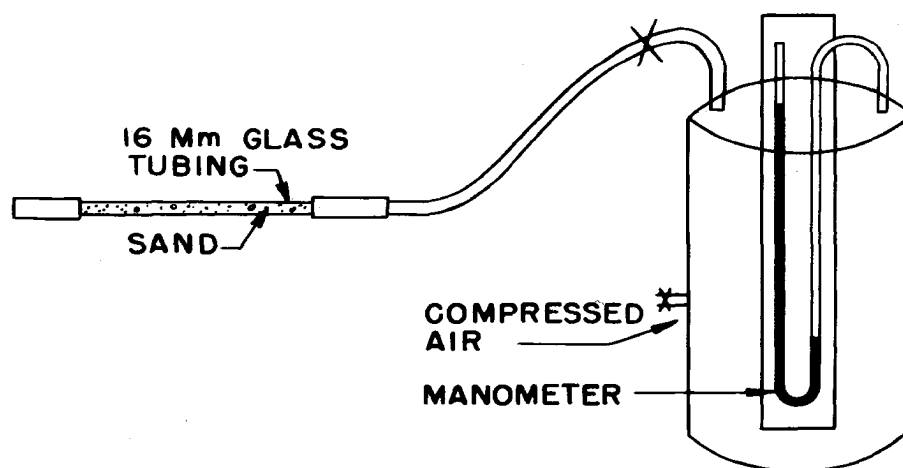


Figure 3. Apparatus for measuring air permeability at a pressure differential of 1 to 40 cm of water.

is observed. The formula used to reduce the data to darcys is

$$k = (2.303uV_tL/AP_a t) \ln h_0/h_1 \quad [5]$$

where u is the viscosity of the air in centipoise, V_t is the volume of the tank in cm^3 , L is the length of the porous medium in cm, A the cross-sectional area of the porous medium in cm^2 , P_a the pressure of the atmosphere in atmospheres, and t the time in seconds for the water manometer to fall from a given height h_0 to a height h_1 , both heights being measured in the same units.

Table 2 shows the results obtained for the air permeability for five different fractions of sand for the two pressure ranges 1.0 to 0.1 mm and 40 cm to 20 cm. The permeability values are the same to within the experimental errors.

Table 2

Air Permeability of Various Size Fractions of Quartz Sand as Measured for Pressure Differentials of 1.0 to 0.1 mm of Water, and 40 to 20 cm of Water

Size Fraction	Permeability	
	1.0 to 0.1 mm of water	40 to 20 cm of water
1.0 - 0.50 mm	137.0 darcys	135.0 darcys
0.50 - 0.42	94.2	93.5
0.42 - 0.25	43.4	44.5
0.25 - 0.15	19.4	17.6
0.15 and smaller	8.2	10.6

It is concluded from the results, shown in Figure 2 and Table 2, that Darcy's law is valid from pressure differentials of 40 cm of water down to 0.018 mm of water and probably lower. Thus, air permeability constants as determined at the upper pressure ranges specified by Kirkham (20) can be employed when very small total pressure differentials are under study as in the present problem. It must be remembered that these pressure differences are taken with atmospheric pressure as a reference.

Differential and Functional Equations

The type of flow here considered will be restricted to the one dimensional case. This case is relatively simple; in addition it applies to a number of practical problems.

Derivation of differential equation of flow

The quantity of gas q , which flows in unit time per unit area in the x -direction in a porous medium and under a total pressure gradient dP/dx , is, as was seen in the last section, given by Darcy's law

$$q = - (k/u) dP/dx, \quad [6]$$

where k is the permeability of the medium, and u the gas viscosity. In equation [6], q is ordinarily in $\text{cm}^3/\text{second}/\text{cm}^2$, k in darcys, u in centipoise, P in atmospheres and x in cm. If there is a mixture of gases, in which only the i th component is of interest, then, if the concentration of this component is c_i , the quantity q_i' of the i th component flowing per unit time per unit area is

$$q_1^i = - (k/u)c_1 \, dP/dx . \quad [7]$$

In equation [7] it is convenient to take c_1 in per cent, the other units staying as before.

If the same component 1 of equation [7] were to move as a consequence of a partial pressure gradient, the total pressure being uniform and constant, then the quantity of gas q_1^p moving per unit time per unit area would be given by Fick's law

$$q_1^p = - D_1 \, dc_1/dx , \quad [8]$$

where D_1 is a constant which depends on the nature of the diffusing gas 1 and upon the gas into which this 1 th component diffuses. The dimensions of q_1^p are the same as q_1^i ; and D_1 has the dimensions $\text{cm}^2/\text{second}$.

Now if there exist simultaneously a pressure gradient and concentration gradient, it is assumed that equations [7] and [8] are additive. The net flow for component 1 is then

$$q_1 = q_1^i + q_1^p .$$

That is,

$$q_1 = - (k/u)c_1 \, dP/dx - D_1 \, dc_1/dx . \quad [9]$$

and this is the basic differential equation of flow.

Functional relationship between pressure and concentration

Let the flow medium be one in which there are no sources or sinks. Then the law of conservation of mass requires that dq_1/dx be zero and equation [9] thus yields, when differentiated on both sides with respect to x ,

$$0 = - (k/u)c_1 \, d^2P/dx^2 - (k/u)(dc_1/dx)(dP/dx) - D_1 \, d^2c_1/dx^2 . \quad [10]$$

Let, for the moment $dP/dx = y$, $D_1 = D$, $c_1 = c$ and $(k/u) = K$. Then division of equation [10] by $-Kc$ yields

$$dy/dx + c^{-1}y dc/dx + (D/Kc)d^2c/dx^2 = 0 .$$

Now let

$$c^{-1}dc/dx = P(x)$$

and

$$(- D/Kc)d^2c/dx^2 = Q(x) .$$

Then

$$dy/dx + Py = Q ,$$

and the solution, found in Dwight's Tables (12), is

$$y = e^{-\int Pdx} [\int e^{\int Pdx} Qdx + b]$$

where b is an arbitrary constant.

But

$$\int Pdx = \int c^{-1}(dc/dx)dx = \ln c + E$$

where E is also an arbitrary constant. Therefore substitution of the value of $\int Pdx$ into the expression for y yields, when the resulting expression for y is integrated,

$$y = (- D/Kc)dc/dx + c^{-1}be^{-E} .$$

That is, replacing y by dP/dx , P by D_1 , c by c_1 and K by k/u , one obtains

$$dP/dx = (- D_1u/kc_1)dc_1/dx + B/c_1 . \quad [11]$$

where $B = be^{-E}$ is an arbitrary constant which remains to be evaluated.

The solution of equation [11] may be obtained by applying again the expression in Dwight's table. The result, as may be verified by differentiation, is

$$P = (- D_1u/k)\ln c_1 + B/c_1 dx + c . \quad [12]$$

where B and C are arbitrary constants, but equation [12] as such will not be further used.

Auxiliary differential equation

Equation [11] involves both c_1 and P as functions of x. Neither of the equations is independent of the other. Therefore an additional independent relation is needed in order that a unique solution be obtainable for equation [11].

To get the auxiliary relation let us consider the total flow of gas q_T of all molecules passing through an element of length Δx of porous medium. Let the pressure difference across this element be ΔP . Now Darcy's law has been proved to be applicable to nitrogen and to air. It would appear therefore that Darcy's law could be applied to whatever combination of gases is moving across the element Δx . At any rate this will be assumed. Therefore, if μ is the viscosity of the mixture of gases, and k the permeability of the medium, one has

$$q_T = - (k/\mu) \Delta P / \Delta x ;$$

and in the steady state this becomes, upon passing over to differentials and then applying the equation of continuity

$$0 = - (d/dx) [(k/\mu) dP/dx] , \quad [13]$$

which is the needed auxiliary equation.

Equation [13] can be further simplified if k and μ can be taken constant. The permeability k can be taken constant if the number, and size of pores, have the same distribution throughout the length of the porous medium. For simplicity such a pore arrangement will be assumed. The viscosity μ will also be assumed to be constant for two reasons. In

the first place gas concentrations often vary only a few per cent in the soil. In the second place even if the gas concentrations do vary more than a few per cent, these variations may be reflected only slightly in the viscosity coefficient, for the reason the viscosity of the components of soil air are approximately the same.

In connection with the above two points, some data are presented. The viscosity of soil air and of its constituents at 20° C, and in centipoise, is (3): air 0.0172, nitrogen 0.0174, oxygen 0.0197, and carbon dioxide 0.0148. The relative viscosity of mixtures of oxygen and carbon dioxide is as follows (3): 100 per cent oxygen, 1.000; 97.5 per cent oxygen, 0.994; 95 per cent oxygen, 0.987; 90 per cent oxygen, 0.976; 85 per cent oxygen, 0.964. These latter values are for 12.2° C, but they will be approximately the same for 20° C. The International Critical Tables from which the above data were taken do not give relative viscosities for mixtures of carbon dioxide in nitrogen. Since, however, nitrogen and oxygen have about the same viscosities, the relative viscosities for oxygen and carbon dioxide should apply, approximately, to mixtures of nitrogen and carbon dioxide.

The above data should now be compared with Table 3. This table gives the composition of normal atmospheric air and normal soil air, together with entries for the three extreme cases, over a year's time, at 1, 3 and 6 foot depth in a silt loam soil.

Table 3

Composition of Atmospheric and Soil
Air (Per Cent by Volume)^a

Kind of Air	N ₂	O ₂	CO ₂
Atmospheric air (33)	79.0	20.97	0.03
Average soil air (33)	79.2	20.6	0.2
Soil at 1 foot depth (5)	81.7	15.3	3.0
Soil at 3 foot depth (5)	92.9	0.25	6.85
Soil at 6 foot depth (5)	84.3	0.2	15.5

^aThe bottom three entries are the extreme cases found over the period of a year.

It appears from Table 3 and the other data, that in the normal root zone of zero to three feet, the viscosity of soil air can be taken as constant. Even in the extreme case at 6 foot depth where Table 3 gives the carbon dioxide to be 15.5 per cent, one sees from the oxygen carbon-dioxide viscosities that the resultant viscosity of the composite soil air would still be about 96.4 per cent of its normal value.

It is thus concluded that k/u , at least as an approximation, may be taken constant; and equation [13] becomes

$$d^2P/dx^2 = 0. \quad [14]$$

It is this latter equation which will now be used in conjunction with equation [11] to determine P and c_1 . Later an example will be given where the theory is modified to take account of viscosity variation in the x direction.

Flow Through a Tube

It appears that the simplest application of equations [11] and [14] would be for flow in a tube containing a uniform homogeneous isotropic porous medium. This case is represented in Figure 4. The tube is of length x_1 and at its left end where $x = 0$, the concentration is c_1^i and the pressure P^i . At the right the respective quantities are c_1^n and P^n . The problem is to find analytically c and P as functions of x . The solution must satisfy equations [11] and [14] and the boundary values shown in Figure 4. Also, when $c_1^n = c_1^i$, the solution must reduce to Darcy's law, and when $P^n = P^i$, to Fick's law.

The solution of equation [14] which satisfies the boundary conditions is quickly found to be

$$P = (P^n - P^i)x/x_1 + P^i ; \quad [15]$$

hence,

$$dP/dx = (P^n - P^i)/x_1 . \quad [16]$$

If the value of dP/dx is now put in equation [11] and the resulting expression integrated, one obtains, upon putting for brevity K for k/u ,

$$c_1 = B_2 e^{-K(P^n - P^i)x/D_1 x_1} + C_2$$

and this becomes, upon utilization of the boundary conditions to evaluate B_2 and C_2 ,

$$c_1 = (c_1^n - c_1^i)(e^{-K(P^n - P^i)x/D_1 x_1} - 1)/(e^{-K(P^n - P^i)/D_1} - 1) + c_1^i . [17]$$

Equations [15] and [17] give the desired solutions of equations [10] and [14] because c_1 and P satisfy the differential equations and boundary conditions.

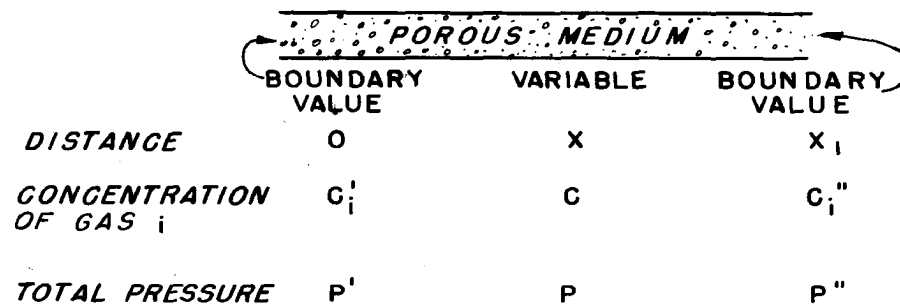


Figure 4. Schematic representation of the one dimensional problem.

To get the quantity of a component of a mixture of gases being transferred through the tube, one now substitutes dP/dx , c_1 and dc_1/dx from equations [16] and [17] into equation [9]. If this is done there results, upon simplification

$$q_1 = [K(P'' - P')/x_1][(c_1'' - c_1')/(e^{-K(P'' - P')/D_1} - 1) - c_1']. \quad [18]$$

It can be shown, when $c_1'' = c_1'$, that equation [18] reduces to

$$q_1 = -K(P'' - P')c_1'/x_1$$

which is, for component 1, Darcy's law as it should be. Also, when $P'' = P'$, equation [18] reduces to Fick's law. To verify the latter case it is necessary to evaluate the indeterminate form $0/0$, which can easily be done by expanding the exponential term.

In equation [18], P'' must be greater than P' , but this condition can always be satisfied by proper choice of the origin of coordinates.

Absorber at one end of tube

When an absorber is placed at one end of a tube filled with a porous material and sealed so that any gas absorbed must move through the tube, there will exist a pressure gradient and a concentration gradient along the tube and there will be mass flow accompanying diffusion flow. Mass flow must occur as will now be shown. Consider the gas to be a mixture of two components at a pressure of one atmosphere. Let the mixture contain initially, say, 20 per cent oxygen and 80 per cent nitrogen. Now let there be at one end of the tube an absorber which absorbs every molecule of oxygen striking it and which thus reduces the concentration of the oxygen there to zero. At the other end of the tube let there be

maintained a mixture of 20 per cent oxygen and 80 per cent nitrogen at atmospheric pressure. Let a steady state be established.

Now, because of absorption of the oxygen, there will be a non-zero oxygen gradient along the tube. Also there will be a non-zero nitrogen gradient, because the nitrogen concentration at the absorber becomes 100 per cent. Therefore nitrogen will flow by diffusion from the absorber end to the other end where the nitrogen percentage is 80 per cent. But, in the steady state the net nitrogen flow at any cross section of the tube must be zero because there is no source at the absorber end. Accordingly there will be mass flow of nitrogen toward the absorber end, and this nitrogen flow will be equal in amount to that which is transferred away from the absorber end by diffusion. The mass transfer of nitrogen can occur only if the pressure is lower than atmospheric at the absorber end. But as a consequence of the pressure differential, oxygen must also flow by mass flow toward the absorber, along with the mass flow of nitrogen.

In summary then, the flow of the gases, when there is the absorber at one end, can be considered as (a) diffusion of oxygen toward the absorber, (b) diffusion of nitrogen away from the absorber, and (c) mass flow of oxygen and nitrogen toward the absorber.

In the problem just discussed it is of most interest to apply the theory to the computation of the quantity of oxygen q_o being transported. Equation [18] is then applicable if subscript i is replaced by subscript o . But to compute q_o it will first be convenient to consider equation [18] with respect to nitrogen flow. This flow q_n has been seen to be zero.

Therefore with subscript 1 in equation [18] being replaced by n, there results

$$0 = [K(P'' - P')/x_1][(c_n'' - c_n') / (e^{-K(P'' - P')/D_n - 1} - c_n')] ;$$

or; since, $(P'' - P')$ is not zero,

$$(c_n'' - c_n') / (e^{-K(P'' - P')/D_n} - 1) - c_n' = 0 ;$$

or

$$c_n''/c_n' = e^{-K(P'' - P')/D_n} . \quad [19]$$

In order to apply boundary conditions to equation [19], the symbols must be better identified. Referring to Figure 4 let us take the absorber to be at $x = 0$. Then the single primed quantities refer to the absorber end of the tube, and the double primed quantities to the open end. The left hand side of equation [19] may now be evaluated. It is, very nearly, 0.8/1.0, since the (partial) pressure of the nitrogen is 0.8 atmospheres, exactly at the open end and 1.0 atmospheres minus a very small quantity, $P'' - P'$, at the absorber end. Thus equation [19] becomes

$$0.8 = e^{-K(P'' - P')/D_n}$$

which is equivalent to

$$(P'' - P') = (D_n/K) \ln 1.25 . \quad [20]$$

Equation [20] gives the pressure difference across the tube. It may also be written

$$P'' - P' = 0.223 D_n u / k \quad [21]$$

since $\ln 1.25 = 0.223$ and $K = k/u$.

Equation [21] shows that the pressure difference across the tube is independent of the tube length. The pressure difference is directly

proportional to the diffusion coefficient and the viscosity, and inversely proportional to the permeability of the porous medium.

A numerical example will illustrate the use of equation [21]. For a porous, dry soil, the constants will be approximately

$$D_n = 0.01 \text{ cm}^2/\text{second}$$

$$u = 0.017 \text{ centipoise}$$

$$k = 10 \text{ darcys .}$$

Therefore

$$\begin{aligned} P'' - P' &= 0.223 \times 1.0 \times 10^{-2} \times 0.017/10 \text{ atmospheres} \\ &= 3.8 \times 10^{-6} \text{ atmospheres} \\ &= 3.9 \times 10^{-2} \text{ mm of water.} \end{aligned}$$

If the permeability were 0.1 darcys, $P'' - P'$ would be 3.9 mm of water.

With the aid of equation [20], the flow rate q_0 of oxygen can now be quickly computed. The right hand side of equation [20] is substituted in equation [18], where i is now o ; and, also, in equation [18], the constant c_o' is set equal to zero. There results

$$q_0 = [D_n(\ln 1.25)/x_1]c_o''/(e^{-(D_n/D_o)\ln 1.25} - 1) , \quad [22]$$

which is independent of both viscosity and permeability but varies inversely with the length of the tube.

In the right hand side of equation [22], D_n/D_o can be taken equal to unity. Also $c_o'' = 0.2$. Putting these values in the equation and performing indicated operations, there results

$$q_0 = - 0.223 D_n/x_1 . \quad [23]$$

This expression may be compared with the rate of flow of oxygen which would be given by Fick's law. The result q_{0F} would be

$$q_{oF} = - 0.20 D_o/x_1.$$

Therefore the error by not taking mass flow into account would be

$$[(0.223 - 0.20)/0.223] \times 100 = 13 \text{ per cent}$$

Measurement of the diffusion coefficient D_o by the absorber method would thus be in error about 13 per cent if mass flow were not taken into account. The error is not exactly 13 per cent because D_n/D_o is not quite equal to unity.

Volatile liquid at one end of tube

When there is a volatile liquid sealed to one end of the tube containing the porous medium, the flow can be analyzed in a manner similar to that used in the case of an absorber at one end. In the present case the volatile liquid will develop its own partial pressure above the liquid and diffusion of the vapor will take place through the porous medium. At the same time, a pressure greater than atmospheric will exist above the volatile liquid. As before the flow may be divided into three divisions: (a) the diffusion of vapor, (b) the diffusion of air in the opposite direction, and (c) the mass flow of all gases in the direction of diffusion of the vapor. Equations [17] and [18] may be applied much as before.

Let subscript a denote the air and v the vapor and let the volatile source be at the end x_1 in Figure 4 so that the double primed subscripts apply to the end where the vapor is generated and the single primed to the open end. Then one has from equation [18], since $q_a = 0$

$$P'' - P' = (D_a/K) \ln c_a'/c_a'' . \quad [24]$$

Again, from equation [18], with v replacing i ; and since $a_v^i = 0$, there results

$$q_v = (K(P'' - P')c_v''/x_1)(e^{-K(P'' - P')/D_v} - 1) . \quad [25]$$

The right hand side of equation [24] is now put in equation [25] with the result

$$q_v = (D_a c_v''/x_1)(\ln c_a^i/c_a'')/(e^{-\alpha} - 1) \quad [26]$$

where, for brevity,

$$\alpha = (D_a/D_v)\ln c_a^i/c_a'' . \quad [27]$$

As an example of the use of the results, carbon disulfide may be taken as the volatile liquid. Its vapor pressure at a room temperature of 27°C is 41 cm of mercury. Therefore, for this vapor, the (partial) pressure of the air at the vapor source is very nearly $76 - 41 = 35$ cm of mercury. The value 35 cm is not quite correct because of the slight build up of pressure at the vapor source due to mass flow. It can be seen now that $c_a^i/c_a'' = 76/35 = 2.16$ and $\ln c_a^i/c_a'' = \ln 2.16 = 0.770$ whence

$$\alpha = 0.770 D_a/D_v .$$

The ratio D_a/D_v can be obtained from Graham's law that states that the diffusion rate of a gas is inversely proportional to the square root of its molecular weight. Therefore, taking air to be made up of nitrogen and, accordingly, of molecular weight 28; and since the molecular weight of carbon disulfide is 76; one obtains

$$D_a/D_v = (76/28)^{1/2} = 1.65 .$$

Hence $\alpha = 0.770 \times 1.65 = 1.27$ and $e^{-\alpha} = 0.281$, and equation [26] becomes

$$q_v = (D_a c_v''/x_1)(0.770)/(0.281 - 1)$$

or

$$q_v = - 1.071 D_a c_v'' / x_1$$

or since $c_v'' = 41/76$ and $D_a = 1.65 D_v$

$$q_v = - 1.767 D_v (41/76) / x_1 . \quad [28]$$

Here again the vapor flow as given by equation [28] may be compared with the amount q_{vF} which would be computed by Fick's law. This flow would be

$$q_{vF} = - D_v (41/76) / x_1 .$$

Thus, use of Fick's law instead of the equation which takes mass flow into account, would result in an error of $0.767/1.767 = 43.2$ per cent.

Note that equation [28] is valid only at 27° C. Equation [23] is valid at different temperatures, but D_a , there, will be a function of the temperature.

Variable viscosity along tube

The theory so far has been given on the assumption that equations [10] and [14] are applicable. These equations depend upon constancy in the viscosity. Equations [9] and [13] must be used if the viscosity is not constant along the tube. In the example where carbon disulfide is used the assumption of constant viscosity may not be justified. The reason the assumption may not be justified is that carbon disulfide and air have quite different viscosities, namely 0.0100, and 0.0183 centipoise, respectively at 27° C. Therefore, since the concentration of the gases varies with x , the viscosity will vary with x .

In order to examine how large the variable viscosity effect might be, equations [9] and [13] will now be used to calculate the pressure P as a function of x in Figure 4. The discrepancy of the pressure

distribution from linearity (compare equation [15]) should then indicate whether the effect of variable viscosity is large.

If it should turn out that the effect is small for carbon disulfide it should also be negligible for soil air, because the concentration of carbon disulfide varies from 54 per cent to zero along a tube of porous medium; whereas in soil only a few per cent variation in oxygen or carbon dioxide concentration would be involved. The figure 54 per cent is the ratio of the vapor pressure of the carbon disulfide to the atmospheric pressure = 41/76, which numbers were noted in the last section.

Jeans (18) has shown how to compute the viscosity of a mixture of gas. The viscosity is the sum of the products of the individual viscosities times their concentration in per cent. Thus, for a mixture of air and carbon disulfide the viscosity u_m is

$$u_m = u_v c_v + u_a c_a .$$

But since $c_a = 1 - c_v$,

$$u_m = u_a + (u_v - u_a) c_v . \quad [29]$$

Equations [9] and [13] are now utilized. Equation [9], upon differentiation with respect to x , with u ($= u_m$) variable, and upon application of the equation of continuity for the steady state, yields

$$c_v \{ (k/u_m) d^2 P / dx^2 + [d(k/u_m) / dx] (dP / dx) \} \\ + (k/u_m) (dc_v / dx) (dP / dx) + D_v d^2 c_v / dx^2 = 0 .$$

Equation [13] yields

$$(k/u_m) d^2 P / dx^2 + [d(k/u_m) / dx] (dP / dx) = 0 . \quad [30]$$

Thus the two differential equations to be solved are equation [30] and

$$(k/u_m) (dc_v / dx) (dP / dx) + D_v d^2 c_v / dx^2 = 0 . \quad [31]$$

One integration for equation [30] yields

$$dP/dx = Au_m/k \quad [32]$$

where A is an arbitrary constant. This equation cannot be solved for P until u_m , as a function of x, is known. To obtain u_m , as a function of x, and also dc_v/dx and c_v , as a function of x, equation [32] is substituted into equation [31] to give

$$d^2c_v/dx^2 + (A/D_v)dc_v/dx = 0.$$

This is solved to obtain

$$dc_v/dx = Be^{-Ax/D_v}$$

and

$$c_v = - (D_v B/A)e^{-Ax/D_v} + E, \quad [33]$$

where B and E are arbitrary constants.

One can now obtain u_m as a function of x by substitution of c_v from equation [33] into the right hand side of equation [29]. The result is

$$u_m = u_a + (u_v - u_a)[(D_v B/A)e^{-Ax/D_v} + E],$$

and this expression for u_m can now be substituted into equation [32] and the result integrated to give

$$P = (A/k)[u_a + (u_v - u_a)E]x + [(u_v - u_a)/kA]D_v^2 Be^{-Ax/D_v} + F, \quad [34]$$

where F is an arbitrary constant.

Equations [33] and [34] are the desired solutions, subject to evaluation of the arbitrary constants A, B, E and F by means of the boundary conditions. These boundary conditions are (compare Figure 4): when $x = 0$, $P = P' = 1$ and $c_v = c_v' = 0$; when $x = x_1$, $P = P''$ and $c_v = c_v''$, P'' and c_v'' being unknown.

Utilizing the boundary conditions and equations [33] and [34] the following four equations can be written:

$$0 = -D_v B/A + E$$

$$1 = [(u_v - u_a)/kA] D_v^2 B + F$$

$$c_v'' = - (D_v B/A) e^{-Ax_1/D_v} + E$$

$$P'' = (A/k)[u_a + (u_v - u_a)E]x_1 \\ + [(u_v - u_a)/kA] D_v^2 B e^{-Ax_1/D_v} + F.$$

The last four equations have as unknowns A, B, E, F and P'' and so there are inadequate relations for the solution. If P'' were known the constants could be determined. The constant P'' can be determined if the above procedure is carried through for c_a instead of c_v . In this event there will again be four arbitrary constants plus P'' as unknowns. But a fifth relation would be available. This relation could be obtained by substituting the values of c_a , dP/dx , and dc_a/dx into equation [9] (with a for i) and then by setting q_a equal to zero, since in the steady state the net air flow is zero. Thus the fifth relation would be available and P'' could be obtained.

Instead of going through this procedure, it is easier to assume as an approximation that $P'' = 1 + 7.07 \times 10^{-6}$ atmospheres, which is the value obtained when the variability of viscosity was neglected. Since a correction effect is here under consideration the use of the approximate value of P'' seems justified.

With use of the noted value of P'' the constants have been evaluated and the variation of P with x, computed. The following values were used in the computations: $k = 10$ darcys, $D_v = 4.75 \times 10^{-2}$ cm²/second, $u_v = 0.100$ centipoise, $u_a = 0.0183$ centipoise, $P'' = 1 + 7.07 \times 10^{-6}$

atmospheres, $x_1 = 10$ cm, and $c_v'' = 54$ per cent. Table 4 shows the calculated pressures along the tube together with values for comparison for the linear case. For the latter case the values of the theoretical

Table 4

Pressure Distribution (in Atmospheres) for Carbon Disulfide Vapor in One Dimensional Flow Through a Ten Centimeter Long Tube of Porous Medium Compared with a Linear Pressure Distribution

Distance from open end of tube	Pressure, carbon disulfide	Pressure, linear case
0 cm	$1 + 0.00 \times 10^{-6}$	$1 + 0.00 \times 10^{-6}$
2	1.55	1.41
4	3.03	2.83
6	4.45	4.24
8	5.79	5.66
10	$1 + 7.07 \times 10^{-6}$	$1 + 7.07 \times 10^{-6}$

pressure at the two ends of the tube were used. It is seen that the deviation is not large. Therefore it would appear that the simpler calculations of the last section would be adequate for most practical cases.

Experimental Verification of Flow Equation

In order to test equation [9], which, it is recalled, is the basic equation for combined mass and diffusion flow, it would seem easier to use equations derived from equation [9], rather than equation [9] itself. For example, the equation applicable to the flow of carbon disulfide as described in the last section might be used. Equation [28] would then apply. The testing procedure would simply involve the measurement of D_v , x_1 and q_v . The experimental values of q_v given by equation [28] would be compared with the theoretical for several samples of different permeability (but the permeability coefficient is not involved in equation [28]).

The procedure, as just outlined, was used in testing the theory. Six samples of sand, ranging in permeability from 5.4 to 143.0 darcys were used. The sand samples (Figure 5) were 10 cm long. They were uniformly packed, with the aid of an electrical vibrator, in glass tubes of 16 mm outside diameter and 14 mm inside diameter. There was a slight constriction in the glass tubes to support a 60 mesh screen against which the sand rested. A screen was also used at the other end of the sample. The sample tube could be sealed in an upright position to a specially made glass evaporating dish by means of a mercury seal. Use of the sample in the upright position does not require modification of equation [28] as will be shown in the Discussion. The glass tube could also be connected, by means of plastic tubing, to equipment for determining the air permeability or to other equipment for determining the

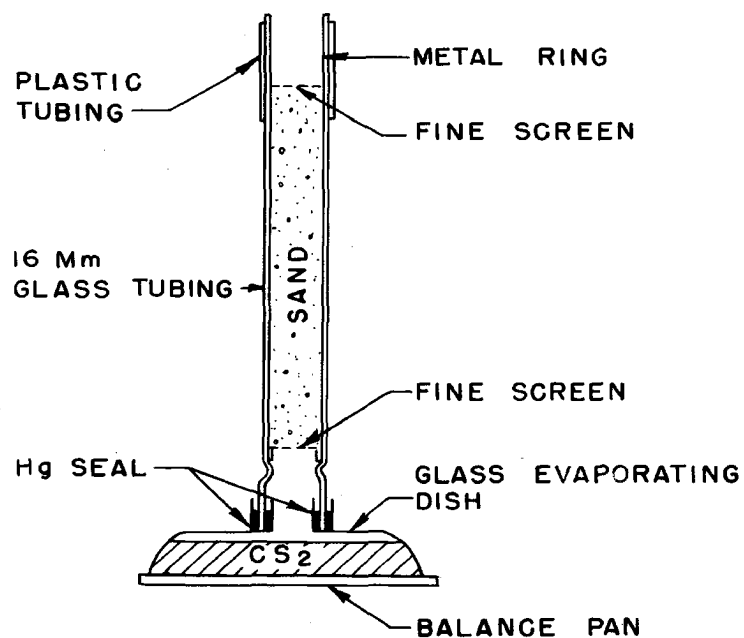


Figure 5. Diagrammatical cross-sectional view of the experimental arrangement for measuring the quantity of carbon disulfide being transferred through porous media.

diffusion coefficient, both of which measurements were made on each sample.

The equipment used for measuring the air permeability has been described (see Figure 3). The apparatus for measuring the diffusion constant is shown schematically in Figure 6 and is essentially the same equipment as described by Taylor (36). Actually the diffusion coefficient D_v of carbon disulfide was not measured, but instead there was measured the diffusion coefficient D_o for oxygen. Oxygen was used because the Beckman oxygen analyzer is available for oxygen and enables the elimination of total pressure gradients which have been troublesome in other methods. The diffusion coefficient D_v of the carbon disulfide, was obtained by applying Graham's law as follows: $D_v = D_o (32/76)^{1/2} = 0.65 D_o$, 32 being the molecular weight of oxygen and 76 that of carbon disulfide.

The quantity of carbon disulfide q_v flowing per unit time was measured by weighing on a balance pan the sample and attached glass evaporating dish. The loss of weight per unit time was a measure of the flow rate. The results from a typical run are shown in Figure 7. Weight of carbon disulfide was converted to volume by the usual method.

It has been indicated that saturated vapor pressure of carbon disulfide will exist at the source end of a porous medium. To test this assumption a separate experiment was run on tubes of sand connected to a source of carbon disulfide. A manometer was connected to the space between the end of the sand column and the liquid carbon disulfide. There was a valve which could shut off the sand from the carbon disulfide

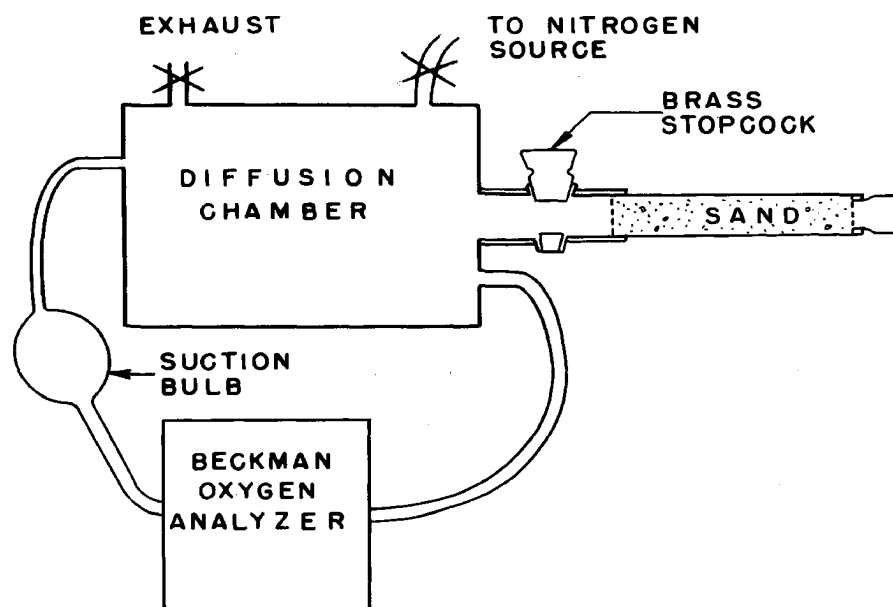


Figure 6. Experimental arrangement used to measure the oxygen diffusion coefficient.

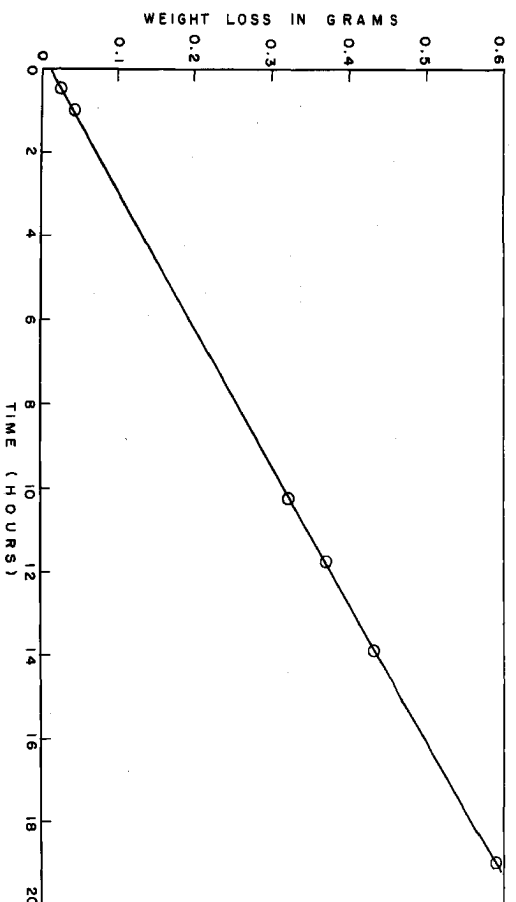


Figure 7. Plot of the weight loss of carbon disulfide against time for the arrangement shown in Figure 5.

source but not the manometer. The manometer remained in contact with the vapor. In the experiment the valve was opened and a steady state permitted to establish itself. At this time the valve was closed and rise of the manometer noted. In no case did the manometer register an increase of more than 1 cm of water. Thus the assumption that saturated vapor will exist at the source end is justified. The saturated vapor pressure of the carbon disulfide at the base of the sand (Figure 5) would thus be, at 27° C, 41 cm of mercury less possibly 1/14 cm of mercury. The value 41 cm is taken from standard tables.

The theoretical and experimental results of the flow rate of the carbon disulfide are shown in Table 5. The measured diffusion coefficients

Table 5

Theoretical and Experimental Values of Flow Rates q_v of Carbon Disulfide Vapor for Porous Media Having Diffusion Coefficients D_v and Permeabilities k (Samples are 10 cm Long and of Diameter 1.4 cm)

Sample No.	D_v cm ² /sec	k darcys	Theoretical q_v cm ³ /sec	Experimental q_v cm ³ /sec
1	0.0180	143.0	0.00246	0.00248
2	0.0242	128.0	0.00331	0.00268
3	0.0200	60.3	0.00274	0.00253
4	0.0239	5.4	0.00328	0.00294
5	0.0207	10.9	0.00284	0.00284
6	0.0292	129.0	0.00402	0.00354

and air permeabilities are also shown. There is satisfactory agreement between the theoretical and experimental values. The per cent discrepancy, in some cases large, was smaller than the 43 per cent noted on page 41. The permeability k does not appear to be correlated either with q_v or D_v . Such a correlation is not expected, as will appear in the Discussion.

Flow Rates of Carbon Dioxide and Oxygen, and Pressure Increase in a Soil Respiration Problem

Equations [17] and [18] will now be applied to a soil respiration problem. The problem is to compute the rate of movement of oxygen and carbon dioxide and the pressure increase in a layer of surface soil of depth x_1 . The layer of soil is taken to be bounded at the top by atmospheric air and at the bottom by moist soil. The layer, itself, is assumed to be dry enough to have negligible respiration. But at depth x_1 , and below, respiration occurs. Furthermore, for each molecule of carbon dioxide which is emitted at depth x_1 in the dry layer, it is assumed that an oxygen molecule from the dry layer goes into the soil water at depth x_1 . Decomposition of organic matter at depth x_1 might be the cause of the situation which is described here in an idealized form.

The flow may be divided into four parts: (a) diffusion of oxygen into the soil layer, (b) diffusion of carbon dioxide out of the soil layer, (c) diffusion of nitrogen into the soil layer, and (d) the mass flow of all gases out of the soil.

The notation of Figure 4 will be convenient. The surface of the soil is taken as $x = 0$. Concentrations and pressure, at depth x_1 are identified with double primes, and at depth $x = 0$, by single primes.

The subscript i in Figure 4 and equations [17] and [18] becomes c, o or n according as carbon dioxide, oxygen or nitrogen, respectively, is the gas in question.

It is assumed that the concentration of carbon dioxide in the atmospheric air is zero. Therefore

$$c_o^i = 0.$$

Two further equations can be written down immediately, by the nature of the problem. They are

$$q_o = -q_c$$

$$q_n = 0.$$

Applying these two in order to equation [18] and putting $c_o^i = 0$, one obtains

$$(c_o'' - c_o^i)/(e^{-K(P'' - P')/D_o} - 1) - c_o^i = c_c''/(e^{-K(P'' - P')/D_c} - 1) \quad [35]$$

and

$$(c_n'' - c_n^i)/(e^{-K(P'' - P')/D_n} - 1) - c_n^i = 0. \quad [36]$$

Solution of equation [36] for $K(P'' - P')$ yields

$$K(P'' - P') = D_n \ln c_n^i/c_n''; \quad [37]$$

and this, when substituted into equation [35] yields, upon solving for c_c'' ,

$$c_c'' = \left[(e^{-(D_n/D_o) \ln c_n^i/c_n''} - 1) / (e^{-(D_n/D_c) \ln c_n^i/c_n''} - 1) \right] [c_o'' - c_o^i e^{-(D_n/D_o) \ln c_n^i/c_n''}]. \quad [38]$$

In this equation D_n/D_o will be taken for purposes of simplification equal to unity, and D_n/D_c can be obtained from Graham's law to yield $D_n/D_c = (44/28)^{1/2}$. Also in equation [38], the concentrations c_n^i will be taken equal to 79 per cent and c_o^i , at 21 per cent.

Equation [38] still contains c_n'' and c_c'' as unknowns. So the solution remains incomplete. But there is another relation, namely

$$c_c'' + c_o'' + c_n'' = 1. \quad [39]$$

because the gas concentrations at depth x_1 must add up to unity. Furthermore, the rate at which respiration is occurring, or another equivalent boundary condition, must be specified to complete the conditions. The rate of respiration will depend upon the temperature, moisture and type of organic matter undergoing decomposition. Let us assume the rate is such that c_o'' has the values shown in Table 6. Then c_o'' is known in equation [39], and c_n'' and c_c'' can be obtained by means of equations [38] and [39]. Also, if D_n/K is specified, then equation [37] will yield the pressure increase ($P'' - P'$). Notice in the solution that depth x_1 does not occur.

Table 6 shows the theoretically computed values of c_n'' , c_c'' and ($P'' - P'$) for two values of D/K and five values of c_o'' .

In Table 6 one sees that if the concentrations of oxygen are maintained at the values specified, the concentrations of nitrogen and carbon dioxide are almost independent of D_n/K . The pressure difference $P'' - P'$ between the respiration depth and the soil surface is, however, directly proportional to D_n/K . This agrees with equation [37], but off hand one might expect that $P'' - P'$ would vary directly as k . One can also observe in the upper half of Table 6 that the differences in oxygen concentrations between the soil surface and depth x_1 are respectively $21 - 0 = 21$, $21 - 10 = 11$, $21 - 15 = 6$, $21 - 17.5 = 3.5$, which are all less than the corresponding carbon dioxide differences 24.97, 13.11, 7.11, 4.18 and 0 per

Table 6

Theoretical Concentrations^a and Pressures^b in Soil
Air for Two Values^c of D_n/K , in a
Respiration Problem

D_n/K	c_o''	c_n''	c_c''	$P'' - P'$
10^{-5}	0	75.03	24.97	0.52×10^{-6}
10^{-5}	10	76.89	13.11	0.27
10^{-5}	15	77.84	7.11	0.15
10^{-5}	17.5	78.32	4.18	0.086
10^{-5}	21	79.00	0	0
10^{-4}	0	75.04	24.97	5.2×10^{-6}
10^{-4}	10	76.89	13.11	2.7
10^{-4}	15	77.84	7.11	1.5
10^{-4}	17.5	78.32	4.18	0.86
10^{-4}	21	79.00	0	0

^aConcentrations are expressed in per cent. c_o'' is the assumed oxygen concentration and c_n'' and c_c'' the corresponding concentrations of nitrogen and carbon dioxide, respectively. Concentrations of nitrogen, oxygen and carbon dioxide at the soil surface are taken respectively equal to 79, 21 and 0 per cent.

^bThe pressure difference $P'' - P'$ is measured in atmospheres in excess of atmospheric pressure.

^cThe diffusion coefficient for nitrogen flow is D_n . The constant K is the ratio k/u , where k is the soil permeability and u the soil air viscosity.

cent. These values are similar to those for the lower half of the table and are as one might expect. They stem from the fact that the carbon dioxide molecules diffuse less rapidly than the oxygen molecules.

Buckingham (7) has presented measured values obtained by Ebermayer, of the concentrations of carbon dioxide, and oxygen, and the values of nitrogen calculated from these, for soil under different vegetation. These values are reproduced in Table 7 and show that the difference in

Table 7

Soil Air Composition in Per Cent at 70 cm
Depth under Different Vegetations^a

Vegetation	Nitrogen	Carbon Dioxide	Oxygen
Beech	78.96	1.19	19.85
Pine	76.93	9.39	13.68
Moss	78.19	7.98	13.83
Sod	78.25	4.13	17.62
Bare ground	77.37	7.02	15.61

^aSource, Buckingham (7)

concentration of carbon dioxide between the depth of sampling and the surface is always greater than the corresponding difference for oxygen. The sets of values are respectively 1.19, 1.15; 9.39, 7.32; 7.89, 7.17; 4.13, 3.38; 7.02, 5.39. In each case the former number is larger than the latter -- in agreement with the theory.

Ebermayer's data can also be used in another interesting manner. Figure 8 shows a plot (triangles) of nitrogen concentration (partial pressure) versus oxygen concentration for the 70 cm depth in the soil as given in Table 7. On the same graph the theoretical values (circles) of nitrogen and oxygen taken from Table 6 are presented. The measured points lie scattered equally about the theoretical curve. It would thus appear from Figure 8 that either respiration was occurring primarily at the 70 cm depth of sampling, or that conditions were otherwise such as to yield approximately the same air composition as for the theoretical case.

Some final interesting calculations have been made in connection with the soil respiration problem described at the beginning of this section. The flow rate q_o of oxygen as given by the exact theory has been computed and compared with the flow rate q_{of} obtained by using the approximate theory. The exact flow rate q_o was obtained from equation [18] with ϕ substituted for 1 and with values of the concentrations, pressures and other needed values as for Table 6. Fick's law, equation [8], was used to calculate q_{of} . The results are shown in Table 8.

One sees in Table 8 that the error made by using the approximate theory is, in all the examples given, small. The error increases with increasing oxygen concentration to a certain point, then decreases again. The maximum error is less than 6 per cent. It appears that errors no greater than 6 per cent will be made in soil respiration problems of the type discussed in this section.

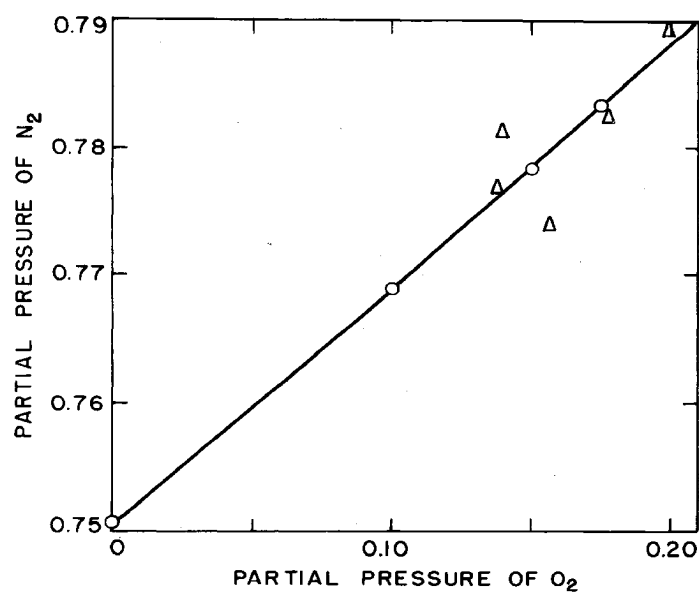


Figure 8. Partial pressure of oxygen versus nitrogen in soil where respiration occurs. The circles indicate calculated points while the triangles are points obtained from the experimental data of Ebermayer (7).

Table 8

Comparison of Oxygen Flow q_0 as Given by Theory which takes Mass Flow into Account, with the Flow q_{0F} which is Computed from Fick's Law Alone; for $D_0/K = 10^{-4}$, Two Values of D_0 and Several Values of c_0'' and for a Depth of 10 cm, for the Respiration Problem of Table 6^a

D_0	c_0''	q_0	q_{0F}	$\frac{q_{0F} - q_0}{q_0} \times 100$
0.01	0	0.00203	0.00210	3.1
0.01	10	0.00105	0.00110	4.8
0.01	15	0.000569	0.000600	5.9
0.01	17.5	0.000349	0.000350	0.2
0.1	0	0.0203	0.0210	3.1
0.1	10	0.0105	0.0110	4.8
0.1	15	0.00569	0.00600	5.9
0.1	17.5	0.00349	0.00350	0.2

^a D_0 is the diffusion coefficient for nitrogen in the soil; $K = k/u$, k is the soil permeability, u the soil air viscosity, c_0'' is the assumed oxygen concentration at 10 cm depth. Units are as follows: q in $\text{cm}^3/\text{cm}^2/\text{sec}$, c_0'' in per cent, D_0 in cm^2/sec , K in $\text{cm}^2/\text{sec}/\text{atmosphere}$.

Effect of Changes in Barometric Pressure on the
Rate of Flow of Carbon Dioxide in Soil

The problem which will now be solved is the same as the one solved in the last section, except that here the barometric pressure, instead of being static, is taken to be increasing at a constant rate with time, and carbon dioxide instead of oxygen is considered. The problem, thus, is to determine the rate of movement of carbon dioxide through the soil when respiration is occurring at a certain depth, and when the barometer is changing as described. By respiration is meant, as before, that for each molecule of carbon dioxide given off, one molecule of oxygen is absorbed.

The method of solving the present problem will not be exact. That is, the exact solution for equation [9], and its appropriate auxiliary equation will not be obtained. Instead the flow of the mixture of soil gases (mass flow) due to the changing barometer will first be considered and this effect then superposed on the diffusion effect which will be calculated by Fick's law. Thus, the interaction of mass flow and diffusion flow will not be taken into account. It will appear that neglect of the interaction is justified.

The soil in the present case is taken as uniformly permeable down to a depth d where there is an impermeable layer, as bedrock. The depth where respiration occurs can be at any level above the impermeable layer.

In order to determine the amount of mass flow, Darcy's law, equation [6], will be used. Accordingly, it will be necessary to determine dP/dx ,

the total pressure gradient in the soil at a distance x of interest from a reference level.

The differential coefficient dP/dx can be obtained if P as a function of x can be determined. This can be done.

The pressure P , it must now be recalled, is the gauge pressure. It can be computed by considering a heat flow problem. The solution to the heat problem in question is given by Carslaw and Jaeger (9) and is for one dimensional flow in a slab, heated at the same constant rate on its two surfaces. The temperature distribution, from the center to the surface of the slab, corresponds to the pressure distribution in the soil air problem. The analogy here results from the fact that air flow and heat flow have the same type of differential equations (20).

Let d (cm) be the depth of the soil to the impermeable layer, a (mm of water/second) be the constant rate of pressure increase at the soil surface, f the fraction of the soil layer occupied by air, K (cm²/second/mm of water) the ratio of soil permeability to air viscosity, t (second) the time and x (cm) the vertical distance measured upward from the impermeable layer. Then the pressure in mm of water at (x, t) is found to be

$$P = at + af(x^2 - d^2)/20660K + (16ad^2f/10330K\pi^3)$$

$$+ \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} e^{-10330Kt(2n+1)^2/4d^2f} \cos (2n+1)\pi x/2d \quad [40]$$

where kappa in Carslaw and Jaeger's equation four on their page 88 has now been replaced by $10330 K/f$. The number 10330 is the assumed value for the normal atmospheric pressure in mm of water.

To evaluate the constant a in equation [40] the barometric pressure record for 1951 for Ames, Iowa, was studied. Three periods were chosen when the barometric pressure changed nearly linearly over the period. A plot of the barometric pressure against time for these three different periods is shown in Figure 9. The rates taken from these plots are 7.56, 3.45, and 1.66 mm of water per hour corresponding to the curve segments labelled a, b and c in Figure 9.

For the other constants in equation [40], these values were taken: $d = 100$ cm, $f = 0.3$, $K = 0.0538$ (cm²/second)/mm of water, which is equivalent to a soil permeability of 10 darcys and an air viscosity of 0.018 centipoise.

When the above values are substituted in equation [40] it is noted that a short time after the barometric pressure wave arrives, all terms beyond the first two are negligible. In fact if $t = 3600$ second the first term in the summation is not greater than $4.77 \times e^{-166}$.

Equation [40] now may be written

$$P = at + af(x^2 - d^2)/20660K . \quad [41]$$

Let P_{x_1} be the pressure at $x = x_1$ and P_{x_2} the pressure at x_2 then

$$P_{x_2} - P_{x_1} = af(x_2^2 - x_1^2)/20660K$$

and this constant pressure difference across the distance $x_2 - x_1$ will cause a constant quantity of gas per unit time to be transferred.

The needed differential coefficient dP/dx for Darcy's law can be written down from equation [41] but it is of interest to tabulate first some pressure differences. This is done in Table 9. The pressure differences are obtained by subtracting the pressure at a depth in question

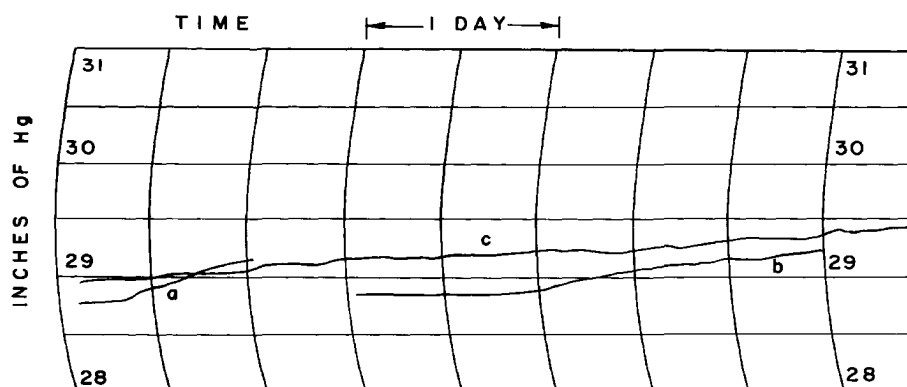


Figure 9. Reproduction of barometric chart for Ames, Iowa, for three different periods.

from the pressure at the soil surface. The three sets of values given correspond to the rates of barometric pressure change determined from Figure 9. Note that the depths in Table 9 are not values of x but of $(d - x)$.

Table 9

Pressure Differences^a in the Soil When the Barometric Pressure is Changing at the Rate of 7.56, 3.45 and 1.66 mm of Water per Hour^b

Depth (cm)	Pressure Difference (mm H ₂ O)		
	7.56 mm H ₂ O/hr	3.45 mm H ₂ O/hr	1.66 mm H ₂ O/hr
0	0.0000	0.0000	0.0000
20	0.0020	0.0009	0.0004
40	0.0036	0.0016	0.0008
60	0.0048	0.0022	0.0011
80	0.0055	0.0025	0.0012
100	0.0057	0.0026	0.0012

^aPressure differences are obtained by subtracting the pressure at a given depth in the soil from the pressure at the soil surface.

^bFor additional conditions see text.

It is apparent from Table 9 that the pressure differences are everywhere small and that little gas transfer by mass movement can therefore be expected. This mass transfer will now be computed by determining dP/dx and substituting the value in equation [6].

From equation [41]

$$dP/dx = 2afx/20660K .$$

Hence, from equation [6],

$$q = - 2afx/20660 , \quad [42]$$

a result independent of K.

Table 10 gives the rates of mass flow q in $\text{cm}^3/\text{cm}^2/\text{second}$ for the same depths and same rates of barometric pressure change shown in Table 9. The rates, as was expected, are small.

Table 10

Mass Flow of Soil Air When the Barometric Pressure
is Changing at the Rate 7.56, 3.45 and
1.66 mm of Water per Hour^a

Depth (cm)	Mass Flow $\text{cm}^3/\text{cm}^2/\text{second}$		
	7.56 mm $\text{H}_2\text{O}/\text{hr}$	3.45 mm $\text{H}_2\text{O}/\text{hr}$	1.66 mm $\text{H}_2\text{O}/\text{hr}$
0	6.10×10^{-6}	2.78×10^{-6}	1.29×10^{-6}
20	4.88	2.23	1.03
40	3.66	1.67	0.77
60	2.44	1.11	0.52
80	1.22	0.56	0.26
100	0	0	0

^aFor additional conditions see text.

The amount of carbon dioxide which is transported by mass flow can be computed from the values in Table 10. It is only necessary to multiply the recorded values by the concentration of the carbon dioxide in the soil at the depth in question.

For example, suppose that respiration is occurring at the 40 cm depth in the soil and that the carbon dioxide concentration there is 0.10. Then, referring to Table 10 one sees that for the rate of barometric pressure change of 7.56 mm of water per hour, the flow rate of carbon dioxide at the 40 cm depth will be $0.10 \times 3.66 \times 10^{-6} = 3.66 \times 10^{-7} \text{ cm}^3/\text{cm}^2/\text{second}$.

The ultimate goal was to obtain the net flow of carbon dioxide. This can now quickly be accomplished. Continuing with the same example of 0.10 per cent concentration of carbon dioxide at 40 cm depth, one finds the diffusion flow from Fick's law to be $D_c(0.10)/40$, where D_c is the diffusion coefficient for carbon dioxide in the soil. The constant D_c may be taken equal to $0.01 \text{ cm}^2/\text{second}$. Therefore, the diffusion flow will be $(0.01)(0.10)/40 = 2.5 \times 10^{-5} \text{ cm}^3/\text{cm}^2/\text{second}$ which is about 100 times as great as the mass flow. Hence interaction effects between diffusion flow and mass flow can be neglected, as well as the mass flow itself. For the lower rates of barometric pressure change in Table 10 the effect of mass flow would be even smaller than in the example given. Also, since it is doubtful that heavier concentrations of carbon dioxide than 10 per cent will exist in the soil above the 40 cm depth (see Table 3), it may be concluded that barometric pressure changes will not be of importance compared with diffusion processes in

the problem of removal of carbon dioxide from the soil. Buckingham (7) reached this same conclusion but in a manner which did not seem completely clear to the present writer.

DISCUSSION

It is a matter of interest to examine the importance of slip flow (see Review of the Literature) when measuring the air permeability of soil. In a moist soil, as it normally occurs in the field, the smaller pores are filled with water. Consequently, only the larger pores contribute to the flow of air. The factor which determines the size of the drained pores is the tension of the soil water. This tension is inversely proportional to the radius of the largest undrained pores. Since the ratio λ/r of the mean free path of the gas molecules to the radius of the pore determines which type of gas flow exists, a simple calculation should reveal when slip flow becomes prominent in some of the pores.

Assuming that the value given by Wilson et al. (38) for the ratio λ/r is correct, namely 0.050, r can be calculated if λ is known. Jeans (18) has given the value of λ for ordinary air at atmospheric pressure as 6×10^{-6} cm. Hence $r = 6 \times 10^{-6} / 0.050 = 1.2 \times 10^{-4}$ cm.

The tension of the soil water which will just drain pores of this size can be calculated by the well known height of rise equation,

$$h = 2T/\rho g r$$

where h (cm) is the tension of the soil water, T (dynes/cm) the surface tension, ρ (gm/cm³) the density of the soil water, and g (cm/second²) the acceleration of gravity. When $r = 1.2 \times 10^{-4}$ cm of water is used in the height of rise equation, one finds the tension h to be 1220 cm of water or 1.2 atmospheres. Thus soil would have to be much drier than the moisture equivalent (one-third atmosphere) -- and in fact drier than it

ordinarily becomes under cropping conditions — before those pores in which the slip factor may be appreciable, will be involved.

Even if the soil is dry enough for the small pores to conduct air, the slip effect will still be negligible in most soils because the pores of this size will conduct only a small percentage of flow. This statement may be based on Poiseuille's law which states that the flow through a capillary of radius r is proportional to the fourth power of the radius. A pore $1/10$ as large as another pore would conduct only $1/10000$ as much air, for equal times and equal pressure differences.

The pores which are involved in free molecular flow will be still smaller than in slip flow. The ratio of λ/r which determines the pore radius when viscous slip flow will have passed over to predominantly free molecular flow has been given by Wilson et al. (38). The value is $\lambda/r = 3.2$. Therefore $r = 6 \times 10^{-6} / 3.2 = 1.9 \times 10^{-6}$ cm and this corresponds to $h = 7.6 \times 10^5$ cm of water tension or 730 atmospheres. This tension is much greater than the tension at the wilting point which is 15 atmospheres. Seven hundred and thrity atmospheres is the tension approximately of water held in air dry soil when the relative humidity is 50 per cent. It is obvious that free molecular flow will not be important in soil aeration problems.

In the Review of the Literature it was noted that Klinkenberg found Darcy's law to give an error of 11 per cent if the permeability of his porous medium was 0.1 darcy. Now, in moist soil the permeability may become as low as 0.1 darcy (13). Nevertheless, the error of 11 per cent would not be expected in the soil, because, as has been brought out

above, the flow will be in pores which are much larger than those in which the slip effect is important. The porous material used by Klinkenberg was not like moist soil. He used fine sand and sintered glass in which the pore space would be that due to small pores.

In view of all the above it appears that Darcy's law should yield the same value of k (not K) for soils regardless of what fluid is used to measure k , if the measuring fluid, gas or liquid, does not swell the pores or displace any soil moisture in the pores. This statement should be true at least as far as effects of slip, or of molecular free flow are concerned. It would be of interest to test Darcy's law on clay powders at very low pressure differentials. It may be that effects not yet considered might influence flow. With the large specific surface of clay, it could be possible that surface effects would introduce anomalies in Darcy's law for gas flow.

Table 5 needs further comment. This is the table which gives the flow rates of carbon disulfide for several samples of porous media. It was noted in earlier reference to this table that the permeability k of the samples did not appear to be related to the flow rates q_v of the vapor or to the diffusion coefficients D_v .

The reason for the lack of correlation of k with q_v is indicated in equation [26] which is the theoretical expression for q_v . This expression does not involve k explicitly nor will it involve k implicitly unless k is a function of $D_a c_v''$ or of c_a'/c_a'' or of D_a/D_v . Now from physical reasoning k is not necessarily related to D_a or D_v because mass flow and diffusion flow are essentially different processes, the

shape and size of pores and the fraction of the pore space being involved differently in the two phenomena. DallaValle (10, p. 263 and 271) discusses the packing arrangements as they are related to permeability. The permeability may vary anywhere from the three point three power to the seventh power of the porosity. DeVries (11), on the other hand, shows that the diffusion coefficient varies nearly linearly with the porosity, the shape of the pores being involved only slightly.

It must yet be examined whether k is a function of c_v'' or of c_a'/c_a'' . It was shown following equation [27] that $c_a'/c_a'' = 1/(1 - c_v'')$. Therefore the momentary discussion comes down to the question: is k a function of c_v'' ? Now, if it is remembered that c_v'' is the vapor pressure of the carbon disulfide at the lower end of the sand column in Figure 5, it will probably also be remembered that this vapor pressure was found to be essentially constant for all the samples tested. That is to say, c_v'' did not vary from sample to sample and hence was invariant with respect to k . It is possible that if more porous samples or shorter ones had been used, c_v'' would not have been found invariant with k .

Two more questions should be answered in connection with Table 5.

(1) Why, with the samples ranging in permeability from 5.4 to 143 darcys, did not the flow rates vary more than from 0.00248 to 0.00354 cm³/second? (2) Should not the effect of gravity have been considered in this problem in view of the fact that vertical, and not horizontal, flow was involved?

The answer to the first question is evident, if one makes the hypothesis that the porosity of the samples did not vary much. For, if

this hypothesis is made, it follows that the diffusion coefficient, and hence flow for the samples would not have varied very much either. The reason the porosity may not have varied much is that porosity is not (but permeability is) a function of the size of the particles. This statement, at any rate, is true of spherical particles. A porous medium made up of spheres all of the same size will have the same porosity as that of another porous medium made up of spheres of another size, provided both media have the same kind of packing. In the carbon disulfide experiment the particles of sand, comprising a sample, had all been screened to about the same size; also, they were all packed in the same manner.

The answer to the second question is: gravity need not be considered because the effect of gravity does not enter into the final flow equation (or into the expression for flow in the other problems discussed where flow was in the vertical direction). That gravity will not be involved is seen by returning to equation [6] and there modifying the equation to take account of gravity. Equation [6] then becomes (compare Muskat, p. 129 (24))

$$q = - (k/u)(d/dx)(P \pm \rho g x) .$$

By comparing the latter equation with equation [6] it seems evident that wherever P appears in the analysis, there should be substituted the quantity $(P - \rho g x)$. If this is done, it will be seen that $\rho g x$ is not involved in the final flow equation, because P itself does not appear in the equation.

In concluding this discussion a result of Van Bavel (37) will be compared with the corresponding result in the present work. The result

in question is the one for the flow of vapor of a volatile liquid through a porous medium. Now a study of Van Bavel's result (his equation thirty three) shows that his equation is only applicable if the volatile vapor has the same diffusion coefficient for the porous medium as has air. The present theory, on the contrary, is more general; it is applicable when the diffusion coefficient of the two vapors may have any values. If Van Bavel's expression had been applied to the problem of the volatilizing carbon disulfide an error of 19 per cent would have resulted. This is seen as follows. His equation in our notation is

$$q_v = (D_v c_a' / x_1) \ln c_a' / c_a'' ,$$

and the values to be substituted in this equation for the carbon disulfide problem are, $c_a' = 1$ and $c_a'' = (76 - 41)/76$. Hence,

$$q_v = - 0.770 D_v / x_1 .$$

The more general theory gives

$$q_v = - 0.952 D_v / x_1 .$$

Therefore the error is $[(0.952 - 0.770)/0.952](100) = 19$ per cent. Van Bavel used ethyl alcohol at 25°C in his experiments. A calculation made as above shows that then the error would be 3.8 per cent, about one-fifth of what it would be for carbon disulfide.

SUMMARY AND CONCLUSIONS

The flow of gases due to a combined concentration and total pressure gradient in soil is of importance in several problems dealing with soil aeration. This paper gives a general theory for gas flow when such phenomena are involved.

Before the theoretical development could be justified, it was necessary to determine the law of flow of gases through soils at very low pressure differentials. It was found that Darcy's law was valid down to pressure gradients as low as 0.00018 mm of water per mm of porous medium, and there were indications that the law is valid down to a pressure gradient of zero. Also, the effect of slip flow and free molecular flow was found to be negligible in its effect on Darcy's law as applied to the flow of gases in ordinary moist soil.

A general differential flow equation was derived by adding terms due to the laws of Darcy and Fick. This equation, together with two auxiliary differential equations, was used in solving the flow problems of interest. The solution of the differential equations yielded the quantity of flow, the gas concentration and the pressure distribution for each component of the flowing gas.

As particular applications of the general differential equations, the following five problems were solved: (a) flow through a tube containing a porous medium when there is an absorber at one end which removes one component of a gaseous mixture; (b) flow through a similar tube with a volatile liquid at one end; (c) the same as (b) except that

the variation in viscosity with gas concentration is to be taken into account; (d) a respiration problem in which carbon dioxide and oxygen are diffusing in opposite directions through soil; and (e) a problem dealing with the importance of mass flow, as compared with diffusion flow, when the barometric pressure is changing linearly with time.

For problem (a) it was found, in a specific example, that the error involved in the measurement of the diffusion coefficient, if a total pressure gradient was not taken into account and diffusion flow only considered, was 13 per cent. In problem (b), with carbon disulfide as the volatile liquid, the error computed in the same manner was 43 per cent. From the results of problem (c) it was concluded that the effect of viscosity changes with concentrations can normally be neglected.

Problem (d) is always present in soil where respiration is occurring. The differences in the rates of diffusion of carbon dioxide and oxygen in soil cause a slight build up of pressure (gauge pressure) in the soil. But in solving the problem it was found that this pressure build up is small and can generally be neglected in its effect upon gas transfer. The error involved was never greater than 6 per cent for conditions which normally might be found in the soil.

The solution of problem (e) showed that the effect of barometric pressure changes, of magnitude normally expected, will have little influence upon the amount of gas transferred through soil. Buckingham (7) reached the same conclusion but in a different way.

In order to test the validity of the general flow equations, some experimental results were obtained for problem (b) when the vapor was

carbon disulfide and the results compared with the theoretical. There was a satisfactory agreement.

The theoretical results of problem (b) were compared with theoretical results, for the same problem, given by another investigator. The latter's theory did not take differences in diffusion coefficients of air and vapor into account. The present theory does. It was found that an error of 19 per cent would result in problem (b) if differences in diffusion coefficients of air and vapor were not taken into account. If the vapor is ethyl alcohol, the error would be 3.8 per cent.

LITERATURE CITED

1. Barr, Guy. A monograph on viscometry, Chapter I, II, and VII, Oxford University Press. 1931.
2. Barrer, R. M. Diffusion in and through solids, Chapter II, Cambridge University Press. 1941.
3. Bircumshaw, L. L. and Scott, V. H. Viscosity of gases. International Critical Tables, 5:1-6. 1929.
4. Blake, G. R. and Page, J. B. Direct measurement of gaseous diffusion in soils. Soil Sci. Soc. Amer. Proc. (1948), 13:37-42. 1949.
5. Boynton, D. and Reuther, W. A way of sampling soil gases in dense subsoil and some of its advantages and limitations. Soil Sci. Soc. Amer. Proc. (1937), 3:37-42. 1938.
6. Brown, G. P., DiNardo, A., Cheng, G. K., and Sherwood, T. K. The flow of gases in pipes at low pressures. J. of Applied Physics, 17:802-813. 1946.
7. Buckingham, E. Contributions to our knowledge of the aeration of soils. U. S. Dept. Agr. Bur. of Soils Bul. 25. 1904.
8. Carmen, P. C. Diffusion and flow of gases and vapours through micropores. I Slip flow and molecular streaming. Proc. Roy. Soc. London, 203:55-74. 1950.
9. Carslaw, H. S. and Jaeger, J. C. Conduction of heat in solids. The Clarendon Press, Oxford. 1947.
10. DallaValle, J. M. Micromeritics. Pitman Publishing Corp., New York, N. Y. 1943.
11. DeVries, D. A. Some remarks on gaseous diffusion in soils. Trans. Int. Congress of Soil Sci. 2:41-43. 1950.
12. Dwight, H. B. Tables of integrals and other mathematical data. The Macmillan Co. New York, N. Y. 1947.
13. Evans, D. D. and Kirkham, Don. Measurement of the air permeability of soil in situ. Soil Sci. Soc. Amer. Proc. (1949), 14:65-73. 1950.

14. Gilbert, P. T. Silicone water-repellents for general use in the laboratory. *Science*, 114:637-640. 1951.
15. Grunberg, L. and Nissan, A. H. The permeability of porous solids to gases and liquids. *J. Inst. Petrol. Tech.*, 29:236. 1943.
16. Hagen, R. M. Movement of carbon disulfide vapor in soils. *Hilgardia*, 14:83-118. 1941.
17. Jacobs, M. H. Diffusion processes. *Ergebnisse der Biologie*, 12:1-160. Verlag von Julius Springer, Berlin. 1935.
18. Jeans, J. Kinetic theory of gases. The Macmillan Co., New York, N. Y. 1940.
19. Keen, B. A. The physical properties of the soil. Longmans, Green, and Co., London. 1931.
20. Kirkham, Don. Field method for determination of air permeability of soil in its undisturbed state. *Soil Sci. Soc. Amer. Proc.*, 11:93-99. 1946.
21. Klinkenberg, L. J. The permeability of porous media to liquids and gases. *Drilling and Production Practice*, p. 200. 1941.
22. Loeb, L. B. Kinetic theory of gases. McGraw-Hill Book Co., New York, N. Y. 1927.
23. Millikan, R. A. The electron, 1st edition. The University of Chicago Press, Chicago, Ill. 1917.
24. Muskat, M. The flow of homogeneous fluids through porous media. Edwards Inc., Ann Arbor, Mich. 1946.
25. Muskat, M. and Botset, H. G. Flow of gas through porous materials. *Physics* 1:1337-1349. 1940.
26. Page, J. B. and Bodman, G. B. Effect of soil physical properties on nutrient availability. In, mineral nutrition of plants. Chapter 6. The University of Wisconsin Press, Madison, Wis. 1951.
27. Penman, H. L. Gas and vapour movements in the soil: I The diffusion of vapours through porous solids. *J. Agr. Sci.*, 30:437-462. 1940.
28. Penman, H. L. Gas and vapour movements in the soil: II The diffusion of carbon dioxide through porous solids. *J. Agr. Sci.*, 30:570-581. 1940.

29. Peterson, J. B. Relations of soil air to roots as factors in plant growth. *Soil Sci.*, 70:175-185. 1950.
30. Raney, W. A. Field measurements of oxygen diffusion through soils. *Soil Sci. Soc. Amer. Proc.* (1949), 14:61-65. 1950.
31. Richards, L. A. Report of the subcommittee on permeability and infiltration. *Soil Sci. Soc. Amer. Proc.* (1951), 16:85-88. 1952.
32. Ridgen, P. J. The specific surface of powders. A modification of the theory of the air permeability method. *J. Soc. Chem. Ind.*, 66:130-136. 1947.
33. Russell, E. J. and Appleyard, A. The atmosphere of the soil, its composition and the causes of variation. *J. Agr. Sci.*, 7:1-48. 1915.
34. Russell, M. B. Soil aeration and plant growth. Soil physical conditions and plant growth. Academic Press, New York, N. Y. 1952.
35. Taylor, S. A. Soil air-plant growth relationships with emphasis on means of characterizing soil aeration. Unpublished Ph. D. thesis, Cornell University Library, Ithaca, N. Y. 1949.
36. Taylor, S. A. Oxygen diffusion in porous media as a measure of soil aeration. *Soil Sci. Soc. Amer. Proc.* (1949), 14:55-61. 1950.
37. Van Bavel, C. H. M. Gaseous diffusion and porosity in porous media. *Soil Sci.*, 73:91-104. 1952.
38. Wilson, L. H., Sibbitt, W. L., and Jakob, M. Flow of gases in porous media. *J. of Applied Physics*, 22:1027-1030. 1951.
39. Yuster, S. T. Homogeneous permeability measurements. *Drilling and Production Practice*, p. 356-363. 1946.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to his major professor, Dr. Don Kirkham, for the helpful guidance rendered during his graduate training at Iowa State College. He also wishes to express his gratitude to Dr. B. Vinograd, Dr. F. F. Blocken, Dr. C. A. Black and Dr. R. S. Hansen, for serving on the Special Committee, and to Mrs. Viola Crellin for the typing of the dissertation.

The author gratefully acknowledges the assistance and encouragement given him by his wife, Frances, during the course of graduate work. Without her help the work could not have been completed.