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Diffusion of Oxygen Through Saturated Porous Media

Paul Fruen
DIFFUSION OF OXYGEN THROUGH SATURATED POROUS MEDIA

BY

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A thesis submitted in partial fulfillment of the requirements for the degree Master of Science, Department of Agronomy, South Dakota State College of Agriculture and Mechanic Arts

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INTRODUCTION

An important characteristic of a soil is its ability to supply oxygen to roots and microorganisms. Bauer (2) discusses several mechanisms for the transfer of oxygen from atmospheric air into soil. He arrives at the conclusion that diffusion is the key to soil aeration.

Much work on diffusion has concentrated on the diffusion of oxygen and carbon dioxide through the soil air. Since most of the growth of roots occurs in moist soil, it appears that some of the diffusion must be through water. Water has a much higher resistance to the flow of oxygen by diffusion than has air. It is likely that this low rate of oxygen diffusion may in many cases limit the respiration of roots surrounded by water or a water film.

The purposes of this investigation are to develop apparatus for the measurement of diffusion through water saturated media, and to compare the effect of porosity on diffusion through water saturated media with that on diffusion through media saturated with gases.
REVIEW OF LITERATURE

Diffusion in Porous Media

The diffusion of gases through soils and similar porous media has been studied by several men who have expressed their results as the ratio of the rate of diffusion through porous media to the rate of free diffusion between the gases. This ratio will henceforth be referred to as $D/D_0$.

Buckingham (3) measured diffusion of air and carbon dioxide through soil. He flowed air across one side of a layer of soil and carbon dioxide across the other side of the layer. The amount diffusing was measured as the loss or gain of carbon dioxide in the flowed gases. He assumed that diffusion and porosity were related by an equation of the form

$$D = k S^n$$

where $D$ was the number of cubic centimeters of each gas passing in opposite directions through a square centimeter area on a layer of soil one centimeter thick across which there existed a partial pressure gradient of one millimeter of mercury, $S$ was the fraction of the soil layer which was filled by the gases, and $k$ and $n$ were constants to be determined from experiments.

He found that $n$ was approximately two and that $k$ was nearly equal to $D_0$, the constant for free diffusion between air and carbon dioxide. These values give the ratio

$$D/D_0 = S^2.$$ 

Penman (9, 10) measured diffusion of carbon disulfide through
granular solids by recording the weight loss from his apparatus as carbon disulfide diffused through a sample and into the air. He also measured diffusion of carbon dioxide through a sample into air. He used a variety of materials including sand, soil, kaolin, steel wool and glass spheres.

After correcting for the impedance of the apparatus, he concluded that for granular solids with $S$ (porosity) between zero and 0.6, with particles approximating spheres, and with isotropic pore space distribution, one could use the relation $D/D_0 = 0.66 S$.

Diffusion of oxygen through porous media was measured by Taylor (13). He used a Beckman Oxygen Analyzer to measure the increase of partial pressure as oxygen diffused from the air into a container of nitrogen. He characterized his media by $\Lambda$, the "equivalent diffusion distance" and arrived at the expression $D = 1/\Lambda^2 D_0$. His $1/\Lambda^2$ is the same as Penman’s $D/D_0$.

For Ontario loam he found $1/\Lambda^2 = 0.668 S$. For quartz sand and for powdered glass, his values were farther from agreement with Penman’s formula $D/D_0 = 0.66 S$.

The effect of impedance of a supporting screen was eliminated by van Bavel (14), with a semi-circular diffusion tube. He measured the changing weight as ethyl alcohol diffused through a sample to the air. Using quartz sand, a mixture of sand and soil, and glass spheres with quartz sand, he concluded that the value for Penman’s $D/D_0$ should be 0.6 S.

Rust, Klute and Giesekeing (11) devised a method for determining the diffusion-porosity relationship which minimized the error arising from the diffusion, through one another, of gases of different diffusivities. They
measured the amount of radioactive carbon dioxide diffusing into a sample saturated with nonradioactive carbon dioxide. Using sand, silica flour and glass beads, they found $D_2/D_1$, which corresponds to Penman's $D/D_o$, to be near $0.04 + 0.60$. 

DeVries (5) used a formula for the electric conductivity of a medium containing ellipsoidal or spherical particles to derive theoretical curves which are very like the relationships between $D/D_o$ and $S$ which have been found experimentally.

The above work was with gases diffusing through dry porous media. The purpose of this work is to determine diffusion of a gas in saturated porous media.

Linear Steady State Diffusion

Diffusion is the movement of a substance in a medium under the influence of forces that arise from concentration gradients.

The amount of material diffusing across a unit area in a unit time is, by Fick's first law (1),

$$ q = -D \frac{\partial C}{\partial x} $$

(1)

where $q$ is the rate of flow in moles/sec, $D$ is the coefficient of diffusion in cm$^2$/sec, $C$ is the concentration in moles/cm$^3$, and $x$ is distance in cm in the direction of diffusion.

The rate of accumulation of the diffusing substance $\partial C/ \partial t$, is described for linear diffusion by Fick's second law,

$$ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} $$

(2)

where $t$ is the time in seconds. When a steady state is reached the concentration at any point no longer changes, that is
\[ \frac{\partial C}{\partial t} = 0 = \partial^2 C / \partial x^2. \]  

(3)

For one dimensional flow equation 3 has the steady state solution

\[ C = Ax + B \]  

(4)

where A and B are constants.

If one takes boundary conditions of diffusion through a plate of thickness L

\[ C = C_1 \text{ at } x = 0 \text{ for all } t \]

\[ C = C_2 \text{ at } x = L \text{ for all } t \]

then one may eliminate A and B in equation 4 to get

\[ \frac{(C - C_1)}{(C_2 - C_1)} = x/L \text{ or } C = (C_2 - C_1) \frac{x}{L} + C_1 \]

where C is the concentration at the position x.

The rate of flow through a unit area of the plate is

\[ q = -D \frac{\partial C}{\partial x} = D \frac{(C_1 - C_2)}{L} \]

(5)

The apparatus used in this investigation was constructed so the above boundary conditions could be approached and equation 5 could be used to relate D to the rate of flow.

The Platinum Electrode

Kolthoff and Lingane (7) describe methods for qualitatively and quantitatively analyzing solutions of electrooxidizable or electroreducible substances. Consider an electrolysis cell containing a silver anode and a platinum cathode in an unstirred potassium chloride solution containing some dissolved oxygen. As the voltage across the cell is gradually increased from zero, the current remains practically zero until the voltage is high enough to cause some oxygen to be reduced at the cathode. At
this point the current begins to increase with increasing voltage.

As the voltage is further increased, the current rises more slowly and finally is almost constant. This nearly constant current is called the limiting current. In this voltage range, the electrode is polarized so that the current does not change when the voltage is varied slightly.

The thing that limits the current of this polarized cell is the rate at which oxygen is diffusing to the cathode. The current is related to the amount of oxygen diffusing by Faraday's Law according to which one Faraday, 96,500 coulombs, of electricity will flow for each gram-equivalent of oxygen reduced.

The limiting current is a measure of the rate of diffusion to the electrode. The rate of diffusion depends on the concentration of the solution. So the current in the polarized cell is a measure of the concentration of oxygen in the solution.

The concentration of potassium chloride and the area of the silver anode both must be large enough so that the anode never becomes polarized.

If the platinum electrode and that part of the solution across which exists the concentration gradient have known dimensions and a simple shape, it may be possible to determine $D$, the diffusion coefficient, directly from the limiting current of the cell.

For one dimensional, steady state, diffusion of a reducible substance from a region where the concentration is $C_1$ to a platinum cathode where the concentration is $C_2$, the diffusion current is

$$i = Dn FA (C_1 - C_2)/L$$

where $i$ is the limiting current in amperes, $D$ is the diffusion coefficient
\[ F \text{ is the Faraday; } n \text{ is the number of gram-equivalents in each mole of the substance being reduced; } A \text{ is the area of the cathode in } \text{cm}^2; \ C_1 \text{ and } C_2 \text{ are concentrations of the reducible substance and are expressed as moles/cm}^3; \text{ and } L \text{ is the distance in cm across which the concentration gradient exists.} \]

**Oxygen Electrode**

Lemon and Erickson (8) made an electrode with a short platinum wire projecting from the end of a closed glass tube. This electrode was used for measuring soil oxygen diffusion. The moist soil formed a bridge from the platinum to a calomel electrode. They maintained 0.8 volts across this cell and found that the steady state current was a good measure of the oxygen supplying power of the moist soil. An essentially steady state was reached in from three to five minutes. They expressed the diffusion rate as the grams of oxygen per minute reaching each square centimeter of platinum electrode.

Clark et al. (4) made an apparatus similar to that of Lemon and Erickson, but with a bead of platinum covered by a gas permeable membrane. This electrode was for use in determining oxygen in blood and tissues. It was stable and sensitive. They found that the increase in current with temperature was linear over the range from zero to fifty degrees centigrade. They maintained 0.6 volts across their cell.

Watanabe and Leonard (15) constructed a cell with a silver anode in a tube and a platinum cathode in the end of the tube. A gas permeable membrane was fastened over the platinum and held tightly against it.
The cell was filled with a dilute solution of potassium chloride and a potential of 0.6 volts was applied to the cell. If a reducible gas was present in those passing through the membrane, it was reduced at the platinum surface and a current flowed in the cell that was proportional to the partial pressure of the gas. They found that the current at a given oxygen level varied directly with the platinum surface area and inversely with the thickness of the membrane. The temperature coefficient was found to be about 5% per degree centigrade at room temperature. They tested their electrode with oxygen in the gas phase and with dissolved oxygen. The electrode measured only dissolved gas and was unaffected by any easily reducible ions in the solution. The electrode easily detected as low as 0.04 parts per million of dissolved oxygen in water.

By testing many membrane materials, they found polyethylene film had satisfactory permeability and gave a cell whose calibration was highly stable for a long period.
MATERIALS AND METHODS

Construction of Apparatus for Diffusion

Diffusion Cell with Two Vessels

A preliminary apparatus was constructed in which the diffusion of oxygen was from a vessel of air-saturated water through a sample of water-saturated porous medium into a vessel of nitrogen-saturated water.

This apparatus and associated stirring and measuring equipment are shown in Figure 1. In it, oxygen diffusion was shown by the decrease in current through a Beckman Oxygen Electrode in the vessel of air-saturated water. A constant temperature bath was used but is not shown.

In order to maintain the concentration gradient across the sample, it was necessary to continuously stir the vessels of air-saturated and nitrogen-saturated water.

A Leeds and Northrup potentiometer was used to measure the voltage drop across a 10,000 ohm resistance in series with the electrode. This drop was proportional to the current and so was proportional to the oxygen concentration. This system was abandoned because of difficulties in stirring, temperature control, and maintaining a steady state.

Diffusion Cell with Platinum Electrode

The cell which was finally used is shown in Figures 2 and 3. Figure 4 shows the cell along with the equipment used to supply the voltage and to record the current.

The body of the cell is constructed from plastic. It contains a silver electrode, a potassium chloride solution and a platform which
supports a platinum disc at the top of the cell. A sheet of polyethylene film is held against the platinum by a tight fitting plastic ring. A second sheet of polyethylene is held 3 mm from the first by another plastic ring which is screwed to the bottom ring. As the apparatus is assembled the sample is placed between the two sheets of polyethylene.

The anode consists of one ounce of silver ribbon 0.005 inches thick. A silver wire welded to the anode leads out of the cell. The cathode is a disc of platinum three inches in diameter and 0.0025 inches thick. A copper wire is soldered to the back of the platinum and leads out of the cell through a hole in the platform.

The platinum is cemented to the platform with insulating varnish. This varnish seal keeps the electrolyte away from the solder joint.

Associated Apparatus

Voltage Control

A voltage divider with a total resistance of 100 ohms is used to apply 0.6 volts across the cell. The power is supplied by two number six dry cells in series. The voltage across the cell is monitored with a Simpson vacuum tube voltmeter. The voltage divider, dry cells, and switch are mounted in a plastic case.

Recording

The current through the diffusion cell is recorded by a Sargent 8-72150 recorder. In the ranges used, the recorder balances itself against the voltage drop across a 1.000 ohm resistance. This drop is recorded on a scale calibrated in microamperes.
Figure 1. Preliminary Diffusion Apparatus
Figure 2. Diffusion Cell
Figure 3. Schematic Diagram of Diffusion Cell
Figure 4. Diffusion Cell with Associated Equipment
PROCEDURE

To determine $D/D_0$ for a sample with the cell illustrated in Figures 2, 3, and 4, the cell was assembled with water in the sample chamber and $i_o$, the steady state current, recorded. The water was replaced by a saturated sample and $i$, the steady state current for diffusion through the sample, was recorded. The factors, $n$, $F$, $A$, $C_1$, $C_2$, and $L$ (equation 6), are the same for both the $i$ and the $i_o$ procedures, therefore we may say $D/D_0 = i/i_o$.

As the cell was assembled a few drops of potassium chloride solution were placed on the platinum which was then covered with a polyethylene membrane. This membrane was held taut by the ring that fitted onto the body of the cell. The water or the water saturated sample was poured onto the polyethylene until the ring was filled. The sample was leveled with a straight edge. Another membrane was placed over the sample and secured under a second ring which was fastened by screws to the tight fitting ring. The polyethylene membranes were trimmed outside the rings then the joints were sealed with beeswax or paraffin.

The cell body was filled with the electrolyte, a saturated potassium chloride solution.

The voltage divider and recorder were connected so that a potential of 0.6 volts was maintained across the cell and so the cell’s current was recorded. The potential across the cell was occasionally adjusted back to 0.6 volts until the current became constant. The room temperature, the recorder scale in use and the sample identification were noted on the recorder chart along with the plot of current versus time.
The equipment was kept in a small room in the interior of the building. The door was kept closed and the lights out so the temperature would stay nearly constant. A separate $i_0$ (the current from diffusion through water) was measured just before each measurement of $i$. The cell was affected by increases in temperature and atmospheric pressure but by taking a separate $i_0$ for each $i$ these effects were minimized. A greyish brown color appeared on the platinum after a few days and a grey coating appeared on the silver. Neither contamination appeared to affect the readings but the platinum was cleaned occasionally.

The porous media used were sand, glass beads, glass wool, kaolinite, and mixtures of these.

The volume of the sample was calculated from the depth and diameter of the sample compartment. There was some difficulty in filling the compartment the same each time. It was especially difficult to get the sample compartment level full of water. Each sample was dried and weighed, and its bulk density was determined. The porosity of each sample was calculated from the formula

$$\text{porosity} = 1 - \frac{\text{bulk density}}{\text{particle density}}.$$  

The particle densities of the sample materials were determined with pycnometer bottles except that the particle density of kaolinite was taken from *International Critical Tables* (6).

The porosities were plotted against $D/D_0$ and the resulting curve compared with Penman's curve for air-saturated porous media.
EXPERIMENTAL RESULTS

Measurements of D/D₀ and porosity were made on materials from Table I. The left hand column lists the materials which were used pure or in mixtures. The center column further characterizes these materials as to their source. The column on the right lists the particle density for each material.

Table II in the left hand column tells what porous materials or mixtures were used as samples. The center column lists the porosity of each sample as calculated from the sample volume, weight and particle density. Different porosities were gotten with 0.0011" glass beads by different amounts of packing. In order to get two different porosities with glass wool one sample was prepared by cutting the glass with a scissors into about 1/16 inch lengths, while the other was prepared by grinding. The ground sample had a lower porosity than the cut sample. The last column lists the experimental values of D/D₀, the ratio of the diffusion current with the porous media to the diffusion current with pure water.

Figure 5 is a plot of D/D₀ versus porosity from the data of Table II. All of the points marked by dots fall approximately on a line. The points marked by crosses are the samples containing kaolinite. They appear to be governed by some different relationship between D/D₀ and porosity. The linear regression of the points marked by dots was calculated and is shown by the solid line. The equation of the line is

\[ Y = 0.026 + 0.67X \]

It does not include the kaolinite points.
<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Particle density</th>
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<tbody>
<tr>
<td>Sand</td>
<td>Ottawa fine sand</td>
<td>2.64</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Clay mineral standard</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>(Birch pit No. 2 Macon, Ga.)</td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>3 M type 130 (0039&quot;)</td>
<td>2.47</td>
</tr>
<tr>
<td>Glass beads</td>
<td>3 M type 380 (0011&quot;)</td>
<td>2.29</td>
</tr>
<tr>
<td>Glass wool</td>
<td>Pyrex brand No. 800</td>
<td>2.49</td>
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### TABLE II. RESULTS FOR MEDIA OF VARIOUS POROSITIES

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<tr>
<th>Porous material</th>
<th>Porosity</th>
<th>D/D₀</th>
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<tr>
<td>1/3 sand, 2/3 .0011&quot; beads</td>
<td>.281</td>
<td>.198</td>
</tr>
<tr>
<td>.0011&quot; beads</td>
<td>.409</td>
<td>.287</td>
</tr>
<tr>
<td>.0011&quot; beads</td>
<td>.426</td>
<td>.333</td>
</tr>
<tr>
<td>.0011&quot; beads</td>
<td>.439</td>
<td>.353</td>
</tr>
<tr>
<td>Glass wool, ground</td>
<td>.746</td>
<td>.485</td>
</tr>
<tr>
<td>Glass wool, cut</td>
<td>.934</td>
<td>.674</td>
</tr>
<tr>
<td>1/5 kaolinite, 4/5 .0039&quot; beads</td>
<td>.642</td>
<td>.281</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>.718</td>
<td>.294</td>
</tr>
</tbody>
</table>
Figure 5. Plot of $D/D_0$ Versus Porosity

Regression line

$Y = 0.026 + 0.67X$
DISCUSSION

The data of Table II indicate that for diffusion of oxygen through some saturated porous media the relationship between diffusion and porosity is near that for dry porous media. The linear regression showed a slope of 0.67 when the kaolinite samples were excluded. This can be compared to the slopes found by Penman (0.66) and van Bevel (0.6). The data fitted this slope for the range in porosity from 0.3 to 0.9. It is expected that in the high porosity range the slope must increase sharply to give $D/D_0 = 1$ for pure water.

The low rate of diffusion through saturated kaolinite may indicate that when a kaolinite particle is wetted its effective cross section for resisting oxygen diffusion is increased. Penman's data for dry kaolin do not show this high resistance to diffusion of oxygen. It is thought that this lowering of $D$ by wetting might be due to the binding of some water on the particle surfaces, to a swelling of the particles or to a change in particle orientation of the particles upon wetting. This is a possibility for further investigation.

The above results now enable one to apply diffusion theory to the liquid as well as to the gas phase in a porous medium. As an example to show how the results from the diffusion cell might be used in a diffusion problem consider a spherical yeast cell, Saccharomyces, surrounded by a spherical shell of water saturated porous media. The question to be considered is what is the greatest shell thickness through which steady state diffusion can supply adequate oxygen for the yeast cell?

The rate of oxygen consumption, $q$, by a yeast cell is $1.8 \times 10^{-12}$
liters/hour \((2.2 \times 10^{-17} \text{ moles/sec})\) (12). If it is assumed that its
density is one, \(b\), the radius, can be calculated from its weight (12) to
be \(3.5 \times 10^{-4} \text{ cm}\). If it is also assumed that the concentration of oxygen
at the cell's surface is zero, and that the concentration, \(C\), of oxygen
at the outer surface of the shell is \(2.2 \times 10^{-7} \text{ moles/cm}^3\) then the rate
of diffusion through a shell of radius \(a\) is given by (1)

\[
q = 4 \pi DCab/(a - b).
\]

(7)

Do for oxygen diffusing in water (6) is about \(1.70 \times 10^{-5} \text{ cm}^2/\text{sec}\). If a
porosity of 0.4 is assumed, \(D\) can be estimated from \(D/D_o = 0.668\). This
gives \(D = 4.5 \times 10^{-6}\). With these values, equation 7 shows that the single
yeast cell can be supplied with adequate oxygen through any thickness
of the porous medium.

As another example under the same conditions, consider an alfalfa
seed of radius \(7.8 \times 10^{-2} \text{ cm}\) which uses \(2.6 \times 10^{-9} \text{ moles/sec}\) (12).
Equation 7 indicates that \(2 \times 10^{-5} \text{ cm}\) is the greatest shell thickness
through which steady state diffusion could supply adequate oxygen to the
seed.
An electrolysis cell for measuring the rate of diffusion of oxygen was developed. The cell provides a readily measurable current which is proportional to the rate of oxygen diffusion through a sample. It is adapted to liquid and saturated granular samples. The results obtained with the cell indicate that the effect of porosity on diffusion in a water-saturated porous medium is similar to the effect of porosity on diffusion in a dry porous medium. The experimental results gave a linear regression with slope .67. This is near Penman's widely used value of .66 for diffusion in dry solids.

SUMMARY
LITERATURE CITED


