# THE ESTIMATION OF DISSOLVED OXYGEN CONCENTRATIONS IN SOILS WITH BARE, STATIONARY PLATINUM WIRE ELECTRODES

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**This is to certify that the**

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# ABSTRACT

## THE ESTIMATION OF DISSOLVED OXYGEN CONCENTRATIONS IN SOILS WITH BARE, STATIONARY PLATINUM WIRE ELECTRODES

by Gerald Hald Brandt

The estimation of oxygen concentration with solid, stationary, platinum wire electrodes was attempted using oscillographic polarography. Studies were conducted both by calibrating electrodes in media equilibrated with gases of known oxygen concentration and by calculating dissolved oxygen concentrations from measured diffusion currents by application of diffusion theory. Linear diffusion was assumed for path lengths that were short compared to the electrode radius.

A square direct current pulse of -0.75 volt was applied to obtain diffusion currents for calibration of the electrodes and for calculation of oxygen concentration. A rectified triangular wave which charged the electrodes from 0 to -0.75 to -1.0 volt in periods from fractions of seconds to seconds was applied to record complete polarograms.

These were tested in 0.01 N KCl solutions, in suspensions of bentonite made up with 0.01 N KCl, and in samples of soil aggregates. These systems were adjusted to various oxygen tensions with gases of known concentration. Measurements were also made in several other air saturated salt solutions and in single aggregates that had been incubated both with and without dextrose.

Diffusion currents that were the average of four individual electrode readings varied in several ways: (1) electrode sensitivity decreased in solutions containing reactive materials such as $Cl^-$; (2) the application of -1.0 volt to electrodes for several hours restored sensitivity of old electrodes and increased the sensitivity of new electrodes; (3) the time allowed for equilibration between the electrode surfaces and the media was important in both oxygen containing and oxygen free samples, particularly where reactive materials were present. Unexplained inherent variability was also prevalent among individual electrode readings.

Glass mounted platinum electrodes with mercury junctions produced maximum products of $\Delta i\sqrt{t}$ at about 0.5 second diffusion time in bentonite suspensions and in most of the salt suspensions. Oxygen concentrations calculated

for aerated dilute salt solutions averaged 9.58 ppm. and ranged from 9.3 to 10.9 ppm. These were slightly higher than the approximate known concentration of 9.0 ppm. at 20°C.

Even though bentonite suspensions yielded diffusion currents that were closely related to oxygen concentration, subsequent measurements in soils were very erratic. Low and erratic oxygen reduction currents were most prevalent in soils either when no electrolyte was added or when adjusted to 20 cm. moisture tension. The electrode surface was apparently charged slowly in soils and oxygen was not reduced at a maximum rate at less than one second after circuit closure.

Relative oxygen concentrations were measured in aggregates wet with 0.01 N KCl to less than 5 cm. moisture tension. Oxygen concentrations were reduced to very low value at 3 mm. below the aggregate surface after 10 hours incubation with dextrose and after 30 hours without dextrose.

A number of problems involved in measuring dissolved oxygen concentrations were defined. A major difficulty in obtaining valid measurements of oxygen concentration with bare platinum wire electrodes involved variability in the electrodes themselves. This problem and other attendant difficulties appear solvable.

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By

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The author wishes to express his thanks to his wife, Evelyn, by dedicating this dissertation to her. This represents only a small token of appreciation compared to the many hours of work, support and sacrifice that she contributed toward its completion.

Thanks is offered to Michigan State University, the Graduate School, the College of Agriculture and the Soil Science Department for providing the facilities for conducting this research and the faculty for guidance of this study. Sincere appreciation is extended especially to Dr. A. E. Erickson for his guidance, encouragement and support.

## TABLE OF CONTENTS

# LIST OF TABLES

Table Page

Appendix Tables

# LIST OF FIGURES

# CHAPTER I

## INTRODUCTION TO THE PROBLEM

The field of soil aeration has experienced a recent rapid change in emphasis from the measurement of oxygen concentrations in the soil air to the measurement of oxygen diffusion rates within the liquid phase. This shift was initiated by two major influences. First, early workers suspected that movement of oxygen through the liquid phase to sites of oxygen consumption restricted aerobic metabolism in both plant roots and soil microorganisms. Secondly, the electrometric reduction of oxygen was applied to soils by Lemon and Erickson (19) and permitted measurement of oxygen diffusion rates. Studies involving the measurement of diffusion rate have demonstrated that the rate of oxygen consumption, and the limiting diffusion rate of oxygen in the liquid phase exert profound environmental influences on microbial populations and plant roots.

Therefore, there is currently a very strong interest in quantitatively characterizing both oxygen availability to biological processes in the soil and the relationship

between oxygen availability and metabolism. This characterization requires measurement or estimation of both oxygen concentrations and oxygen diffusion rate. Concentrations of oxygen need to be examined at the surface of roots and in the vicinity of microorganisms while they are actively using oxygen. By relating such measurements to plant and microbial responses in variously aerated liquid media and soil cultures, a more complete understanding of aeration as it is related to soil-plant and soil-microbial relationships should result.

Oxygen availability in soils is easily characterized in either the saturated state or the air-dry state. In saturated conditions dissolved oxygen is rapidly reduced to very low concentrations (21, 27, 29), while in dry conditions aeration is not a limiting factor. However, at moisture contents slightly below saturation, difficulties are encountered in precisely characterizing oxygen availability. In the soil, local conditions of oxygen stress are located adjacent to aerobic sites. Plant roots and microorganisms within the soil matrix must compete for available oxygen in this heterogeneous and dynamic environment.

To describe the environment as it relates to metabolism within plant roots, a measurement of average oxygen concentrations and average oxygen diffusion rates using platinum electrodes would perhaps be most relevant. Roots, reasonably, will be found in both aerobic and moderately anaerobic microenvironments. Consequently, the extent of aerobic metabolism within roots should be governed by the ratio of the aerobic to the anaerobic environments adjacent to roots. A measure of both average concentration and diffusion values should reflect the conditions of oxygen availability as they influence total root metabolism.

Oxygen availability within microenvironments must be characterized in a much more detailed but somewhat hypothetical manner. Models of the macro- and microstructure may be constructed using idealized physical matrices. Currie (4) presented such a model. Calculations based on his theoretical matrix gave hypothetical concentration gradients that should have been found within aggregates if bulk oxygen consumption rates that he measured were representative of use rates within aggregates, and if oxygen was consumed at a uniform rate throughout the aggregate. Anaerobic interiors were predicted by his models for larger aggregates with given physical properties. Similar models could be constructed for aggregate systems with moisture films and menisci incorporated at various moisture tensions. By imposing a condition of uniform oxygen consumption in one case and a condition of surfacial consumption in another case, quite different aerobic:anaerobic ratios would be obtained. To test these models, a method of measuring oxygen concentrations within moisture films and aggregates would be required.

According to the brief discussion above, measurements of oxygen concentration and of oxygen diffusion rate should be very useful for studying the relationships between dissolved oxygen and respiring bodies within the soil. In addition, these measurements can be combined with appropriate diffusion theory to calculate a purely physical aeration parameter for a given soil matrix. This parameter should be an effective diffusion coefficient for the liquid and solid phases of the soil that would be derived either from existing diffusion theory or from experimentally derived functions.

This investigation was initiated to study methods for measuring dissolved oxygen concentrations in soil systems.

## CHAPTER II

## REVIEW OF LITERATURE

### Polarographic Measurement of Oxygen

The dissolved oxygen content of liquids has been determined by polarographic methods since the work of Heyrovsky in 1924 (10). Dropping mercury electrodes have been used for many studies in liquids, and solid electrodes have been used for measuring oxygen dissolved in systems containing particles of solid or colloidal material where the dropping mercury electrode cannot be used. Because this study was concerned with the measurement of oxygen dissolved in the liquid phase of soils, only solid, stationary platinum electrodes were considered in this review.

Polarographic techniques for measuring dissolved oxygen were reviewed by Kolthoff and Lingane (14). In sections on platinum electrodes these authors draw heavily from studies by Laitinen and Kolthoff (16, 17). Their studies showed that exact mathematical analysis can be applied to diffusion currents only when they are obtained from recessed platinum electrodes. Even then, such

electrodes needed to be positioned with the recess pointed downward to that the accumulation of reduction products did not interfere with electrode kinetics. They showed that diffusion to solid platinum wire electrodes was unsymmetrical in liquids and could not be subjected to exact mathematical analysis. Convection currents that resulted from the accumulation of reaction products were suggested as the cause of high diffusion currents from bare platinum wire electrodes. In spite of these difficulties, solid platinum wire electrodes were reported to have a number of practical advantages. Consequently, various modifications of the method have been adopted for the estimation of relative dissolved oxygen concentrations and diffusion currents in animal tissue, in soils, in fermentation systems, in waste products, and in many other types of media (5, 7, 19, 27).

The technique was adapted to measure oxygen tensions in animal tissue by Davies and Brink (5) in 1942. They made both absolute diffusion measurements with recessed linear diffusion platinum electrodes and relative measurements with bare electrodes. Current readings were obtained after 20 seconds of circuit closure. Electrodes with bare platinum surfaces exhibited a decrease in calibration current with increased exposure to blood. Similar irreproducibility for bare platinum electrodes has been reported elsewhere (14). Davies and Brink reported that a semipermeable covering over the electrode recess greatly improved reliability. Similar membrane coverings are now used with commercial electrodes that measure relative oxygen concentrations in tissue.

A unique application of the principle of oxygen reduction at a solid platinum electrode was made in soil science by Lemon and Erickson (19) who proposed that the electrode would simulate oxygen consumption by a plant root. Maximum oxygen flux rates (called oxygen diffusion rates) were calculated from steady-state diffusion currents with the mathematical model for linear diffusion given by Kolthoff and Lingane (14) as obtained from Fick's First Law:

$$i_t = nFAf_{x=0,t} = nFAD\left(\frac{\partial C}{\partial x}\right)_{x=0,t} \qquad (1)$$

Similarly, the current at any time could be calculated using the expression:

$$i_t = nFCA\sqrt{D/\pi t} \qquad (2)$$

where: $i_t$ = electrode current in amperes at time t.

$f_{x=0,t}$ = moles of oxygen diffusing to the electrode at time t.

$C$ = initial uniform oxygen concentration.

D = diffusion coefficient of oxygen in cm.$^2$/sec.

n = number of electrons used per molecule of oxygen electrolyzed.

A = area of the electrode in cm.$^2$.

F = the Faraday, 96,500 coulombs.

Examination of equation (2) indicates that a plot of $i_t$ against $1/\sqrt{t}$ should yield a straight line and that the product of $i\sqrt{t}$ should be constant for cases where the linear diffusion model applies.

In recent years, a new field within polarography, called oscillographic polarography by Heyrovsky (11), has developed. The currents from short times and a variety of applied signals can be recorded photographically using standard oscilloscopes. This technique is yet untouched for measurements of oxygen concentrations in natural media.

## Oxygen Diffusion Rates and Plant Response

The oxygen diffusion technique using platinum electrodes was adapted to routine field measurements by Van Doren (31, 32). He studied some relationships between oxygen diffusion rates and plant growth, and summarized data on critical oxygen diffusion rates and on periods of growth that are most sensitive to conditions of oxygen stress. These data were reported in earlier literature for tomatoes, sugar beets, peas, wheat, potatoes, oats, and corn. In the summarized studies, oxygen diffusion rates were controlled or altered by varying aggregate size and moisture tension or moisture tension alone.

This same method of controlling oxygen diffusion rate was used in a greenhouse study with peas by Cline and Erickson (2). Growth, yield, and chemical composition of peas were related to oxygen diffusion rate up to a critical diffusion level. Coarse roots and few nodules developed under low oxygen supply.

The influence of periodic oxygen deficiency on growth and yield of plants was discussed in a review article by Erickson and Van Doren (8). Periods of oxygen deficiency that accompanied rainfall on field soils were responsible for suppressing optimum growth and yield. Stage of growth, light intensity, temperature, and fertility influenced the magnitude of depressed growth from short periods of oxygen deficiency.

In more recent studies by Letey _et al_. dissolved oxygen concentrations and diffusion rates were controlled by varying the partial pressure of oxygen in the soil atmosphere. They observed responses in plant growth, root growth, water use and nutrient uptake. When the roots of cotton, sunflower, green beans (23), and snapdragons (30) were placed in nitrogen atmospheres, both shoot and root growth were markedly inhibited. Snapdragon (22) responded to increasing oxygen availability with increased water uptake and decreased Na uptake, while barley (25) showed no change in Na or Ca + Mg. The uptake of both K and P increased in barley and snapdragon under conditions of increasing oxygen availability. With sunflower and cotton, increased oxygen availability stimulated uptake of Ca and P and inhibited Na uptake, and in sunflower, K uptake was also stimulated (24). The above workers have studied effects of both soil and air temperature on relationships between oxygen diffusion rates and plant response (24, 26). Low oxygen diffusion rates in the presence of higher air temperatures were shown to be more detrimental to shoot growth than with lower air temperatures. Under conditions of oxygen stress the water uptake capacity of roots decreased. An increased water requirement at higher temperatures in the presence of a reduced water supplying capacity was apparently responsible for the decreased shoot growth observed. They also found that O.D.R. increased 1.8 percent per degree centigrade rise in soil temperature.

The preceding studies have suggested that oxygen availability to plant roots affects growth and ultimately crop yield by influencing water and nutrient uptake as well as root development. Therefore, it should prove most interesting to examine the relationships between plant metabolism and the aeration status of roots. Kenefick (13), in 1959, measured the accumulation of ethanol in roots of sugar beet plants. He showed that ethanol accumulated in considerable quantities with the entire plant under low oxygen tensions and in much smaller quantities when only the roots were anaerobic. The accumulated ethanol was removed from the plant by transpiration from the leaves and was transpired actively while only the tap roots were placed in anaerobic conditions.

A recent study was conducted with tomatoes (9) to investigate changes in plant metabolism that accompany conditions of oxygen stress in soils. Ethanol accumulation was clearly related to low oxygen diffusion rates. However, oxidative decarboxylation of pyruvate was not the first inhibited step in anaerobic metabolism. Abnormal accumulations of several metabolic intermediates and by-products were observed by $C^{14}$ and chromatographic techniques.

The studies cited above establish conclusively that the diffusion measurements obtained with platinum microelectrodes are a reliable measure of the rate at which oxygen can be supplied to plant roots from the liquid phase of soils. This is true over the range of moisture contents where oxygen may be limiting to crop growth.

## Availability of Oxygen to Plant Roots

A theoretical approach to the relationships between dissolved oxygen and plant roots has been presented in a sequence of papers by Lemon (18), Lemon and Wiegand (20), Weigand and Lemon (33), and Covey and Lemon (3). They used the model of diffusion through a uniform cylindrical shell to calculate oxygen concentrations present at the surface of roots, $C_r$. Their calculations of $C_r$ were used to predict whether oxygen availability at roots was optimal or suboptimal in accordance with known critical oxygen levels in solution. When cotton was grown on Miller clay at moisture tensions in the 1 to 4 atmosphere range, cotton yield showed some correlation with calculated values of $C_r$ (33).

Lemon (18) showed that the problems of oxygen supply in the soil and oxygen demand by plants cannot be theoretically separated. He pointed out that critical oxygen concentrations, $C_r'$, are those that reduce axial root concentrations to zero. Thus, metabolic uptake of oxygen is a hyperbolic function of increasing oxygen concentration. The rate of oxygen uptake by roots increases until the dissolved oxygen concentration at the root surfaces is equal to $C'_r$ and then the uptake rate levels off at a maximum. Because this critical dissolved oxygen concentration must be maintained at root surfaces before aerobic metabolism predominates within roots, oxygen concentration is fundamental to the problem of plant responses to dissolved oxygen.

The calculation of $C_r$, using the method proposed by Covey and Lemon (3), involves several assumptions. Among the most damaging to the theory are two: (a) that the geometry of the root and of the water sheath around the root is of cylindrical symmetry; (b) that the oxygen sink strength exterior to the root is negligible. Covey and Lemon pointed out that the assumed geometry does not hold for a single measurement but tends to be approached on the average. Diffusion currents diverged from the model in all cases at diffusion times greater than three minutes. The authors recognized that the model cannot be true to nature because the root-liquid and liquid-gas interfaces possess geometries that are unique and complex for each single measurement.

The second limiting assumption, that the microbial population represents a negligible oxygen sink, is contrary to evidence. In soil systems, oxygen diffusion measurements have reflected significant fluctuations in the microbiological demand for molecular oxygen (1). In pure culture studies polarographic measurements showed that dissolved oxygen concentrations were reduced to almost zero in less than 80 seconds in cultures of *Serratia marcescens* (21). This organism is involved in the aerobic decomposition of proteins. Almost complete oxygen removal in a period of 40 minutes has been observed in a suspension of the fungus *Pencillium chrysogenum* (28). These pure cultures undoubtedly consumed oxygen at a higher rate than is normal for the general microbial population in soils. However, in the rhizosphere the activity of the microbial population greatly exceeds that of the normal soil population. It is to be expected that sizeable oxygen sinks exist externally to root surfaces.

The importance of obtaining valid values for oxygen concentrations at the surface of roots was emphasized by Lemon and Weigand (20) in a recent review of studies on root respiration as related to oxygen availability in the surrounding media. As they point out, the rate of oxygen consumption is greatest at the growing root tip for many plants and that roots display a lag in returning to normal metabolism after anaerobic conditions have been encountered. The latter phenomenon may be related to the "leaky" conditions which roots develop in anaerobic environments.

## Summary

The need for a method to estimate or measure dissolved oxygen concentrations in the solution phase of soils has arisen (a) from a desire to relate responses that have been observed with diffusion measurements in soil-plant studies to $O_2$ partial pressure studies in pure cultures, (b) from studies relating biochemical responses to oxygen diffusion rates, (c) from attempts to calculate critical oxygen concentrations at root surfaces, (d) from microbiological studies that suggested the presence of local microclimates, (e) from theoretical calculations for oxygen concentrations in microenvironments, and (f) from a desire to further explore the purely physical relationships between dissolved oxygen and the soil matrix.

# CHAPTER III

# CONSIDERATIONS IN THE MEASUREMENT OF DISSOLVED OXYGEN CONCENTRATIONS IN SOILS

The search for methods for measuring oxygen concentrations at root surfaces and within microenvironments must be guided by theoretical concepts regarding the nature of these environments, their geometry, and their abundance. The relationships to be characterized between oxygen availability and biological processes of the soil must also be considered. This section contains discussions of the nature of oxygen availability within microenvironments, the relationship of average dissolved oxygen concentrations to root respiration, and the general nature of the measurement with reference to the steady-state sink as contrasted to a short-term oxygen sink.

## $pO_2$ Gradients in Microenvironments

Currie (4) recently presented profiles of oxygen concentration that would have been expected within respiring aggregates of different radii with given physical properties

(Figure 1). Oxygen consumption rates for the whole soil body were assumed to apply to individual crumbs within that body. He also assumed that oxygen was consumed at a uniform rate at all depths in aggregates and subsequently predicted that oxygen was deficient in the center of aggregates above a given diameter. Optimum crumb size was nicely demonstrated by his model, but the scheme may only approximate the profile of oxygen tensions within an aggregate. If oxygen consumption were largely a surfacial phenomenon, then anaerobic interiors would be predicted for much larger aggregate volumes than would be predicted with the model of uniform consumption. With the proper micro-technique, the model of uniform respiration could be tested against that of surfacial oxygen consumption. This same micro-technique might also be used for detecting the presence or absence of $pO_2$ gradients in moisture films and menisci either by direct measurement or by inference from studies in capillary tubes.

To accurately characterize oxygen status in microhabitats, the method must incorporate small electrode size with a technique for accurately determining electrode position. The values obtained should make it possible to relate variations in microbial activity to position dependent variations in oxygen availability.

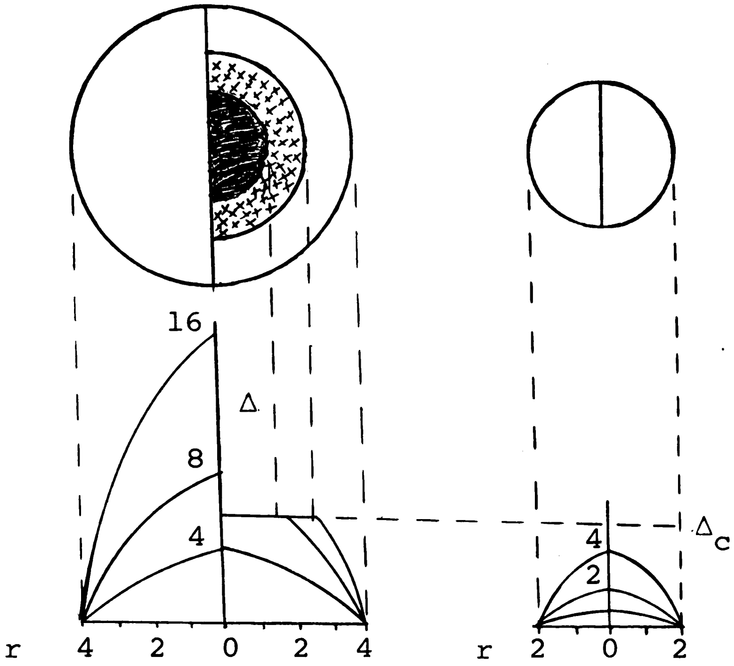

Figure 1. Oxygen profiles in respiring aggregates of different radii.

The vertical axis gives radial concentration changes for three values of Sc/Dc (the respiratory activity of a crumb/coefficient of diffusion in the crumb). The left-hand grid gives concentration gradients, Δ, where low $O_2$ concentrations would not inhibit growth and the right-hand grid gives concentration gradients, where a critical oxygen concentration, $\Delta_c$, inhibits growth (from Currie, 4).

## Average $pO_2$ Values

Tedious characterization of minute environments could not be expected to yield values of oxygen availability which would correlate with gross plant response. It seems reasonable to assume that oxygen diffusion within roots and movement of anaerobic and aerobic metabolites within roots are capable of "averaging" the effect of local microclimates on root respiration. Therefore, a measure of the average concentration of oxygen in the soil solution would seemingly be a more realistic measure of oxygen tension at root surfaces. Such an average measurement of concentration can be obtained by using larger platinum electrodes similar to those which have been used for diffusion measurements (19). One of the great difficulties of such a method is that the large electrode will not detect the decrease in oxygen concentration caused by the rhizosphere population immediately adjacent to the root. It appears possible that a microtechnique may be used to detect decreases in oxygen concentrations at the root surface caused by aerobic respiration among the microorganisms and within the plant root. Surfacial root concentrations may in turn be related empirically to average oxygen concentrations in soils.

## The Nature of Methods for Measuring Dissolved Oxygen

The preceding two sections described some of the relationships between dissolved oxygen and biological processes in the soil that could be studied with a method to measure dissolved oxygen concentrations. Measurement within microenviornments was thought desirable for characterizing microbial responses and average oxygen concentrations were considered necessary when studying plant responses to oxygen. In either case the only requirements placed upon a possible method were that it accurately reflect oxygen concentration in a heterogeneous medium like the soil, and that it can be miniaturized.

Because the soil is made up of a solid, liquid and gaseous matrix, the measurement must be made with electrodes held firmly in place. Thus, solid, stationary platinum electrodes need to be used. Of all the platinum electrode designs that were available, only two were of interest because of the requirements that they be stationary, miniaturizable, and make intimate contact with the soil. One electrode of interest was the Beckman physiological oxygen analyzer which is a very small electrode mounted in a hypodermic needle. This electrode is calibrated in liquids of known oxygen concentration prior to making readings of relative oxygen concentration in other materials. The electrode can be used in very specialized situations such as measuring oxygen concentrations in aggregates and plant stems, but is too expensive to use routinely. The method which would be most useful in soil studies should be adaptable to routine measurements that could be obtained along with diffusion data.

Therefore, wire electrodes similar to those used for diffusion measurements were of primary interest and consequently were used in this study.

The remainder of this section will be devoted to discussion of how a concentration measurement with platinum wire electrodes might differ from measurements of diffusion current. The nature of diffusion currents and their meaning in soils will first be considered, then possible means of obtaining estimates of dissolved oxygen concentration follow.

## Diffusion Measurements

Oxygen diffusion to bare platinum wire electrodes in liquid was described in Chapter II as unsymmetrical. Studies by Laitinen and Kolthoff (16) attributed this response to convection currents in the liquid adjacent to the electrode surface. Because of this interference, diffusion to wire electrodes in liquids under normal conditions cannot be analyzed mathematically.

The soil, on the other hand, is a solid matrix rather than a liquid medium. This property minimizes the interference from convection currents and might facilitate the mathematical analysis of diffusion currents obtained from soils using special techniques.

The method currently used to measure oxygen diffusion rates in soils applies -0.65 volt to an electrode system consisting of an Ag:AgCl reference cell and a platinum electrode (31). Diffusion of oxygen to the platinum electrode approaches a steady-state diffusion rate after 3 to 5 minutes circuit closure. This was interpreted by Wiegand and Lemon (33) as being the time required to expand the diffusion sphere around the electrode in the liquid phase to the air-liquid interface where an equilibrium of dissolved oxygen concentration was maintained by gaseous diffusion.

Steady-state diffusion currents have been converted to oxygen diffusion rates by using linear diffusion theory (19). The resulting values are more appropriately called maximum flux rates rather than pure diffusion rates. That is, the calculation in this case gives the amount of oxygen approaching the wire electrode surface under steady-state conditions. It does not yield a true diffusion rate that is characteristic for the oxygen supplying medium because the diffusion to the electrode is cylindrical rather than linear. Therefore, oxygen concentrations cannot be calculated with the same mathematics used to calculate oxygen flux rates to the electrodes at normal diffusion times.

## Oxygen Concentration Measurements

The most direct means of obtaining oxygen concentrations from soil systems would be to calibrate stationary wire electrodes in media of known oxygen concentration at some shorter diffusion time. This would be a usable scheme if the attendant properties of the calibrating medium were similar to those of soils and if bare platinum electrodes could be made sufficiently reliable.

Another means of obtaining dissolved oxygen concentrations from soils is to calculate them from diffusion theory. This was attempted by Covey and Lemon (3) using cylindrical diffusion mathematics on transient diffusion currents. Their method is limited by the lack of uniform geometry and by oxygen sinks external to the roots as discussed previously (page 13). It would be desirable to construct another rational model and test the two methods against one another with plant response. Both plant yield and the presence of certain metabolites which accumulate under varying conditions of anaerobiosis might be used to test the models.

An alternate theoretical method for calculating initial oxygen concentrations should attempt to overcome the two major limitations in Covey and Lemon's model. The influence of the geometry of moisture films adjacent to the electrode surface and the affect of competing oxygen sinks, should be minimized. Both of these improvements might be realized at short diffusion times when the diffusion path length is small enough to be unaffected by moisture film geometry or competing oxygen sinks. The possibility that linear diffusion mathematics might produce valid oxygen concentrations also arises when diffusion path lengths are reduced to values that are small compared to the electrode radius. This method may also avoid convection currents that occur in liquids from the formation of reaction products.

## Studies Undertaken

In the investigations of the following three chapters, estimation of oxygen concentration was attempted both by experimental calibration of electrodes and by mathematical analysis of diffusion currents. In these studies two kinds of waves were applied to platinum wire electrodes. A square, direct current pulse was applied to obtain the diffusion currents at short times reported in Chapter IV. In this chapter diffusion currents are compared to oxygen concentration both by experimental calibration and by linear diffusion theory. In Chapter V the triangular wave was applied to obtain oxygen reduction currents. These were compared to oxygen concentration by experimental calibration only. Chapters IV and V are primarily concerned with measurements in homogeneous media, namely, bentonite suspensions and various dilute salt solutions. Diffusion data from soils, a heterogeneous medium, are reported in the next chapter, Chapter VI. Experimental calibration, theoretical analysis, and relative measurements were used to determine if diffusion currents recorded from soils were similar to those from homogeneous media.

Both Chapters IV and V are arranged similarly. The necessary theory and the principles involved in using the particular kinds of applied waves are discussed briefly. These are followed by descriptions of necessary circuitry and general methodology used in all studies within the chapter. Sections within these chapters present specific additional procedures.

# CHAPTER IV

# ANALYSIS OF DIFFUSION CURVES AT RELATIVELY SHORT TIMES

The possibility of reducing nonsymmetrical diffusion which is normally encountered with bare platinum wire electrodes to linear diffusion by measuring diffusion currents at relatively short diffusion times, led to studying the early phase of normal diffusion curves. This chapter is devoted to certain theoretical aspects of linear diffusion at short diffusion times and to testing the assumption that nonsymmetrical diffusion reduces to linear diffusion at short diffusion times in both homogeneous and non-homogeneous media.

## Application of Linear Diffusion Theory

### Diffusion Path Lengths

Linear diffusion mathematics permits the calculation of concentration gradients at any diffusion time and at any distance from the electrode. The following function was given by Kolthoff and Lingane (14) as obtained from the electrode surface at selected diffusion times.

$$\frac{C_{x,t}}{C} = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-y^2} \, dy \qquad (3)$$

The integral on the right, is the well known "error function" for which the above authors give numerical values. $C_{x,t}$ is the concentration of the material diffusing to the electrode at distance x and time t, C is the initial uniform concentration, and y is the integration variable. In this case, $z = x/2\sqrt{Dt}$ where D is the diffusion coefficient of oxygen. The value for soils, $D = 2.33 \times 10^{-5}$ $cm^2$ $sec^{-1}$, determined by Covey and Lemon (2) was used. After plotting $C_{x,t}/C$ vs z, as in Figure 2, the value for $C_{x,t}/C$ can be obtained by calculating z for any values of x and t.

These calculations for z values were made at diffusion times of 0.01, 0.1, and 1.0 second. Concentration ratios were read from Figure 2 and graphed in Figure 3 (page 29) to demonstrate the magnitude of diffusion path lengths encountered at diffusion times of one second or less. At one second of diffusion time the oxygen concentration at 100 μ from the electrode surface would be 0.84 of the bulk equilibrium concentration. One hundred microns is equal to

about one-third of the radius of an electrode made from 22 ga. platinum wire (r = 0.3219 mm). This ratio between diffusion path length and electrode radius is presented schematically in Figure 4 by a scale drawing increased one hundred fold. Diffusion from a distance of 100 μ or less to the electrode surface should be approximately linear. However, at slightly greater diffusion path lengths cylindric geometry would seemingly begin to contribute to diffusion currents. The above discussion suggests that if a short linear phase of diffusion does occur to wire electrodes, then diffusion times of one second and less should be examined for this linear phase.

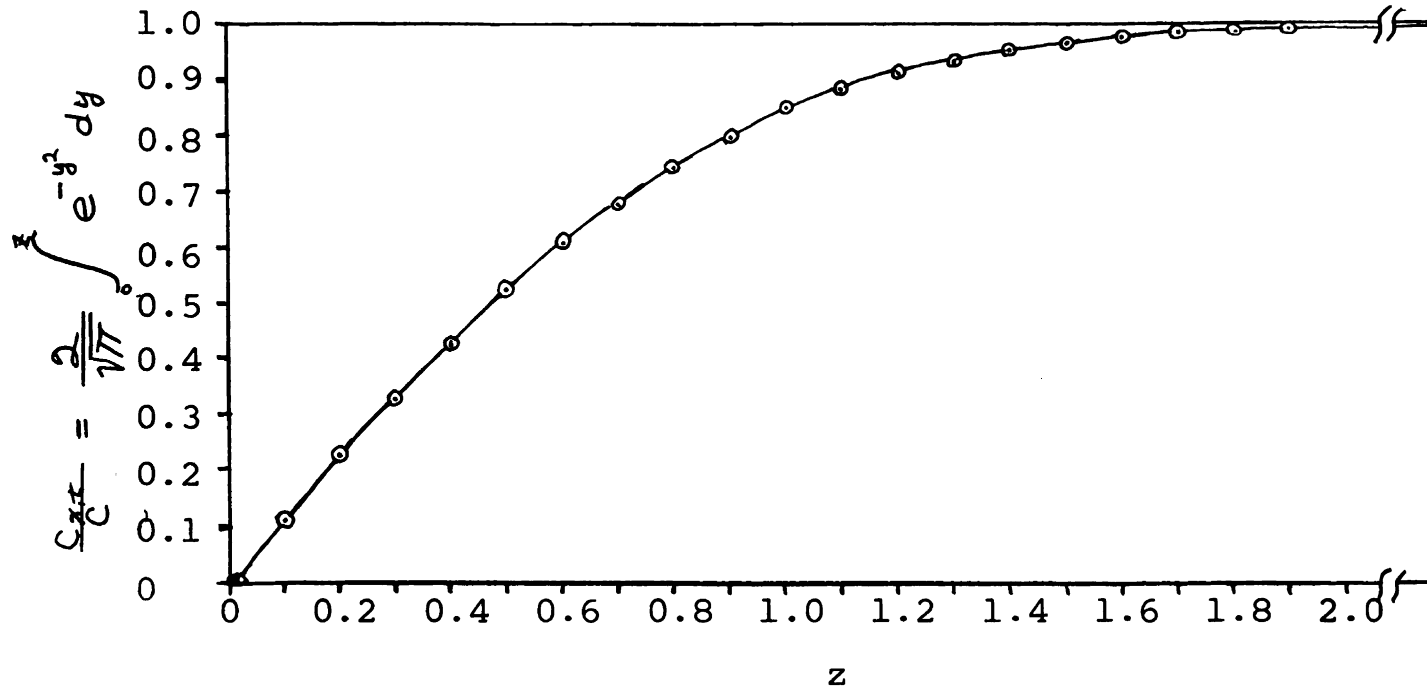

Figure 2. Concentration ratios for values of z in the "error function." (Values are from Kolthoff and Lingane, 12.)

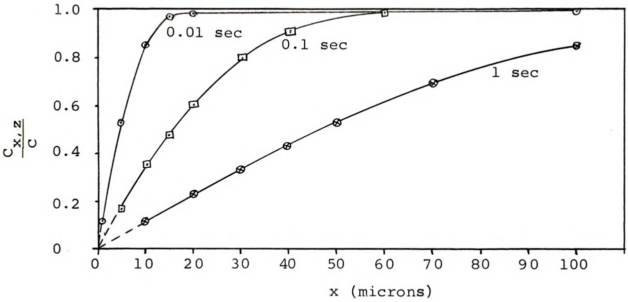

Figure 3. Oxygen concentration gradients up to 100 microns from the electrode surface for 0.01, 0.1 and 1.0 second of diffusion.

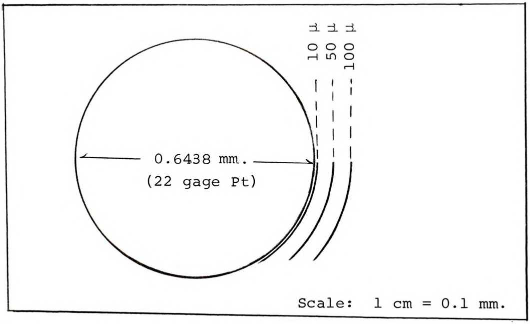

Figure 4. Diffusion shells of 10, 50 and 100 microns thickness drawn parallel to the surface of 22 ga. platinum wire (in cross section).

## Expected Limitations

Diffusion currents from short times may be confounded with transient properties encountered while the electrode surface becomes charged. First of all the electric double layer must charge to an emf. that is sufficiently negative to produce rapid oxygen reduction before the electrode behaves as an absolute sink. If the lag in charge buildup is sufficiently long, the real diffusion time will be somewhat less than circuit closure time. Secondly, the electrolyte structure will become more and more ordered as charge accumulates. This may effect changes within the double layer in the diffusion coefficient and diffusion rate of oxygen. Short-time reduction currents might be influenced further by oxygen adsorbed on the platinum surface.

Diffusion currents measured in this chapter were interpreted in light of the above complications and interference from them was overcome whenever possible.

## The Apparatus

A polarograph was needed that would produce and record diffusion currents at times of one second and less. It was necessary first to generate a direct current pulse to charge the electrodes. Then a technique for automatically presenting the diffusion curve on an oscilloscope and recording the curve was required. This apparatus was developed from two basic electronic instruments: a low frequency function generator and an oscilloscope. A simplified schematic diagram of the instrumental hook-up used with these basic units is given in Figure 5.

## General Description of the Circuit

The pulse generator. Preliminary studies were conducted to determine the approximate range of operating characteristics that were required in the pulse generator. These studies demonstrated that a negative voltage could be applied to the electrodes for only one hundredth of the

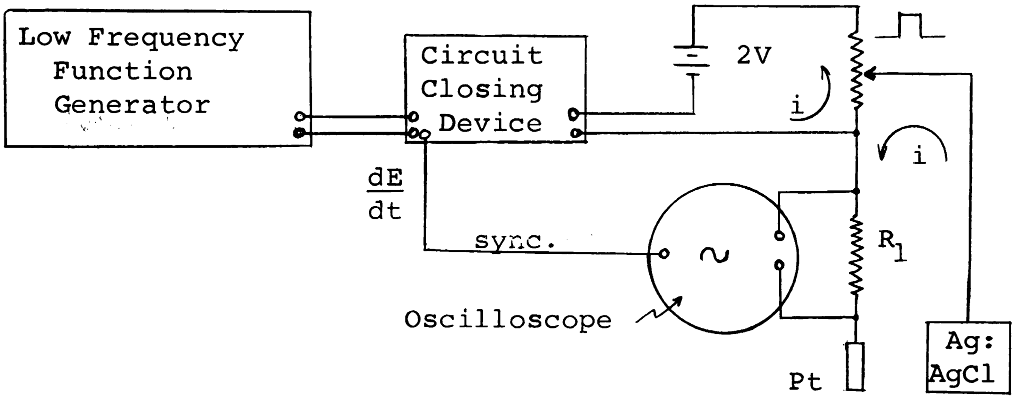

Figure 5. Simplified schematic diagram of the oscillographic polarograph that applies a direct current square wave to the electrodes. A detailed schematic appears on page 35.

total time between pulses to allow full recovery of oxygen concentration at the electrode surface. With a lower ratio of "off-time to on-time" reduction currents declined during successive pulses. A similar criterion was established from triangular wave data in Figure 25 on page 112.

A widely versatile pulse generator that possessed the above requirement was made from several separate parts. The square wave from a low frequency function generator was fed to a circuit closing device (Figure 5). This device contained a relay that closed the voltage control circuit, which in turn contained a voltage source and a voltage divider. By using these components the pulse could be varied in duration, frequency and amplitude. Pulse duration was adjustable from 0.1 to 50 seconds. The longest cycle time of the generator, 100 sec./cycle, limited the maximum pulse duration to 50 seconds. The pulse recurrence time was adjustable from 0.1 to 99.9 seconds. Both the pulse duration and the pulse recurrence time were adjustable between the above extremes.

The voltage source and the voltage divider were placed in series with the circuit closing relay. They provided voltage from zero to two volts to charge the electrode circuit. The voltage source needed only to supply sufficient current so that the electrodes in the circuit would exert an insignificant influence on the applied voltage.

The electrode circuit was arranged so that pulses could be applied either automatically as governed entirely by the pulse generator or manually as controlled by a manual switch. The manual switch merely closed the electrode circuit prior to pulse generation.

The recording device. Diffusion curves were recorded using techniques from oscillographic polarography. The oscilloscope trace was synchronized with the pulse applied to the electrodes by a capacitive pulse from the circuit closing device (Figure 5). This facilitated automatic presentation of the diffusion curve. A "Polaroid" camera was then used to record the curve.

The oscilloscope was coupled to the electrode circuit by inserting a precision (± 1%) resistor across the scope terminals in series with the platinum electrode. If a 1000Ω resistor was used, the observed pulse amplitude in millivolts could be read directly as microamperes current flow to the electrode. One hundred microamperes flowing through a 1000Ω resistor will decrease the applied voltage by 0.1 volt and thus seriously alter an applied voltage of -0.65 volt. When currents were in the 20 to 30 microampere range, a 1000Ω resistor was used for convenience, but at higher current flows smaller precision resistors down to 120Ω were used.

## Detailed Circuit Operation

Both a block diagram and a detailed schematic diagram of the circuits used are given in Figure 6. A Hewlitt-Packard model 202 A low frequency function generator was used. This instrument can be set to produce sine, square, and triangular waves ranging in frequency from 0.008 to 1,200 cps with an amplitude up to 30 volts peak-to-peak. The square wave output was used and fed to the switching circuit. This circuit contained a differentiating network consisting of a variable resistor and a bank of capacitors from 2 to 20 microfarads. The differentiating network received the square wave and produced a capacitive pulse that could be varied in duration by adjusting the resistance and the capacitance. The positive pulse of the differentiated wave was used to cause the tube of the switching circuit to conduct as well as to synchronize circuit closure with the scope trace. The amount of grid voltage required to make

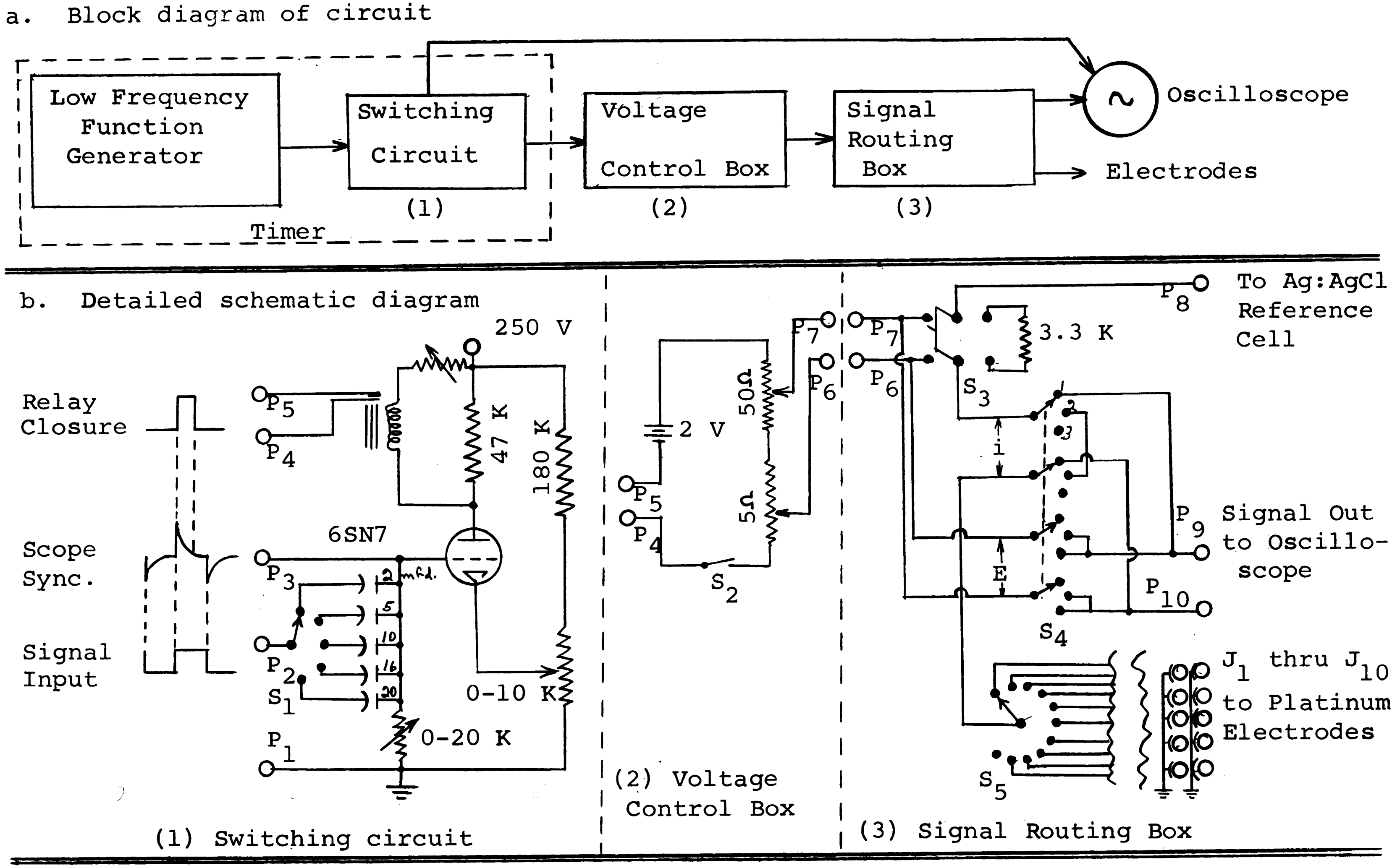

Figure 6. A block diagram (a) and detailed schematic diagram (b) of the apparatus used to apply a square d.c. pulse and measure current at short diffusion times.

the tube conduct could be adjusted with the 10 K bias resistor. As the tube was driven to conduct, the increased current flow was accompanied by a decreased voltage across the tube and an increased voltage across the plate circuit containing the relay. The relay was thus closed and remained so until the tube was near cut-off again. The duration of relay closure was governed by (a) the amplitude of the square wave, (b) the combination of adjusting the resistance and the capacitance in the differentiating circuit, (c) the adjustment of the tube bias, and (d) the adjustment of the resistor in series with the relay coil. The frequency of relay closure was dependent only on the frequency of the square wave produced by the function generator. The timer was capable of producing relay closure times from 0.1 to 50 seconds in duration and open-circuit times up to 99.9 seconds with 0.1 second closure. The first one hundredth second of the square pulse was distorted by relay "chatter." This difficulty was minimized by adjusting the relay, the differentiating circuit, and the amplitude of the input signal.

The leads from the relay in the switching circuit were connected to the voltage control circuit by $P_4$ and $P_5$. This circuit contained a 2 volt battery, a switch, and two variable resistors for adjusting the output voltage. A $5\Omega$ resistor was placed in series with a $50\Omega$ resistor to provide more accurate voltage adjustment. They were normally adjusted to give voltages between 0.6 and 0.8 volt at $P_6$ and $P_7$.

The signal routing box included three switches each with separate functions. The purpose of $S_3$ was to connect the platinum and the Ag:AgCl electrodes with the applied signal or to place them in a stand-by condition, coupled to one another through a 3.3 K resistor. By setting $S_4$ to position 1, the current flowing to the platinum electrodes was routed through $P_9$ and $P_{10}$ to the oscilloscope where a precision resistor ($\pm$ 1%) was placed across the scope terminals to convert current to voltage. With $S_4$ at position 2 the applied voltage was routed to the oscilloscope with the platinum electrode in the circuit. Position 3 of the same switch excluded the platinum electrodes from the circuit while the voltage was being measured. Switch 5 allowed for rapid switching between 10 different electrodes which were connected by shielded leads to $J_1$ through $J_{10}$. An open position between each electrode contact in this switch permitted all electrodes to be left in an "open" position, that is, uncoupled with the Ag:AgCl reference cell.

## Electrodes Used

Three different types of electrodes were used in the studies of this chapter. Epon[1] insulated electrodes similar to those used in routine field diffusion measurements, were constructed by fusing platinum wire to larger gauge copper wire and insulating with a plastic sheath on the shank and Epon adhesive for a seal to the platinum. The other electrodes were mounted in glass. One set had fused copper-platinum junctions and another set had mercury junctions. A diagram of each electrode is given in Figure 7. All the electrodes had exposed platinum tips 4 mm. long made from 22 ga. wire (d = 0.6438 mm.) unless otherwise specified.

New electrodes were made at the beginning of this sequence of studies and, prior to use, were stored for about 12 hours coupled to a Ag:AgCl reference cell with an applied voltage of -1.0 volt.[2]

---

[1] Epon adhesive VI, Shell Chemical Corporation.

[2] A rectified traingular wave (Figure 22, page 107) produced low oxygen reduction currents when applied to new electrodes. The sensitivity of these electrodes increased markedly after a negative voltage had been applied with the electrodes stored in 0.01 N KCl for up to twelve hours.

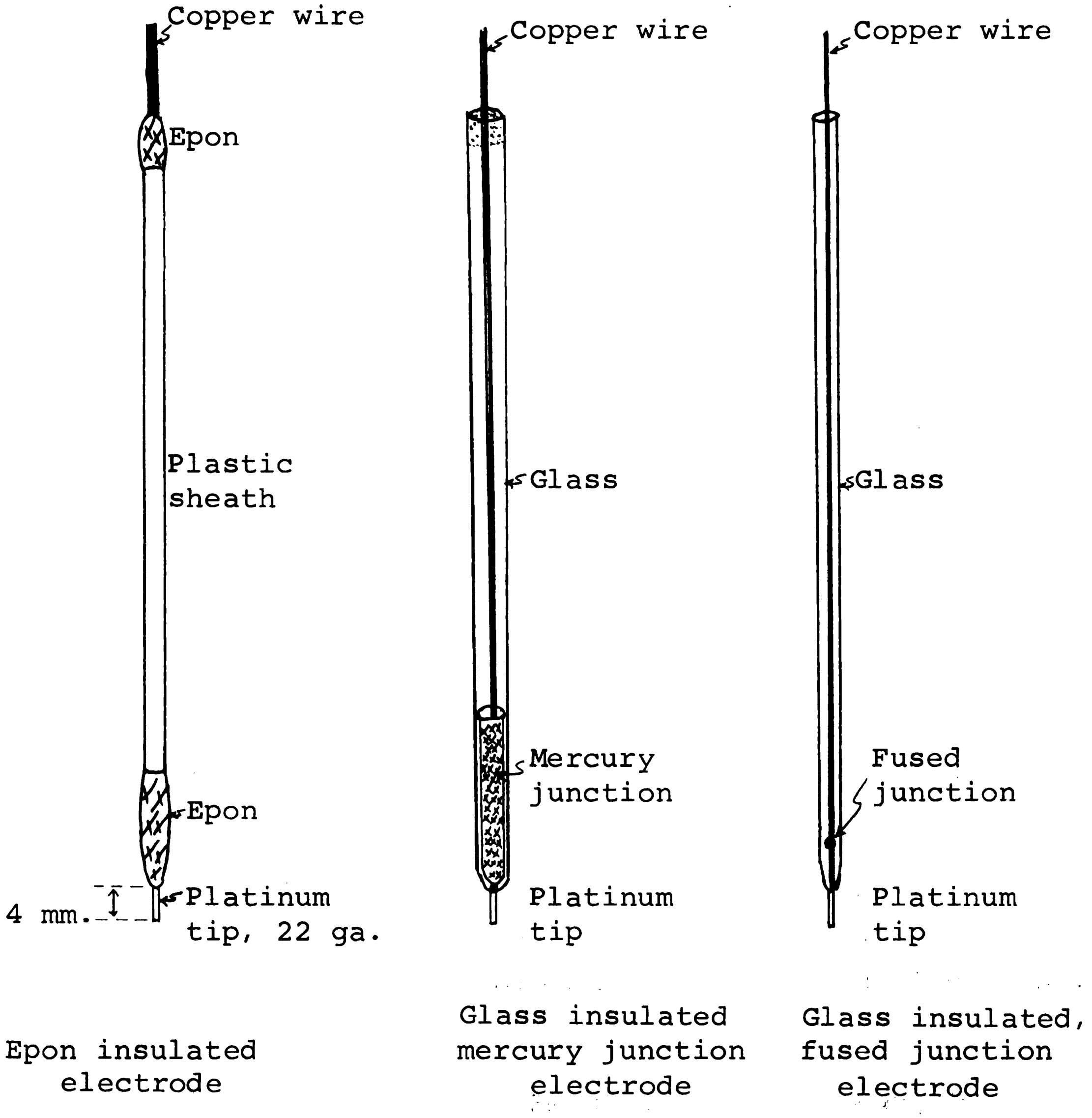

Figure 7. Diagram of three kinds of electrodes studied.

## The Procedure

Currents were read from photographs of total and residual current curves similar to the curves given in Figure 8. The top curve was recorded from an aerated liquid and the bottom curve was recorded from an oxygen free (nitrogen saturated) sample of the same liquid. The base line at the bottom represents zero current flow to the platinum electrode. In some cases both the total reduction current and the residual current amplitudes were measured from the base line so that trends in the residual current could be observed. In other cases only difference measurements were made and converted into oxygen diffusion currents. Oxygen diffusion currents, labeled $\Delta i$, were measured from each pair of photographed curves at several diffusion times. In the photograph of Figure 8 the diffusion ranged from 0 to 0.9 second and diffusion currents could be measured at 0.1 second intervals.

Data were gathered in this way from several types of media including: (1) 3% bentonite made-up in 0.01 N KCl, (2) various salt solutions of 0.01 N strength and (3) soil. Average values of $\Delta i\sqrt{t}$ were calculated from oxygen diffusion currents that were recorded from four different electrodes. These products were examined for constancy to

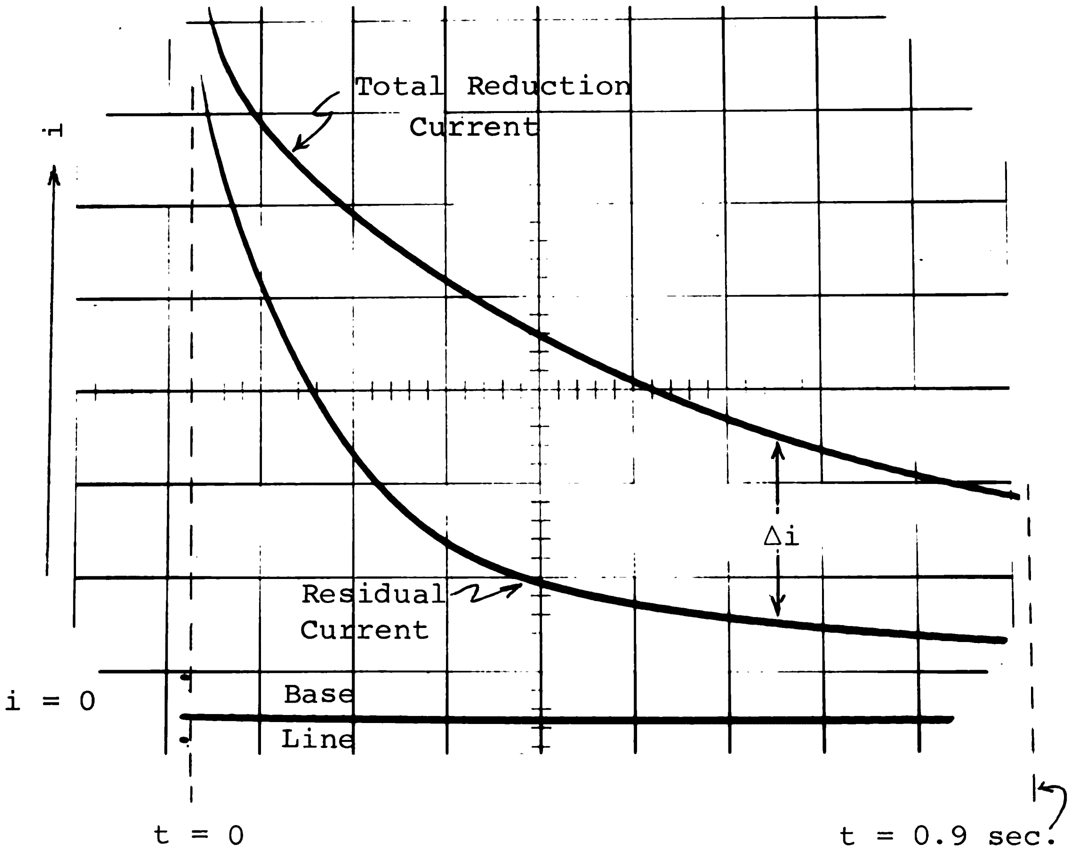

Figure 8. Typical diffusion curves from air saturated and nitrogen saturated media.

The curves are records of total reduction current on top and residual current on the bottom with a common base line. The time base along the horizontal axis was set at 0.1 sec./cm. for this photograph.

test for phases of linear diffusion.

All readings were gathered at approximately 20°C.

## Results and Discussion

The objective of the study presented in this chapter was to test for evidence of linear oxygen diffusion by application of linear diffusion theory to oxygen reduction currents obtained during short time intervals. Studies were first conducted with Epon insulated electrodes (Figure 7) at an applied voltage of -0.65 volt. Measurements were then made at more negative applied voltages and also with glass mounted electrodes.

### Preliminary Studies with Epon Insulated Electrodes

#### Measurements in KCl, clay suspensions, and soil.

Diffusion currents were recorded from three different air saturated media: 3% bentonite in 0.01 N KCl, 0.01 N KCl alone, and Kalkaska sand adjusted to 10 cm. moisture tension. Total reduction and residual current curves were recorded from four different electrodes in each of the above media. Separate pairs of curves were collected at three ranges of time. Currents at diffusion times between 0.01 and 0.08 second were recorded at a sweep time of 0.01 sec./cm. on the oscilloscope. Currents at diffusion times between 0.1 and 0.8 second were recorded at a sweep time of 0.1 sec./cm. Currents at diffusion times between 2.5 and 30 seconds were recorded at the slow sweep time of 5 sec./cm.

Individual and average values of $\Delta i$ and the products of $\Delta i\sqrt{t}$ appear in Tables 1 through 3 for diffusion times of 0.01 and 30 seconds for each media. Measurements in bentonite (Table 1) and in 0.01 N KCl (Table 3) produced diffusion currents with similar trends. Both began at high current values and generally decreased over the range of diffusion times studied. In Kalkaska sand adjusted to 10 cm. moisture tension (Table 2), diffusion currents were all very low. On the average these diffusion currents from soils decreased from short to longer diffusion times but the results for individual electrodes were erratic. In these soil samples no supporting electrolyte was added so only the cations in the soil were present to charge the electrode surface.

Two transition points appear in all the data of Tables 1 through 3. That is, a different pair of diffusion curves were used to measure the currents at 0.08 second than were used at 0.10 second. This also applies to currents at the transition between 0.8 second and 2.5 seconds. Careful

Table 1. Oxygen diffusion currents from air saturated 3% bentonite in 0.01 N KCl.

| | Oxygen diffusion current in microamperes[a] | | | | | |
|---|---|---|---|---|---|---|
| | Electrode number | | | | | |
| Diffusion time (sec.) | 20 | 21 | 22 | 23 | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
| .01[b] | 30.9 | 16.7 | 22.2 | 28.6 | 24.6 | 2.5 |
| .02 | 32.7 | 16.3 | 23.5 | 29.0 | 25.6 | 3.6 |
| .04 | 33.6 | 16.6 | 25.0 | 29.0 | 26.1 | 5.2 |
| .06 | 33.2 | 15.8 | 26.0 | 28.8 | 25.9 | 6.4 |
| .08 | 34.6 | 15.2 | 26.0 | 28.1 | 26.0 | 7.4 |
| .10 | 29.0 | 16.7 | 24.0 | 27.7 | 24.4 | 7.7 |
| .20 | 26.8 | 16.7 | 21.1 | 24.0 | 22.2 | 9.9 |
| .30 | 24.0 | 16.7 | 19.6 | 20.7 | 20.3 | 11.2 |
| .40 | 25.0 | 17.0 | 18.2 | 19.6 | 19.9 | 12.6 |
| .50 | 21.6 | 16.3 | 16.7 | 18.1 | 18.2 | 13.1 |
| .60 | 20.4 | 16.5 | 15.7 | 17.2 | 17.5 | 13.6 |
| .80 | 18.7 | ---- | 14.1 | 16.3 | 16.4 | 14.7 |
| 2.5 | 8.1 | 9.25 | 12.0 | 19.9 | 13.3 | 21.1 |
| 5.0 | 7.4 | 14.1 | 10.0 | 15.2 | 11.7 | 26.3 |
| 7.5 | 6.2 | 12.0 | 9.3 | 13.2 | 10.2 | 28.0 |
| 10 | 5.3 | 10.8 | 8.3 | 12.0 | 9.1 | 28.9 |
| 15 | 4.8 | 9.0 | 7.1 | 10.2 | 7.8 | 30.2 |
| 20 | 4.8 | 7.6 | 6.6 | 8.6 | 6.9 | 30.9 |
| 25 | 4.4 | 6.8 | 6.0 | 7.4 | 6.2 | 30.8 |
| 30 | 3.8 | 6.3 | 5.5 | 6.5 | 5.5 | 30.4 |

[a] These were obtained at the beginning of a sequence including soil, 0.01 N KCl and bentonite again with Epon insulated electrodes at -0.65 volt applied.

[b] Three separate sets of diffusion curves consisting of both an air saturated curve and a $N_2$ saturated curve were recorded to collect the above data. A sweep time of 0.01 sec./cm. was used for diffusion times from 0.01 to 0.08 second, 0.1 sec./cm. for diffusion times from 0.1 to 0.8 second, and 5 sec./cm. for diffusion times from 2.5 to 30 seconds.

Table 2. Oxygen diffusion currents from Kalkaska sandy loam adjusted to 10 cm. moisture tension and equilibrated with air.

| | Oxygen diffusion current in microamperes[a] | | | | | |
|---|---|---|---|---|---|---|
| | Electrode number | | | | | |
| Diffusion time (sec.) | 20 | 21 | 22 | 23 | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
| .01[b] | ---- | 6.5 | 17.6 | 11.2 | 11.8 | 1.2 |
| .02 | ---- | 5.5 | 17.6 | 10.2 | 11.1 | 1.6 |
| .04 | 2.7 | 6.9 | 19.5 | 12.0 | 10.3 | 2.1 |
| .06 | 4.2 | 6.9 | 21.4 | 11.2 | 10.9 | 2.7 |
| .08 | 5.1 | 6.9 | 20.5 | 10.2 | 10.7 | 3.1 |
| .10 | 4.6 | 2.3 | 20.4 | ---- | 9.1 | 2.9 |
| .20 | 5.5 | 3.7 | 16.6 | ---- | 8.6 | 3.9 |
| .30 | 4.6 | 4.2 | 15.7 | ---- | 8.2 | 4.5 |
| .40 | 4.6 | 4.2 | 13.0 | ---- | 7.3 | 4.6 |
| .50 | 4.2 | 4.2 | ---- | ---- | 4.2 | 3.0 |
| .60 | 4.2 | 4.6 | ---- | ---- | 4.4 | 3.5 |
| .80 | 4.6 | 3.7 | ---- | ---- | 4.2 | 3.7 |
| 2.5 | 2.7 | 6.5 | 4.1 | 4.6 | 4.5 | 7.1 |
| 5.0 | 4.6 | 5.1 | 4.6 | 3.7 | 4.5 | 10.1 |
| 7.5 | 5.1 | 3.7 | 5.1 | 3.7 | 4.4 | 12.1 |
| 10 | 5.5 | 2.8 | 5.1 | 3.7 | 4.3 | 13.6 |
| 15 | 4.6 | 2.3 | 5.5 | 4.2 | 4.1 | 16.0 |
| 20 | 3.7 | 1.8 | 5.1 | 4.2 | 3.7 | 16.6 |
| 25 | 4.2 | 1.8 | 5.1 | 4.6 | 3.9 | 19.5 |
| 30 | 3.7 | 1.4 | 5.1 | 4.2 | 3.6 | 19.8 |

[a] Currents are from Epon insulated electrodes with -0.65 volt applied.

[b] See Table 1.

Table 3. Oxygen diffusion currents from air saturated 0.01 N KCl.

| Diffusion time (sec.) | Oxygen diffusion currents in microamperes[a] | | | | | $\Delta i\sqrt{t}$ |
|---|---|---|---|---|---|---|
| | Electrode number | | | | Average $\Delta i$ | |
| | 20 | 21 | 22 | 23 | | |
| .01[b] | 45.6 | 15.7 | ---- | 22.2 | 27.8 | 2.8 |
| .02 | 46.2 | 14.8 | ---- | 22.2 | 27.8 | 3.9 |
| .04 | 46.2 | 14.8 | ---- | 20.4 | 27.1 | 5.4 |
| .06 | 44.8 | 13.9 | ---- | 20.4 | 26.4 | 6.5 |
| .08 | 43.0 | 13.3 | ---- | 20.4 | 25.6 | 7.3 |
| .10 | 18.8 | 17.6 | 25.8 | 24.0 | 21.6 | 6.8 |
| .20 | 18.2 | 17.2 | 23.3 | 20.4 | 19.8 | 8.9 |
| .30 | 15.6 | 17.6 | 20.0 | 17.6 | 17.7 | 9.8 |
| .40 | 14.4 | 18.2 | 18.1 | 16.7 | 16.9 | 10.6 |
| .50 | 13.0 | 18.0 | 16.7 | 15.7 | 15.9 | 11.2 |
| .60 | 11.8 | 18.2 | 14.8 | 14.8 | 14.9 | 11.6 |
| .80 | 11.1 | 16.6 | 13.0 | 16.7 | 14.3 | 12.8 |
| 2.5 | 9.2 | 10.2 | 7.6 | 13.0 | 10.0 | 15.9 |
| 5.0 | 8.3 | 8.3 | 7.6 | 10.2 | 8.6 | 19.3 |
| 7.5 | 6.9 | 6.8 | 6.6 | 8.8 | 7.3 | 20.0 |
| 10 | 6.1 | 6.3 | 6.5 | 7.8 | 6.7 | 21.2 |
| 15 | 5.3 | 5.5 | 5.5 | 7.4 | 5.9 | 23.0 |
| 20 | 4.9 | 5.1 | 4.8 | 7.8 | 5.6 | 25.3 |
| 25 | 4.6 | 4.7 | 4.6 | 7.4 | 5.3 | 26.6 |
| 30 | 4.5 | 4.4 | 4.4 | 6.9 | 5.0 | 27.8 |

[a] See Table 2.

[b] See Table 1.

examination of the currents at these two points shows that changes in diffusion currents were abnormally large in many instances. For example: at the transition between 0.8 and 2.5 seconds (a) electrode 20 in Table 1 shows an abnormally large current decrease, (b) the current for electrode 23 in Table 1 increased, (c) electrode 21 gave an increase in Table 2, and (d) in Table 3 electrode 21 gave an abnormally large decrease.

In the data of this section electrodes varied in some way from one reading to the next. The detailed data for each electrode (not presented) that were used to calculate the diffusion currents in Tables 1 through 3 were examined to see if the variability arose from variations in the total reduction current or from variations in the residual current. The residual current was fairly constant from one reading to the next, but the total current fluctuated considerably. Therefore, abnormal changes in oxygen diffusion currents resulted mostly from variation in total reduction current. This directly reflected changes in the amount of oxygen reduced at the electrodes. Vigorous stirring of the electrodes for a short time had been assumed to effect equilibration between oxygen containing media and the adsorbed oxygen on the platinum surface. These results suggest, however, that chemical equilibrium must also be established.

The average corrected currents from Tables 1 through 3 were subjected to a test for linear diffusion by plotting $\Delta i\sqrt{t}$ against t (Figure 9a) and $\Delta i$ against $1/\sqrt{t}$ (Figure 9b). The average current values produced curves which were fairly smooth in spite of the variability observed between individual pairs of diffusion curves.

Bentonite suspensions produced higher oxygen reduction currents than KCl alone (Figure 9). This should suggest that the oxygen concentration of air saturated 0.01 N KCl was below that of the air saturated bentonite. If the oxygen concentration of bentonite was truly higher, then molecular oxygen adsorbed by the colloidal particles in the clay suspension may have been responsible. Soil samples of Kalamazoo sandy loam that had been wet with distilled water and adjusted to 10 cm. moisture tension seemed to contain a smaller oxygen concentration than both bentonite and 0.01 N KCl, as expected.

The relation between oxygen diffusion currents at very short diffusion times was more apparent in the plot of $\Delta i$ vs. $1/\sqrt{t}$ given in Figure 9b. At very short diffusion times (with $1/\sqrt{t}$ greater than 5 or t less than 0.04 second)

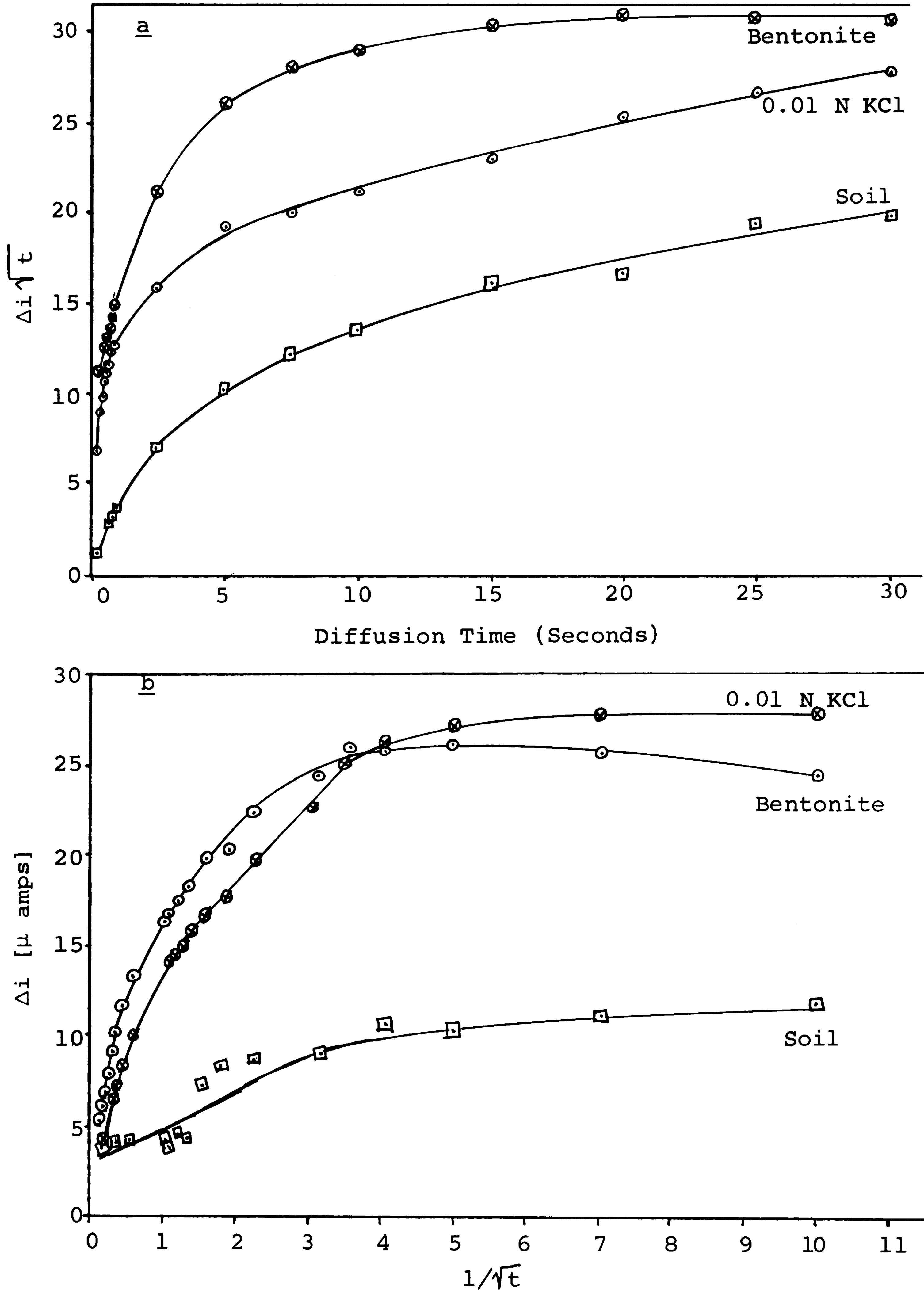

Figure 9. Tests for linear diffusion in the data of Tables 1, 2 and 3. Epon insulated electrodes were used at an applied voltage of -0.65 volt.

the oxygen diffusion current from 0.01 N KCl was greater than from bentonite, indicating that the double layer next to the platinum surface charged more rapidly in the absence of a colloid. Between values for $1/\sqrt{t}$ of 1 and 3 (t = 0.1 to 1 second) there may have been a linear phase in the KCl curve. This did not occur in either of the other media.

On the whole, the data contained in Figure 9 indicated that oxygen diffusion to a cylindrical platinum electrode had no linear phase at short diffusion times when Epon insulated electrodes with fused junctions were used at an applied voltage of -0.65 volt. According to the section on expected limitations (page 30), factors other than oxygen diffusion rate may have interfered with the rate at which oxygen was reduced in the early phase of the diffusion curve. The rate of charge build-up in the double layer and the kinetics of the reduction mechanism may both have interfered.

Electrode "drift" and variability. After the readings in Tables 1, 2, and 3 were gathered, a second group of diffusion curves were recorded for aerated bentonite. A pair of curves for each electrode were recorded at a sweep time of 0.2 sec./cm. and diffusion currents were measured at times between 0.1 and 1.8 seconds (Table 4).

A casual examination of the currents from individual electrodes in Tables 1, 3 and 4 shows that no two electrodes produced exactly the same diffusion currents. To demonstrate this point a summation of corrected diffusion currents was compiled for diffusion currents between 0.1 and 0.8 second (Table 5). The summations over diffusion currents from the initial bentonite sequence were calculated from the individual currents in Table 1, those from the sequence in 0.01 N KCl were calculated from currents in Table 3, and those from the final sequence in bentonite were calculated from Table 4. The summation of currents for individual electrodes varied for each electrode within a sequence. They also varied from one diffusion curve to the next that were recorded with the same electrodes in different sequences. The average values in the last column decreased fifteen percent from 138.9 to 115.8. These represent the averages from the initial and the final bentonite sequences, respectively. Davies and Brink (5) similarly reported 15% variability in diffusion currents from platinum electrodes used to measure oxygen tensions in biological media. The average values given in Table 5 for the two bentonite sequences decreased because of 37% and 24% decreases in the oxygen

Table 4. Oxygen diffusion currents from air saturated 3% bentonite in 0.01 N KCl.

| Diffusion time (sec.) | Oxygen diffusion currents in microamperes[a] |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | Electrode number |  |  |  | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
|  | 20 | 21 | 22 | 23 |  |  |
| 0.1[b] | 24.0 | 7.4 | 10.0 | 13.0 | 13.6 | 4.5 |
| 0.2 | 25.8 | 7.4 | 14.9 | 14.8 | 15.7 | 7.0 |
| 0.3 | 26.8 | 10.2 | 17.3 | 16.7 | 14.8 | 8.2 |
| 0.4 | 25.3 | 12.0 | 19.3 | 16.7 | 18.3 | 11.6 |
| 0.5 | 24.5 | 13.0 | 20.6 | 16.7 | 18.7 | 13.5 |
| 0.6 | 21.8 | 12.6 | 20.7 | 15.8 | 17.7 | 13.7 |
| 0.8 | 20.4 | 11.3 | 21.5 | 14.8 | 17.0 | 15.2 |
| 1.0 | 18.3 | 9.8 | 20.4 | 13.9 | 15.6 | 15.6 |
| 1.2 | 16.7 | 9.6 | 20.4 | 13.5 | 15.1 | 16.6 |
| 1.4 | 15.7 | 8.9 | 19.8 | 13.0 | 14.4 | 17.0 |
| 1.6 | 14.8 | 8.7 | 18.8 | 11.6 | 13.5 | 17.1 |
| 1.8 | 13.9 | 8.0 | 18.1 | 11.4 | 12.9 | 17.3 |

[a] Diffusion currents were taken at the end of a sequence, including bentonite, soil, 0.01 N KCl, and bentonite again. Epon insulated electrodes were used with an applied voltage of -0.65 volt.

[b] One sweep time of 0.2 sec./cm. was used for all data.

Table 5. Summations of the oxygen diffusion currents at times from 0.1 to 0.8 second for the data contained in Tables 1, 3 and 4.

| Description of sequence | Summation of oxygen diffusion currents in microamperes |  |  |  |  |
|---|---|---|---|---|---|
|  | Electrode number |  |  |  | Average |
|  | 20 | 21 | 22 | 23 |  |
| Initial bentonite | 165.5 | 116.0 | 129.4 | 143.6 | 138.9 |
| 0.01 N KCl | 102.9 | 123.4 | 131.7 | 125.0 | 121.1 |
| Final bentonite | 168.6 | 73.0 | 124.3 | 108.5 | 115.8 |

sensitivity of electrodes 21 and 23, respectively. Little variability was observed in electrodes 20 and 22. In KCl the diffusion currents for three electrodes were approximately equal, but electrode 20 was comparatively low.

The nature of electrode variability needed to be examined more carefully. Therefore, diffusion currents were recorded from aerated bentonite suspensions after the electrodes had been exposed to different treatments. The same electrodes that had been used for all the preceding data were used. The first column of diffusion currents reported in Table 6a was brought forward from Table 4. Currents reported in the second column of Table 6a were recorded after the electrodes were stored at -1.0 volt for 3 days and had become coated with a black material. The electrodes were then acid washed and wiped clean with cheese cloth, and the diffusion currents in column 3 were recorded.

Storing electrodes at -1.0 volt coated them with a black material and increased their sensitivity to oxygen according to column 3 of Table 6a. The same treatment for a shorter period of time was used on new electrodes with low sensitivity. Treating the electrodes by acid washing and wiping them clean, decreased the sensitivity of all

Table 6a. Average oxygen diffusion currents from aerated 3% bentonite suspensions in 0.01 N KCl.

| | $\Delta i$ for 21% $O_2$[a] | | |
|---|---|---|---|
| Diffusion time (sec.) | From Table 4 | Stored with -1.0 volt[b] | Cleaned with wiping and acid washing |
| 0.2 | 15.7 | 24.3 | 11.7 |
| 0.4 | 18.3 | 21.1 | 9.4 |
| 0.6 | 17.7 | 19.9 | 8.2 |
| 0.8 | 17.0 | 18.6 | 7.4 |
| 1.0 | 15.6 | 17.7 | 7.0 |
| 1.2 | 15.1 | 16.6 | 6.6 |
| 1.4 | 14.4 | 15.9 | 6.3 |
| 1.6 | 13.5 | 15.4 | 6.0 |
| 1.8 | 12.9 | 14.3 | 5.9 |

[a] All diffusion currents given are the averages of four readings.

[b] The data in Table 4 were first obtained. Then, -1.0 volt was applied to the electrodes until they were coated with a black material, and the currents in this column were recorded. The diffusion currents in the next column resulted after electrodes had been acid washed and wiped clean.

the electrodes.

Among the individual electrode currents used to calculate the averages in Table 6a, the lowest currents were not always produced by the same electrode. For example in Table 4 electrode 21 produced the lowest currents. After 3 days storage at -1.0 volt electrodes 20, 21 and 23 produced oxygen reduction currents that were very similar, but electrode 22 was lowest.[1] On the other hand, acid washing and wiping caused electrode 23 to produce very low oxygen reduction curents.[2]

The measurements reported in this section clearly demonstrate that variability was obtained from "drifts" in oxygen sensitivity for a group of electrodes. Secondly, large changes in sensitivity were induced by the treatment applied to the electrodes prior to gathering diffusion data. Lastly, individual electrode sensitivities changed from one set of readings to the next. One electrode may have been the most sensitive in one set and the most insensitive in another.

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[1] Data not presented.

[2] Data not presented.

Measurements in oxygenated clay suspensions. Calibration of membrane electrodes has been used to measure oxygen concentrations in a variety of liquid media. If bare platinum electrodes would produce sufficiently reliable results, then a similar technique could be used to obtain dissolved oxygen concentrations with bare wire electrodes (Chapter III, page 23). This section contains corrected diffusion currents from 3% bentonite suspensions equilibrated with atmospheres of 5, 10, 15 and 21% $O_2$. Diffusion currents for 0.2 to 1.8 seconds were recorded at a sweep time of 0.2 sec./cm., and those for 0.5 to 4.0 seconds were recorded at a sweep time of 0.5 sec./cm.

The average diffusion currents for 5, 10, and 15% $O_2$ suspensions decreased systematically between the currents reported for 0.2 to 1.8 seconds and those reported for 0.5 to 4.0 seconds (Table 6b). The one second diffusion currents in the sequence from 0.2 to 1.8 seconds were 7.8, 9.8 and 12.6 microamperes in 5, 10 and 15% $O_2$ suspensions, respectively. In the sequence from 0.5 to 4.0 seconds, currents of 5.8, 6.6 and 9.1 microamperes were recorded, giving an average decrease of 2.9 microamperes.

Diffusion currents for each individual electrode were examined to see if this decrease was caused by

Table 6b. Average diffusion currents from variously oxygenated 3% bentonite suspensions in 0.01 N KCl.

| Diffusion time (sec.) | Average $\Delta i$[a] | | |
|---|---|---|---|
| | 5% $O_2$ | 10% $O_2$ | 15% $O_2$ |
| 0.2[b] | 10.3 | 13.0 | 16.9 |
| 0.4 | 8.8 | 11.7 | 15.5 |
| 0.6 | 9.0 | 11.0 | 14.2 |
| 0.8 | 8.4 | 10.3 | 13.3 |
| 1.0 | 7.8 | 9.8 | 12.6 |
| 1.2 | 7.3 | 9.4 | 12.1 |
| 1.4 | 7.1 | 9.1 | 11.7 |
| 1.6 | 6.8 | 8.8 | 11.0 |
| 1.8 | 6.5 | 8.4 | 10.1 |
| | | | |
| 0.5 | 4.8 | 7.9 | 10.2 |
| 1.0 | 5.8 | 6.6 | 9.1 |
| 1.5 | 7.9 | 5.8 | 8.0 |
| 2.0 | 8.2 | 5.5 | 7.7 |
| 2.5 | 8.6 | 5.2 | 7.1 |
| 3.0 | 8.9 | 4.8 | 6.9 |
| 3.5 | 9.2 | 4.6 | 6.5 |
| 4.0 | 9.4 | 4.4 | 6.4 |

[a] Comparable data for 21% $O_2$ appears in Table 6a, columns one and two.

[b] Separate pairs of diffusion curves were used to obtain the data for the two ranges of diffusion time.

insufficient equilibration time between the electrodes and media. Data from electrode 21 (Table 7) were representative of the sequence. The measured distance on film and the calculated current in microamperes were included for both the total reduction curves and the residual curves. The total reduction currents in the column headed 15% $O_2$ were nearly the same for both diffusion curves. However, the residual currents were 4.6 and 3.7 microamperes lower at 0.5 and 1.0 second diffusion time with the curve from 0.2 to 1.8 seconds than with the curve from 0.5 to 4.0 seconds. A similar change in residual current was also noticed on many occasions by visual observation of the scope trace.

The mechanics of recording the two residual curves were different. Immediately prior to recording the first residual curve, adsorbed oxygen was removed from the electrode by applying a single 2 second pulse of -0.65 volt while it was positioned in the $N_2$ saturated medium. The residual current for the longer times was recorded after the electrodes were left in the $N_2$ saturated suspension while several instrumental adjustments were made. Thus, a longer period of equilibration was allowed prior to recording the curve at longer diffusion times. Some complex was apparently formed on the platinum surface during

Table 7. Total, residual, and oxygen diffusion currents from 15% $O_2$ bentonite suspensions using electrode 21.

| Diffusion time (sec.) | Distance on film (mm.) | | Δi in μamps | | $\Delta i^a$ |
|---|---|---|---|---|---|
| | 15% $O_2$ | $N_2$ | 15% $O_2$ | $N_2$ | |
| 0.2 | 33.8 | 23.0[b] | 62.5 | 42.5 | 20.0 |
| 0.4 | 30.0 | 21.0 | 55.5 | 38.8 | 16.7 |
| 0.6 | 28.0 | 20.0 | 51.8 | 37.0 | 14.8 |
| 0.8 | 26.5 | 19.5 | 49.0 | 36.0 | 13.0 |
| 1.0 | 25.5 | 19.0 | 47.2 | 35.2 | 12.0 |
| 1.2 | 24.9 | 18.8 | 46.0 | 34.7 | 11.3 |
| 1.4 | 24.2 | 18.2 | 44.8 | 33.7 | 11.1 |
| 1.6 | 23.6 | 18.0 | 43.6 | 33.2 | 10.4 |
| 1.8 | 23.2 | 18.0 | 43.0 | 33.2 | 9.8 |
| | | | | | |
| 0.5 | 29.0 | 23.0 | 53.8 | 42.6 | 11.2 |
| 1.0 | 26.2 | 21.0 | 48.5 | 38.9 | 9.6 |
| 1.5 | 24.8 | 20.0 | 45.8 | 37.0 | 8.8 |
| 2.0 | 24.0 | 19.5 | 44.4 | 36.1 | 8.3 |
| 2.5 | 23.1 | 19.0 | 42.8 | 35.1 | 7.7 |
| 3.0 | 22.2 | 18.2 | 41.1 | 33.6 | 7.5 |
| 3.5 | 21.9 | 18.0 | 40.6 | 33.4 | 7.2 |
| 4.0 | 21.6 | 17.8 | 40.0 | 32.9 | 7.1 |

[a] These Δi values appear in Table 6b.

[b] The vertical sensitivity of the oscilloscope was set at 2 mv/cm. and a 120Ω resistor was across the input terminals in series with the platinum electrode. The camera reduced the screen image slightly, 0.9 cm. = 1 cm. The current in microamperes was calculated as follows:

$$\mu a = (\text{mm. on film}) \left[\frac{1000}{120}\right] \left[\frac{1}{0.9}\right] \left[\frac{\text{Scale factor}}{10}\right] .$$

With the scope set at 2 mv./cm. and a 120Ω resistor across the input terminals:

$$\mu a = (\text{mm. on film})1.85$$

equilibration that contributed to the residual current.

Diffusion currents from various oxygen concentrations in bentonite, reported in Tables 6a and 6b, were plotted against oxygen concentration in Figure 10. Currents at 1.0 second were taken from the data recorded between 0.2 and 1.8 seconds. The plot was fairly linear over the range of concentrations studied but sensitivity was very low. The oxygen reduction current from 21% $O_2$ suspensions was only 8 microamperes higher than from 5% suspensions. This was equivalent to only 4.3 mm. on a film in a maximum field of about 70 mm.

The influence of applied voltage. In the preceding data, the rate at which oxygen was reduced at the platinum surface may have been influenced by the rate of charge accumulation in the electrodes double layer (page 30). Because the charging rate should increase at higher negative voltages, oxygen diffusion currents were recorded at -0.65, -0.70, -0.75 and -0.80 volt to examine the influence of applied voltage on $\Delta i \sqrt{t}$. Measurements were obtained from 3% bentonite suspensions made-up in 0.01 N KCl with the same four electrodes that were used in the preceding studies.

The products of $\Delta i \sqrt{t}$ increased with each increase in

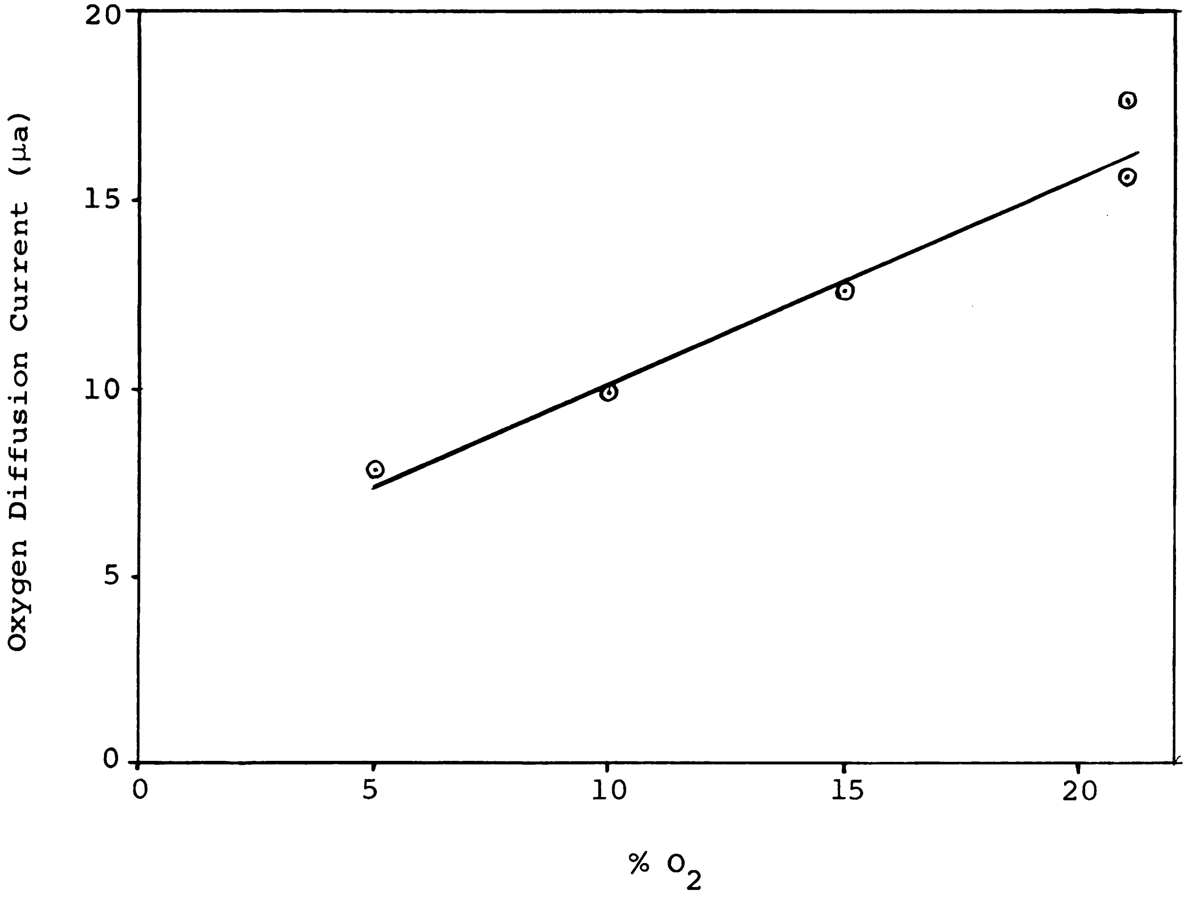


Figure 10. One second diffusion currents plotted with oxygen concentrations from bentonite suspensions.

Platinum electrodes with a fused junction mounted in Epon and plastic insulation were used with an applied voltage of -0.75.

Diffusion currents for 21% $O_2$ were given in Table 6a and the rest were given in Table 6b.

negative applied voltage (Figure 11). An increase of 5 μa · $sec.^{1/2}$ resulted when the voltage was changed from -0.65 to -0.70, but only small increases were obtained with the next two increases in negative voltage to -0.75 and -0.80 volt. Because the curves for -0.70 and -0.75 volt were almost the same, the applied voltage used for the remainder of the studies in this chapter was -0.75 volt.

Even though increased currents were recorded at more negative voltages, the double layer was apparently not charged fast enough at any of the applied voltages to produce constant products of $\Delta i\sqrt{t}$ (Figure 11). This generalization resulted from the observation that $\Delta i\sqrt{t}$ increased gradually with time. Bentonite, KCl, and soil measurements with Epon insulated electrodes produced similar trends in the data of Figure 9 (page 49).

Summary. Measurements in this section with Epon insulated platinum electrodes produced no phase of linear diffusion at an applied voltage of -0.65 volt. Oxygen diffusion currents from oxygenated clay suspensions were fairly linear with oxygen concentration but electrode sensitivity was low. Thus, experimental calibration was the only way that oxygen concentration was obtainable using

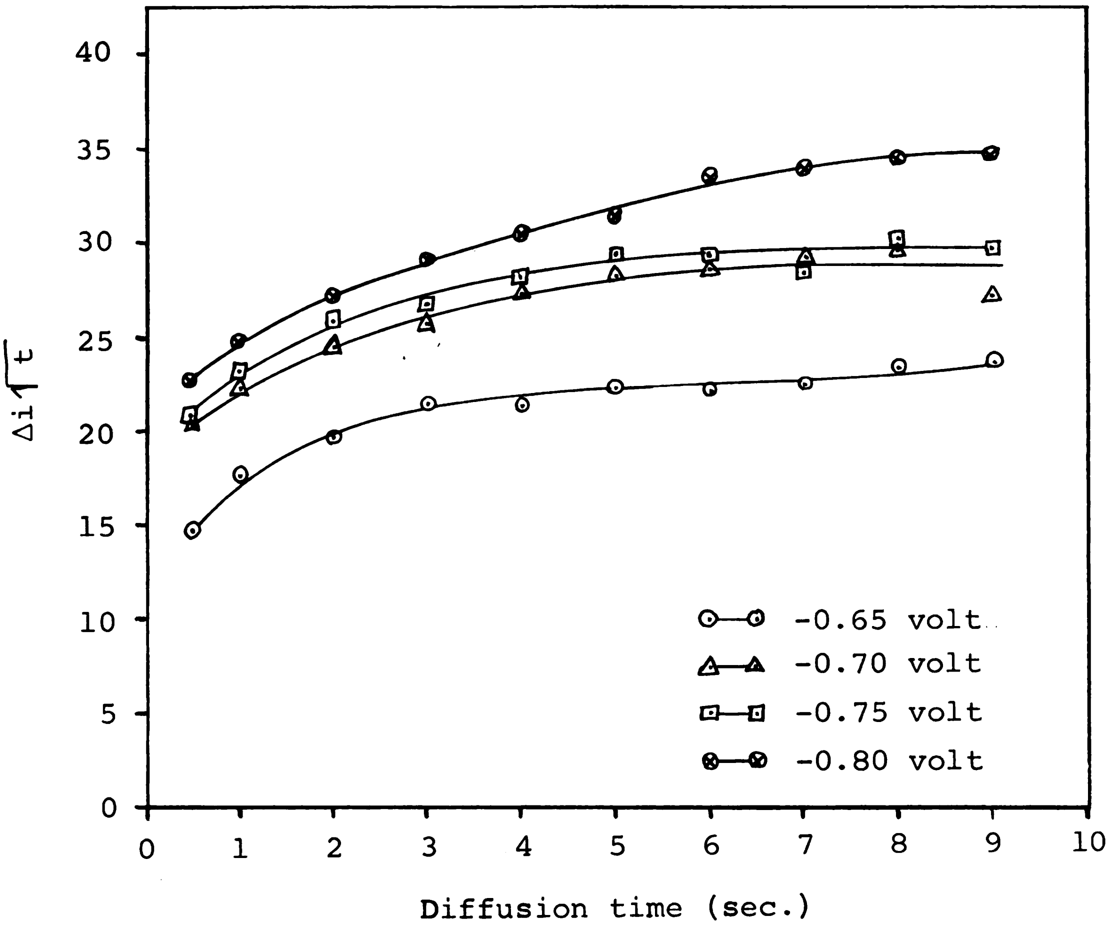


Figure 11. Influence of applied voltage on $\Delta i\sqrt{t}$ from bentonite suspensions.

Epon insulated electrodes were used.

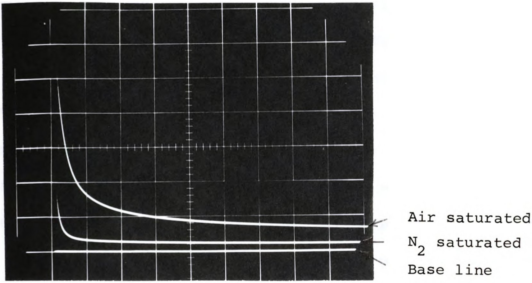
Epon insulated electrodes. However, the high residual currents and low sensitivity of these electrodes make them undesirable for measurement of oxygen concentration by any method.

Diffusion currents varied because of (a) the prior treatment of electrodes, (b) the equilibration time allowed between the electrode and media both in oxygen containing and oxygen free suspensions, and (c) some kind of inherent electrode characteristic.

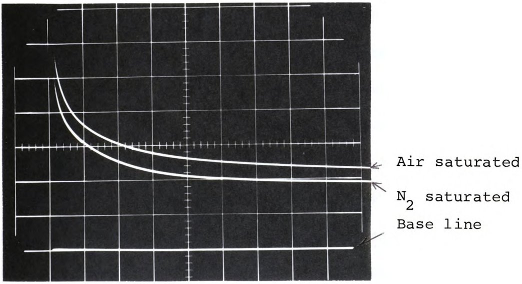
## Comparison of Three Electrode Types

In the data of the preceding sections, higher than normal residual currents were obtained with the Epon insulated electrodes. If "current leakage" through the insulating material was responsible for the high residual currents, then glass electrodes might produce considerably different diffusion currents. In the photographs of Figure 12, the residual currents from glass insulated electrodes were about one-tenth of the residual currents from comparable Epon insulated electrodes.

As a result, the influence of electrode construction on oxygen diffusion currents was studied with three electrode types (Figure 7, page 39). Two types were platinum electrodes



(a) From glass insulated platinum electrodes.



(b) From Epon insulated platinum electrodes.

Figure 12. Total and residual curves for glass insulated and Epon insulated electrodes.

Both electrodes had fused junctions. The electrode used for the curves in (b) had plastic "spaghetti" insulation on the shank and Epon adhesive to seal the plastic to the platinum tip.

The curves were recorded from 3% bentonite in 0.01 N KCl.

mounted in glass; one group had mercury junctions and the other group had fused Pt:Cu junctions. The third electrode type, Epon insulated electrodes, was represented by data from Figure 11. All of these electrodes were stored with an applied voltage of -1.0 volt in 0.01 N KCl prior to use to increase their sensitivity. Measurements were made using four electrodes of each type at -0.75 volt applied.

Mercury junction electrodes produced products of $\Delta i\sqrt{t}$ (Figure 13) that were about 40 $\mu$a · sec.$^{1/2}$ at one second and decreased gradually to about 21 $\mu$a · sec.$^{1/2}$ at 5 seconds. They were then constant between 5 and 9 seconds. Two sets of data were recorded for these electrodes. One set, labeled Pt:Hg-1 was obtained after the electrodes had been stored for 12 hours at -1.0 volt. The other set, labeled Pt:Hg-2, was obtained with the same electrodes after they became coated with a black material from prolonged storage at -1.0 volt. This treatment decreased electrode sensitivity somewhat at shorter diffusion times but the change was small.

Fused junction electrodes gave products of $\Delta i\sqrt{t}$ of 21 $\mu$a · sec.$^{1/2}$ that were almost constant from 1 to 9 seconds and that were equal to the products from mercury junction electrodes between 5 and 9 seconds. The Epon

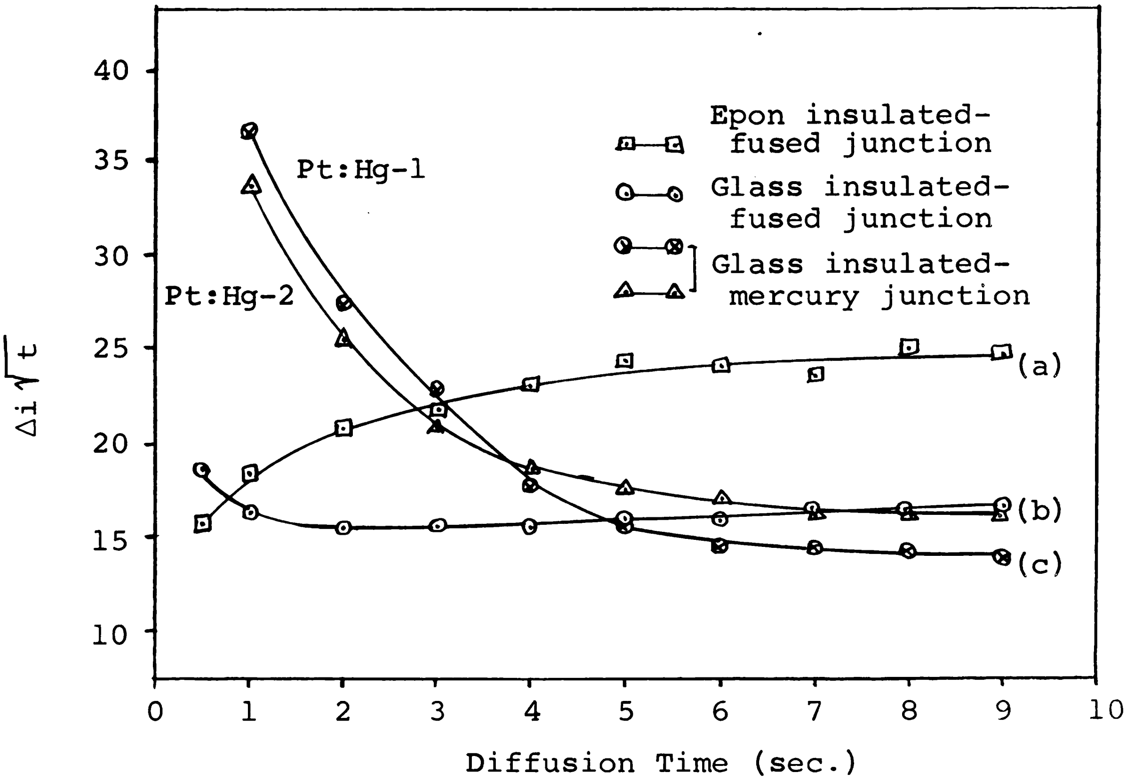


Figure 13. Influence of electrode type on $\Delta i\sqrt{t}$.

Two sets of data, labeled Pt:Hg-1 and Pt:Hg-2, were included for glass insulated, mercury junction, platinum electrodes.

The oxygen diffusion currents were recorded from aerated 3% bentonite in 0.01 N KCl at an applied voltage of -0.75 volt.

insulated electrodes responded differently than both types of the glass electrodes. The product of $\Delta i\sqrt{t}$ increased gradually from 20 to 30 over the 9 second period. Both junction resistance and high "leakage" current apparently interfered with the rate of charge accumulation at the surface of Epon insulated platinum electrodes. This characteristic renders them unsuitable for short term diffusion curve analysis and perhaps for oxygen concentration measurements by experimental calibration.

A difference in response between the two glass insulated electrodes was apparent only at diffusion times of less-than five seconds. In this early phase the diffusion currents from mercury junction electrodes were higher and at one second were twice the currents from fused junction electrodes. This difference suggested that resistance in the fused junction limited high diffusion currents at short times by slowing the double layer charging rate. The fact that $\Delta i\sqrt{t}$ from mercury junction electrodes decreased to equal those from fused junction electrodes, was not understood. The reaction rate at short diffusion times may have been slowed by both the accumulation and the counter diffusion of reaction products. The constant value for $\Delta i\sqrt{t}$ between 5 and 9 seconds may represent an equilibrium between diffusion of reactant and counter diffusion of reduction products.

The preceding discussion suggested that the period between 5 and 9 seconds where $\Delta i\sqrt{t} = 21\ \mu a \cdot \sec.^{1/2}$ was not a phase of simple linear diffusion. However, because constant and equal products were obtained during this period from both types of glass insulated electrodes, the phase must be examined further. This was accomplished by calculating the oxygen concentration from $\Delta i\sqrt{t}$ with linear diffusion theory and comparing the resulting value with a known oxygen concentration.

The concentration of oxygen in 3% bentonite should be about the same as that in 0.01 N KCl, namely 9.0 ppm. at 20°C. The calculation for the dissolved oxygen concentration was made with the following expression derived from linear diffusion theory:

$$\text{ppm } O_2 = \frac{(\text{moles } O_2/\text{cc.})(\text{G.M.W.})(10^6)}{\text{g./cc.}} = \left[\frac{\Delta i\sqrt{t}}{nFA\sqrt{D/\pi}}\right]\left[\frac{(\text{GMW})(10^6)}{\text{g./cc.}}\right]. \quad (4)$$

When $\Delta i\sqrt{t} = 21 \times 10^{-6}$ ampere $\cdot$ sec.$^{1/2}$, the concentration was calculated as 3.9 ppm. $O_2$. Other values used in the calculation were: $D = 2.33 \times 10^{-5}$ cm.$^2$/sec., $n = 4$, and $d = 0.0834$ cm$^2$. An oxygen concentration of 3.9 ppm. is less than half of the approximate known quantity.

As a result of the preceding findings the diffusion currents between 6 and 10 seconds in Figure 13 probably do not represent a phase of linear oxygen diffusion for the following reasons: (a) the value for $\Delta i\sqrt{t}$ during this phase yielded oxygen concentrations which are less than half of their approximate known value, (b) diffusion from 6 to 10 seconds should reflect the cylindrical electrode geometry (page 28), and (c) the decrease in $\Delta i\sqrt{t}$ from a maximum at 0.6 second indicated that counter diffusion or other interfering factors may have produced the lower constant phase.

Therefore, a calculation for oxygen concentration was made using the approximate diffusion current at one second from the mercury junction electrodes, even though $\Delta i\sqrt{t}$ was not constant at that time. With $\Delta i\sqrt{t} = 40 \times 10^{-6}$ ampere $\cdot$ $\text{sec.}^{1/2}$ the calculated concentration was 7.5 ppm. $O_2$, which is much closer to the real concentration.

Diffusion times between 0.1 and 1.0 second were earlier proposed as those that may give rise to a linear diffusion phase (page 28). Because one second diffusion currents from mercury junction electrodes produced a reasonable oxygen concentration for bentonite suspensions, additional measurements were made at less than one second with these electrodes.

## Studies With Glass Insulated Electrodes

Equilibration time. Diffusion currents at less than one second were needed from mercury junction electrodes. At the same time, a procedure was needed for obtaining valid and reproducible diffusion currents so that some of the variability that had been observed with Epon insulated electrodes (page 55) could be avoided. Therefore, diffusion at less than two seconds was studied under conditions of equilibrium and non-equilibrium between electrodes and bentonite suspensions. Equilibrium was assumed to have been established after the electrodes stood "open circuited" for five minutes in aerated as well as in oxygen free bentonite suspensions. Non-equilibrium was assumed for only 30 seconds equilibration with air saturated bentonite. For non-equilibrium in $N_2$ saturated bentonite suspensions, only 5 seconds equilibration was allowed after removal of chemisorbed oxygen.

The detailed procedure follows. Each electrode was first placed in air saturated bentonite and a single 2 second voltage pulse was applied. The electrode equilibrated with the medium for 5 minutes before the first diffusion curve was recorded. The electrode was then moved to oxygen free bentonite. Chemisorbed oxygen was removed with a few 2 second pulses of -0.75 volt. After brief stirring a non-equilibrated residual curve was recorded. An equilibrated curve of residual current was recorded after the electrode was in $N_2$ saturated media for 5 minutes. Then, the electrode was transferred to the air saturated bentonite again and stirred for about 30 seconds. A non-equilibrated diffusion curve was then recorded. This was repeated for each of the four electrodes used.

Three possible combinations of the average diffusion and average residual currents were plotted as products of $\Delta i\sqrt{t}$ in Figure 14. The highest products were obtained from electrodes that had been equilibrated in aerated bentonite and that had been exposed only briefly to the $N_2$ medium (curve a). Equilibration in oxygen free bentonite increased the residual current and thus decreased oxygen diffusion currents for the shorter times (curve b). During this added time a reducible substance was apparently formed on the electrodes. Stirring the electrodes for only 30 seconds in oxygen containing bentonite greatly decreased the oxygen diffusion currents (curve c). These findings confirm the earlier observation (page 48) that chemical equilibrium must be established between the electrode surface and

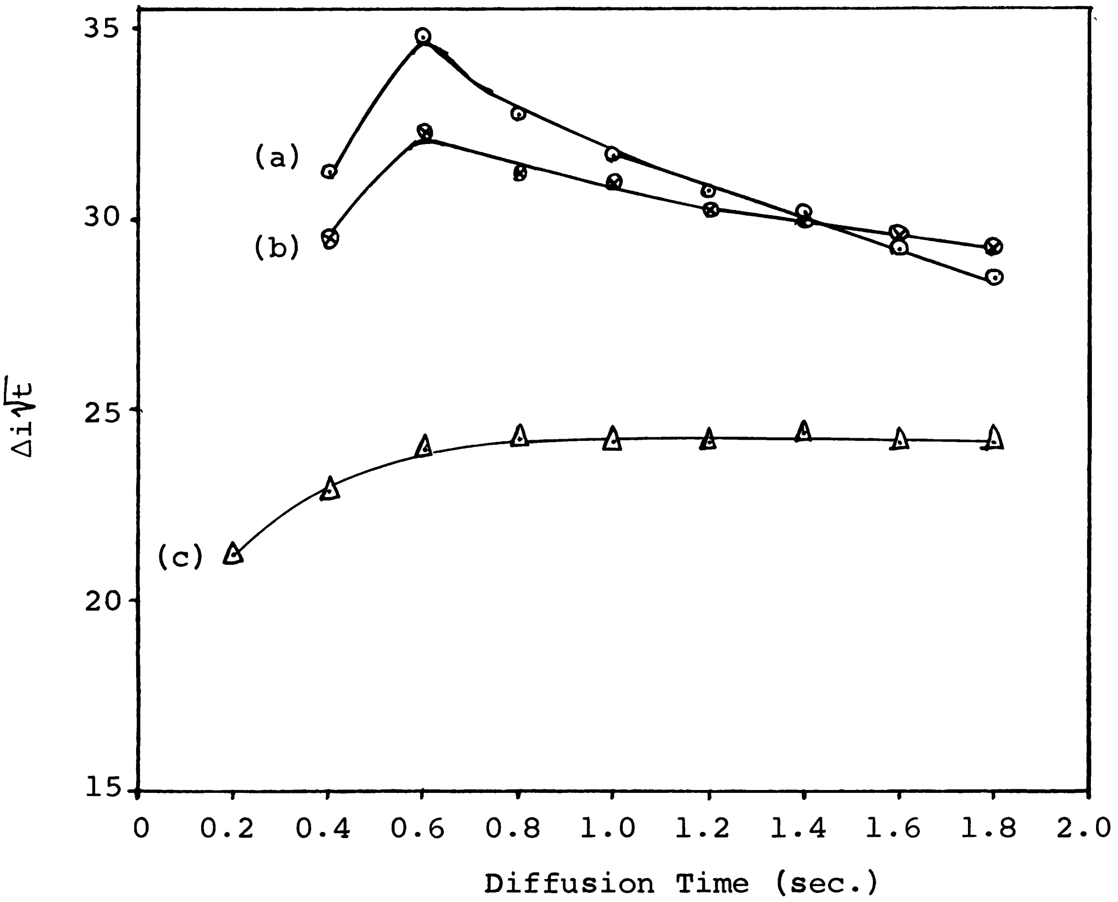


Figure 14. The influence of chemical equilibrium between the electrode surface and the bentonite suspension on $\Delta i\sqrt{t}$.

Measurements were obtained from 3% bentonite in 0.01 N KCl using 4 glass insulated platinum electrodes with mercury junctions.

Curve legend and electrode treatments:

| Curve legend | Equilibration time prior to recording curve | |
|---|---|---|
| | Air saturated | $N_2$ saturated |
| (a) | 5 minutes (equilib.) | *5 seconds (non-equilib.) |
| (b) | 5 " " | 5 minutes (equilib.) |
| (c) | 30 seconds (non-equilib.) | 5 " " |

*A few 2 second pulses of -0.75 volt were applied to remove chemisorbed oxygen and then about 5 seconds elapsed before the measurement.

bentonite suspensions containing KCl before reproducible oxygen diffusion currents can be recorded. This applies to recording total reduction currents as well as residual currents.

In the remainder of this chapter, all the measurements were made using the procedure that produced the highest products of $\Delta i \sqrt{t}$ in Figure 14. This was accomplished under conditions of equilibrium in media containing oxygen and conditions of non-equilibrium in oxygen free media. This method was selected prior to discovering that equilibrium needed to be established in both oxygen containing and oxygen free media when reactive materials were present. The individual steps of the adopted procedure were as follows. An initial 2 second voltage pulse was applied to the electrodes to remove any effects of oxygen in the previous media. After 5 minutes of equilibration, the oxygen reduction curve was recorded. Residual current curves were recorded shortly after three 2 second pulses of -0.75 volt had been applied to the electrodes to remove reducible chemisorbed oxygen.

The measurements at shorter times in Figure 14 were an extension of the measurements with mercury junction electrodes at longer times in Figure 13 on page 67.

Because curve (a) of Figure 14 was recorded using the same techniques that were used with the readings in Figure 13, this curve was used to relate the findings in the two figures. In Figure 14, the initial rise in $\Delta i\sqrt{t}$ to about 35 $\mu a \cdot sec.^{1/2}$ at 0.6 second probably resulted from charging of the double layer. The subsequent decrease in $\Delta i\sqrt{t}$ after 0.6 second in Figure 14 was apparently the early part of the phase in Figure 13 that decreased gradually until five seconds where $\Delta i\sqrt{t}$ became constant. The cause for this response was suggested as being interference by reduction products (page 69). The above relationship between the two sets of data seems relevant even though the maximum values of $\Delta i\sqrt{t}$ were somewhat different.

The combined results in Figures 13 and 14 indicate that the electrode process during short diffusion times was complex and difficult to analyze for a linear phase because of factors that interfere with the rate of diffusion to the electrode and the rate of oxygen reduction at the electrode surface. Interference may have been caused by any of the stages of the electrode process. These were summarized by Koryta (15) as being (a) diffusion, (b) chemical reaction by which the reducible or oxidizable (electroactive) form of the depolarizer is formed, (c) the transfer of this particle through the ionic part of the double layer, (d) the preformation of the particle at the electrode surface (i.e., suitable orientation, adsorption, etc.), (e) the electrode reaction proper, and (f) the processes in which the product of the electrode reaction takes part.

Even though short term diffusion and reduction of oxygen at platinum electrodes appear to be complex, the possibility of obtaining a short linear phase at less-than one second still remained. Therefore, additional studies of the maximum in $\Delta i\sqrt{t}$ that appeared at 0.6 second in Figure 14 were conducted.

Double layer charging rate. All the data in the preceding studies with mercury junction electrodes were gathered from clay suspensions made-up in 0.01 N KCl. An applied voltage of -0.75 volt was used. Measurements were made in this section to see if increasing the negative voltage applied to the electrodes and removing the colloid from the electrolyte would allow the double layer to charge faster. A shift of the maximum in $\Delta i\sqrt{t}$ to shorter time was assumed to indicate a faster charging rate. Oxygen diffusion currents were recorded from aerated 0.01 N KCl at two applied voltages, -0.75 and -0.80 volt. In Figure 15, the product

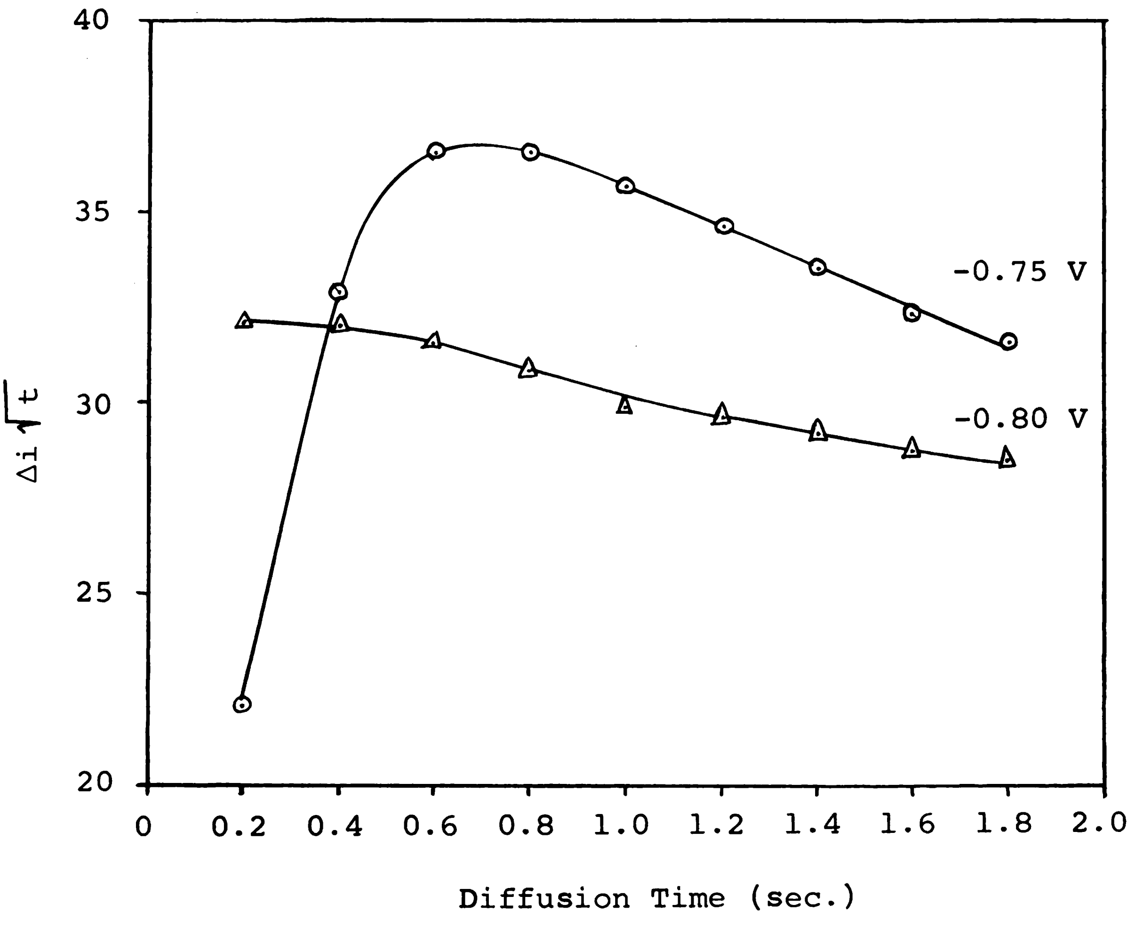


Figure 15. The influence of applied voltage on $\Delta i\sqrt{t}$ for glass insulated electrodes.

Measurements were made using four glass insulated platinum electrodes with mercury junctions.

of $\Delta i\sqrt{t}$ at -0.75 volt was very similar to that obtained from bentonite in 0.01 N KCl (Figure 14, page 73). The presence of clay apparently did not influence the charging rate in earlier data. At -0.80 volt the electrode sensitivity decreased perhaps because $H^+$ was reduced to $H_2(g)$. This may have blocked some of the active sites used for oxygen reduction at -0.75 volt. Therefore, with mercury junction electrodes, -0.75 volt is the largest negative voltage that can be applied to the electrode without encountering interference from other reactions.

Measurements in oxygenated clay suspensions and KCl. The studies in this section were conducted to determine if maximum products of $\Delta i\sqrt{t}$ at less than one second were related to oxygen concentration. Oxygen diffusion currents were recorded from suspensions of 3% bentonite in 0.01 N KCl that had been oxygenated with 5, 10, 15 and 21% $O_2$ in the equilibrating gases. The products of $\Delta i\sqrt{t}$ given in Figure 16 were calculated from the average of four oxygen diffusion currents. Platinum electrodes of the mercury junction type were used.

At less than 0.2 second, the relationship between $\Delta i\sqrt{t}$ and % $O_2$ was almost inverse. Then a short phase

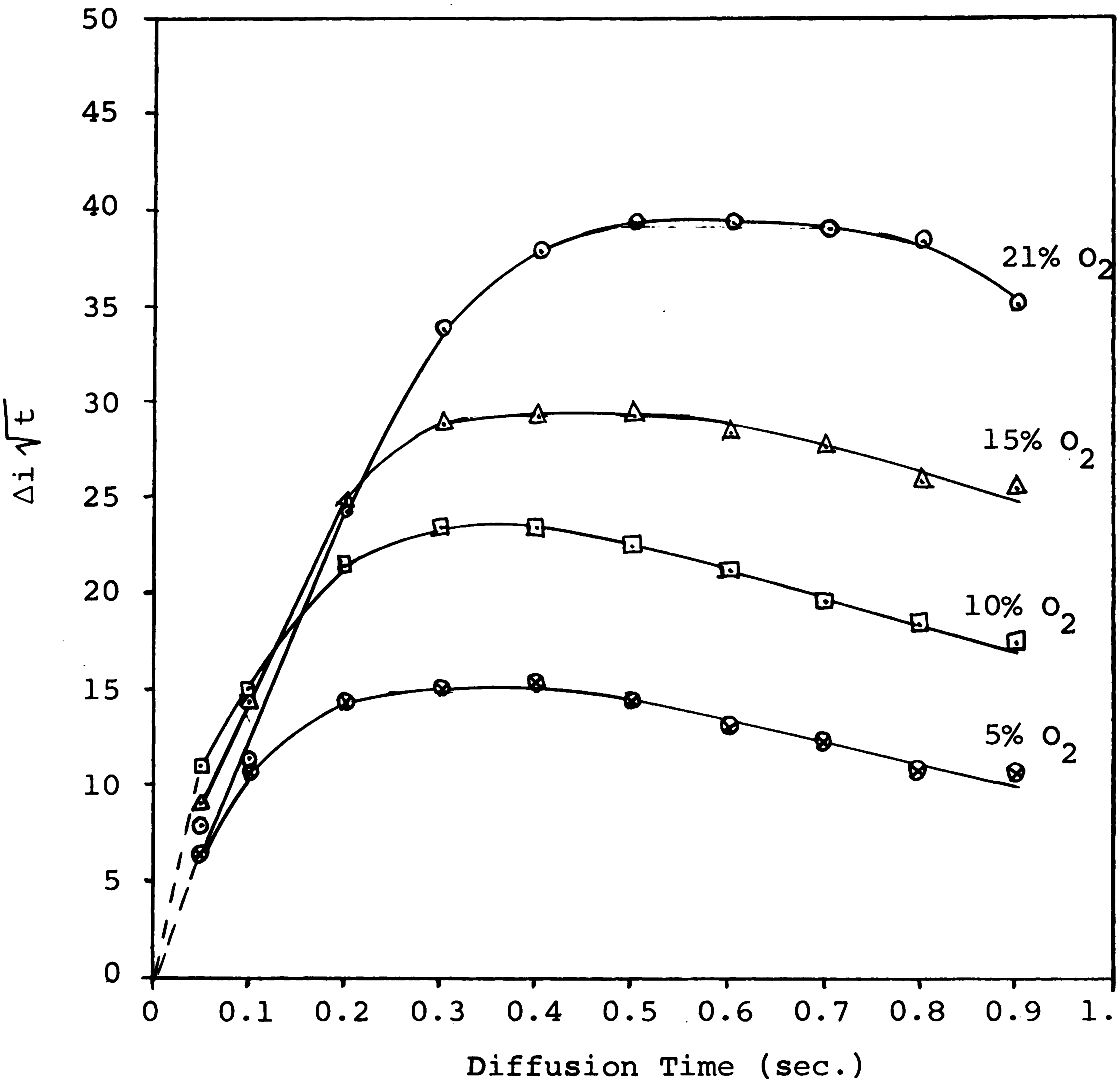


Figure 16. Variation of $\Delta i\sqrt{t}$ with oxygen concentration and time from bentonite suspensions.

Diffusion curves were obtained at -0.75 volt with four platinum electrodes mounted in glass with a mercury junction.

where $\Delta i\sqrt{t}$ was constant appeared at each oxygen concentration. Phases of constant $\Delta i\sqrt{t}$ were positioned at longer times for higher oxygen concentrations and appeared between 0.4 and 0.8 second in 21% $O_2$, 0.3 and 0.6 second in 15% $O_2$, 0.3 and 0.5 second in 10% $O_2$, and 0.2 to 0.5 second in 5% $O_2$. The presence of these constant phases suggested that diffusion was nearly linear between the above designated times. In air saturated bentonite the average product of $\Delta i\sqrt{t}$ was 39.5 $\mu$a · sec.$^{1/2}$. This was reproduced within ± 10% on four separate occasions.

Diffusion currents at 0.5 second time were approximately on the plateau of the curves for each oxygen concentration in Figure 16. These currents were plotted with oxygen concentration (Figure 17). The plot was linear from 5 to 21% oxygen and average currents ranged from 20 to 56 microamperes. These currents were three times higher than comparable currents from Epon insulated electrodes (page 60).

Diffusion currents for each individual electrode were also given in Figure 17. These ranged from 14 to 26 $\mu$amperes at 5% $O_2$ and from 46 to 54 $\mu$amperes at 21% $O_2$. Individual reduction currents from electrodes I, III, and IV were almost as linear with $O_2$ concentration as the average

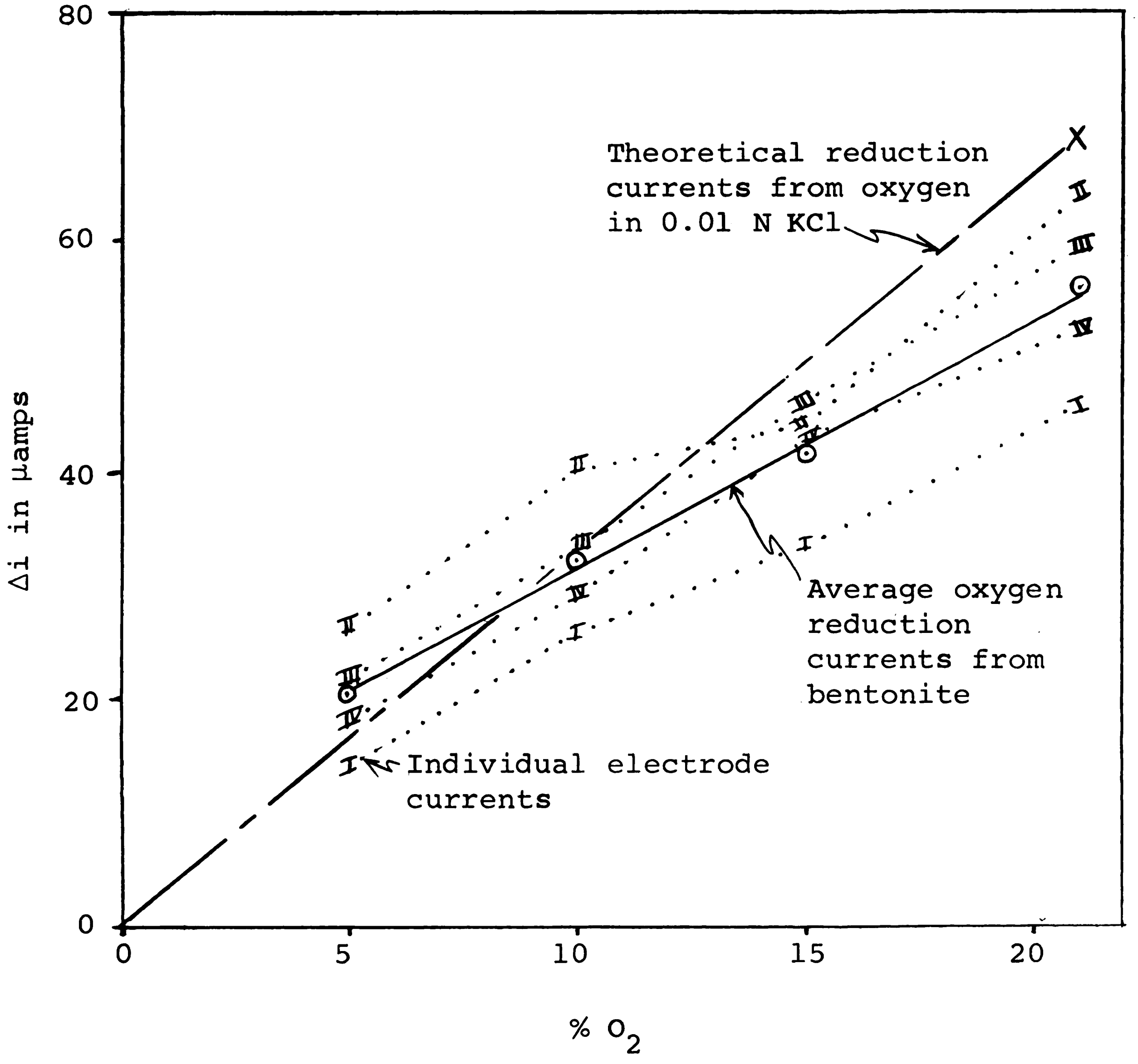


Figure 17. Oxygen diffusion currents with oxygen concentrations in bentonite suspensions.

Diffusion curves were obtained from 3% bentonite in 0.01 N KCl using bare platinum electrodes mounted in glass with a mercury junction. Individual electrode currents are designated with the electrode numbers, I, II, III and IV.

diffusion currents, but electrode II was erratic. These were electrodes of similar size that had been exposed to similar treatments.

The linear extrapolation of the curve for each electrode intersected zero percent $O_2$ between about 5 to 12 μamperes. This anomaly was caused by not permitting the electrodes to equilibrate with the $N_2$ saturated bentonite. On two previous occasions in this study (pages 47 and 72), diffusion currents were decreased by up to 10 μamperes after the electrodes equilibrated for five minutes with nitrogen saturated bentonite made up in 0.01 N KCl. Reducible substances that contributed to residual currents formed on electrode surfaces during equilibration. If each diffusion current given in Figure 17 were decreased by 0 to 10 μamperes, then the plot of average $\Delta i$ values with $O_2$ concentration would nearly have intersected zero current at zero oxygen concentration.

The actual oxygen diffusion currents from bentonite were compared to theoretical diffusion currents from the oxygen content of aerated 0.01 N KCl (Figure 17). These currents were calculated with equation 4 (page 69) using the known concentrations of $O_2$ in 0.01 N KCl as 9 ppm. at 20°C (Table 8). Oxygen concentrations were also calculated for bentonite suspensions equilibrated with 5, 10, 15 and 21% $O_2$ using the diffusion currents in Figure 17. The bentonite concentrations were below those for 0.01 N KCl except for the value at 5% $O_2$. If each diffusion current was corrected for the 5 to 10 μampere error in the residual current, then a recalculation of the 5% $O_2$ concentration in bentonite gave less than 2 ppm. rather than 2.65 ppm. as calculated from the uncorrected current value. With this correction, all the concentrations in bentonite were below those known for 0.01 N KCl. The suggestion of page 48, that the $O_2$ concentration of bentonite in equilibrium with 21% $O_2$ was above that of KCl, was not substantiated.

Table 8. Oxygen concentrations calculated from actual reduction currents in bentonite suspensions compared to known concentrations in 0.01 N KCl at 20°C.

| % $O_2$ | Dissolved oxygen concentration in ppm. at 20°C | |
|---|---|---|
| | 0.01 KCl | Calculated from average diffusion currents for 3% bentonite in 0.01 N KCl |
| 5 | 2.1 | 2.65 |
| 10 | 4.3 | 4.1 |
| 15 | 6.4 | 5.4 |
| 21 | 9.0 | 7.4 |

Because the known oxygen concentrations of KCl have been used as a reference in this study, an experiment was conducted to see if 0.01 N KCl would produce data similar to that for bentonite in Figure 16, page 79. A different set of glass insulated platinum electrodes with a mercury junction were used after thorough cleaning and storing at -1.0 volt for 20 minutes. Reduction currents were recorded for variously oxygenated solutions of 0.01 N KCl in the order of 21, 5, 10, and 15% $O_2$ with the procedure used above (described on page 74). Products of $\Delta i\sqrt{t}$ were calculated from average oxygen diffusion currents and presented in Figure 18.

Some rather interesting comparisons can be made between the KCl data of Figure 18 and the plots of $\Delta i\sqrt{t}$ for bentonite in Figure 16. The curves for both aerated solutions have similar plateaus. However, the maximum value of $\Delta i\sqrt{t}$ in KCl was about 54 $\mu a \cdot sec.^{1/2}$ and in bentonite suspensions it was 39.5 $\mu a \cdot sec.^{1/2}$. This difference may have arisen from greater electrode sensitivity in the KCl readings or from the characteristic dissolved oxygen concentrations in the two media. A concentration calculation for aerated 0.01 N KCl (Figure 18) with $\Delta i\sqrt{t}$ of 54 $\mu a \cdot sec.^{1/2}$ gave 9.9 ppm. $O_2$. Decreasing the corresponding diffusion current by 5 $\mu$amps of residual current, gave 9.2 ppm. in 0.01 N KCl. This agrees very well

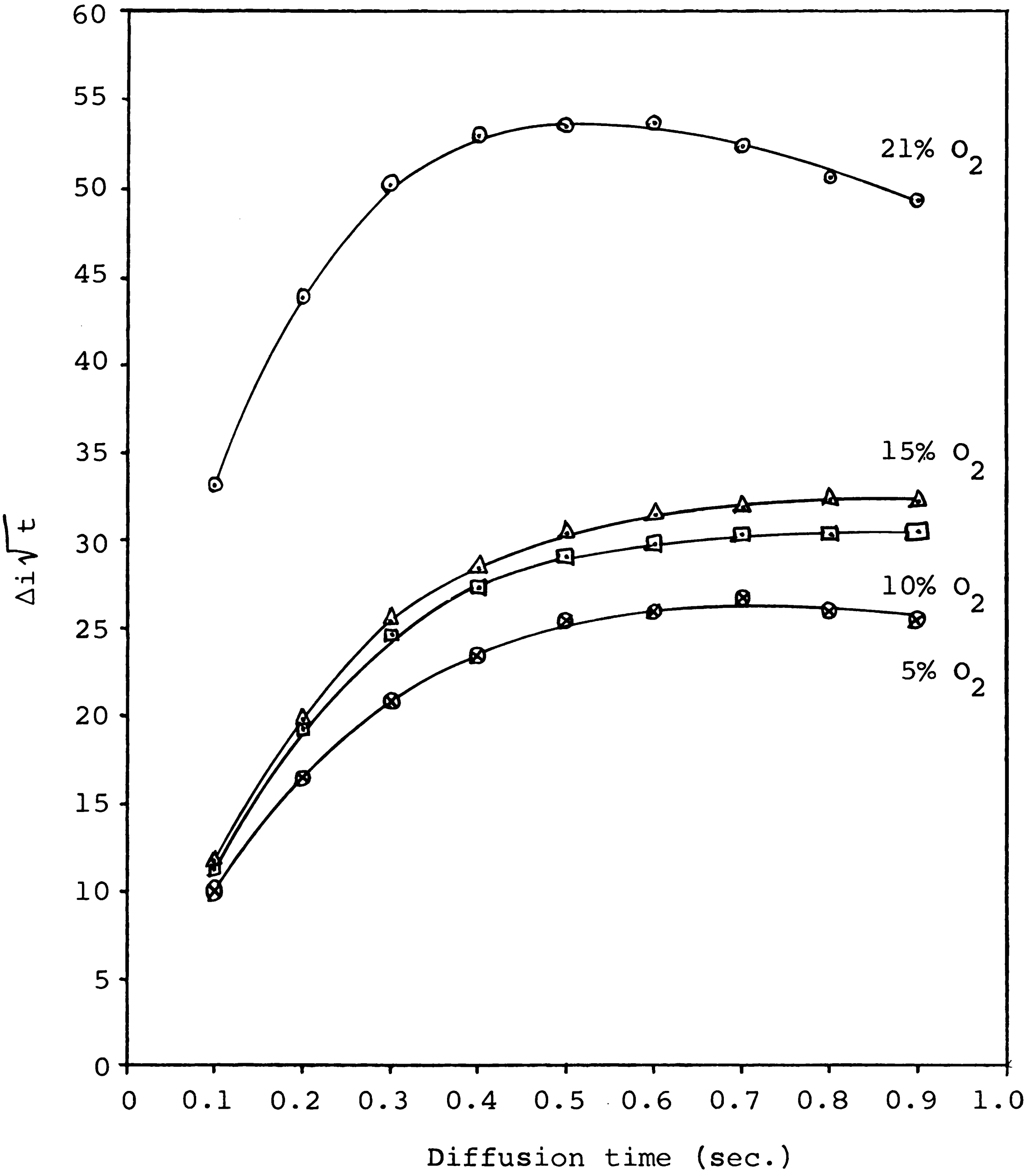


Figure 18. Variation of $\Delta i\sqrt{t}$ with oxygen concentration and time from 0.01 N KCl.

Diffusion curves were obtained at -0.75 volt applied to platinum electrodes mounted in glass with mercury junctions. The curves were obtained in the order of 21, 5, 10 and 15% after the electrodes had been stored at -1.0 volt for 20 minutes.

with the known concentration of 9.0 ppm.

As the readings progressed from 5 to 10 to 15% $O_2$ solutions, diffusion currents became anomalous when compared to those for bentonite suspensions in Figure 16. The maxima in $\Delta i\sqrt{t}$ at 0.5 were absent in the curves for these lower oxgyen concentrations and almost equal products of $\Delta i\sqrt{t}$ were produced at 10 and 15% $O_2$. The bunching of the diffusion currents for 5, 10 and 15% $O_2$ was caused partly from the 5% values being high. These responses were very puzzling and led to gathering more data from 0.01 N KCl with a different set of electrodes. Measurements were first made in 15% $O_2$ solutions and then in 21% $O_2$ solutions. Products of $\Delta i\sqrt{t}$ of 25 and 27 were calculated for 15 and 21% $O_2$ samples, respectively. These again showed a marked decrease in sensitivity to oxygen with increased exposure to KCl. As a result, the findings reported in Figure 18 were apparently characteristic for the techniques used to obtain measurements in KCl even though the results could not be satisfactorily explained. The 5 minute equilibration time with the media containing oxygen called for by the procedure on page 74, accounted for most of the electrode's exposure to KCl. This was in an open circuit position, that is, the electrodes were not coupled with the Ag:AgCl reference cell.

The decrease in sensitivity must have been caused by the deposition of a complex involving the ions in solution and the platinum surface that interfered with obtaining "normal" oxygen diffusion currents.

Measurements in various salt solutions. In the preceding sections, measured oxygen diffusion currents were influenced by exposure of platinum electrodes to KCl. This led to a study on the effect of various other salt solutions on diffusion currents. Diffusion currents were recorded from a group of 0.01 N salt solutions including $Na_2CO_3$, $Na_2SO_4$, $MgSO_4$, KCl, $Li_2SO_4$, NaCl and $K_2SO_4$ in that order. In the first six of these salt solutions, two sets of readings were recorded after different electrode treatments. The electrodes were pretreated by storing at -1.0 volt in 0.01 N KCl for 20 minutes. At this point an error was encountered in the procedure. The electrodes were uncoupled from -1.0 volt but were left in 0.01 N KCl while the first sequence of readings was being completed. They should have been transferred to distilled water. Consequently, diffusion currents from the first sequence in each salt solution reflected some KCl "poisoning" from standing in the KCl with no applied negative voltage. After pretreatment, diffusion curves were recorded from one salt solution and the electrodes remained in that salt for one-half hour before the second set of diffusion curves were recorded. The first set was labeled (1) and the second set was labeled (2) in Figures 19 and 20. The four electrodes used in KCl (Figure 18) and the technique described on page 74 were used in this study.

The effect of equilibrating electrodes in non-reactive salts and the influence of $Cl^-$ "poisoning" on diffusion currents are demonstrated by the data in Figures 19 and 20. The trend in data for $Na_2CO_3$ and $Na_2SO_4$ in Figure 19 was characteristic for the sequence. Equilibration of the electrodes in $Na_2CO_3$ for one-half hour between curves (1) and (2) increased their sensitivity. Diffusion currents were first recorded from $Na_2CO_3$ and then from $Na_2SO_4$. Therefore, curve (1) from $Na_2SO_4$ was recorded after curve (2) from $Na_2CO_3$. Between these two sets of data the electrodes were stored in 0.01 N KCl for 20 minutes at -1.0 volt and were also "open circuited" in KCl while the readings for curve (1) in $Na_2SO_4$ were in progress. The products of $\Delta i \sqrt{t}$ decreased from curve (2) in $Na_2CO_3$ to curve (1) in $Na_2SO_4$ apparently from the exposure to KCl.

After one-half hour in $Na_2SO_4$, the electrodes produced

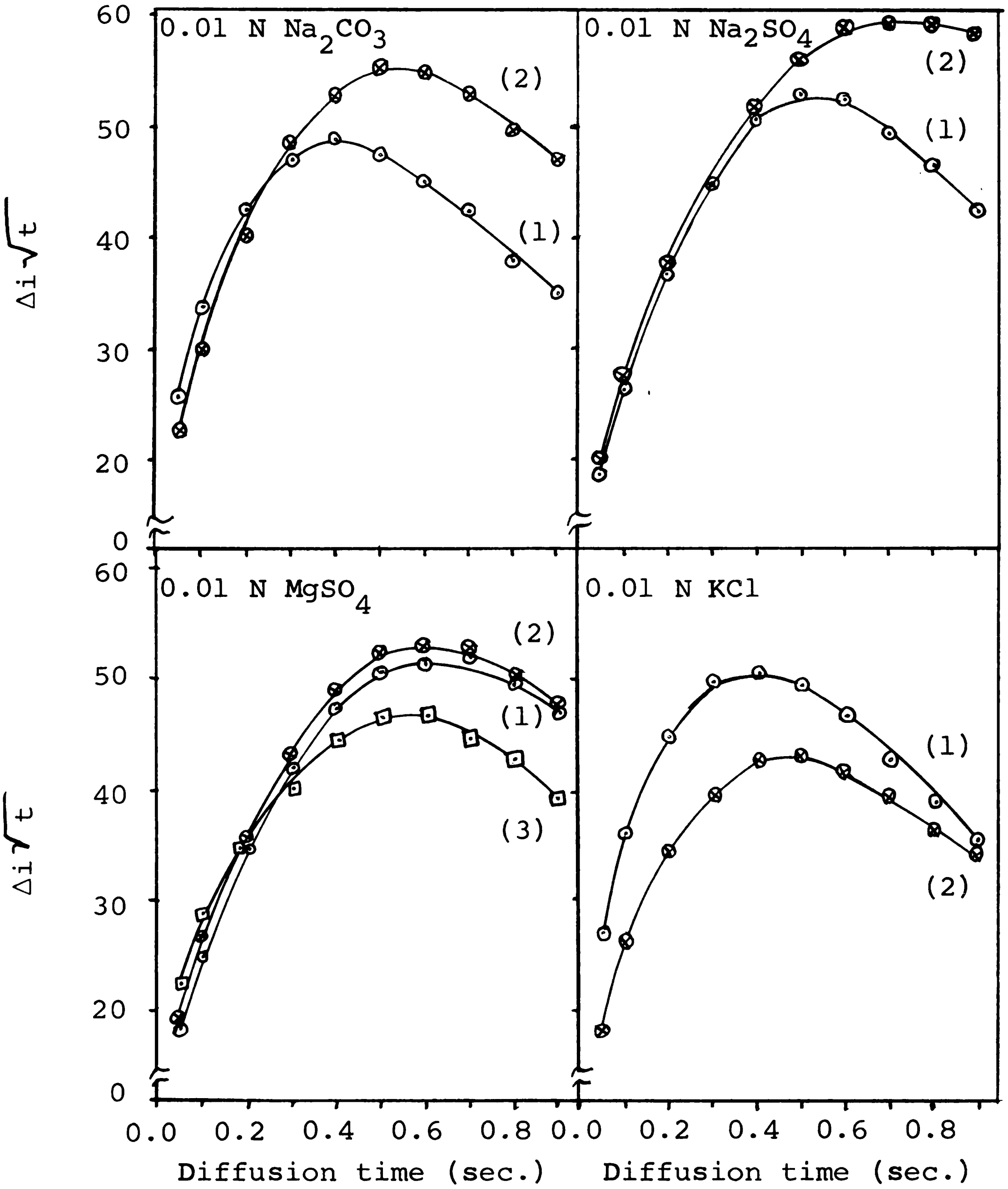


Figure 19. Variation in $\Delta i\sqrt{t}$ from 0.01 N $Na_2CO_3$, $Na_2SO_4$, $MgSO_4$ and KCl using different electrode treatments.

The electrodes were stored in 0.01 N KCl at -1.0 volt for 20 minutes and open circuited in KCl for a short time prior to recording curve (1). The electrodes were left for one-half hour in the salt in which the measurement in curve (1) were made and then curve (2) was recorded. Curve (3) in $MgSO_4$ was obtained after curve (2) in 0.01 N KCl.

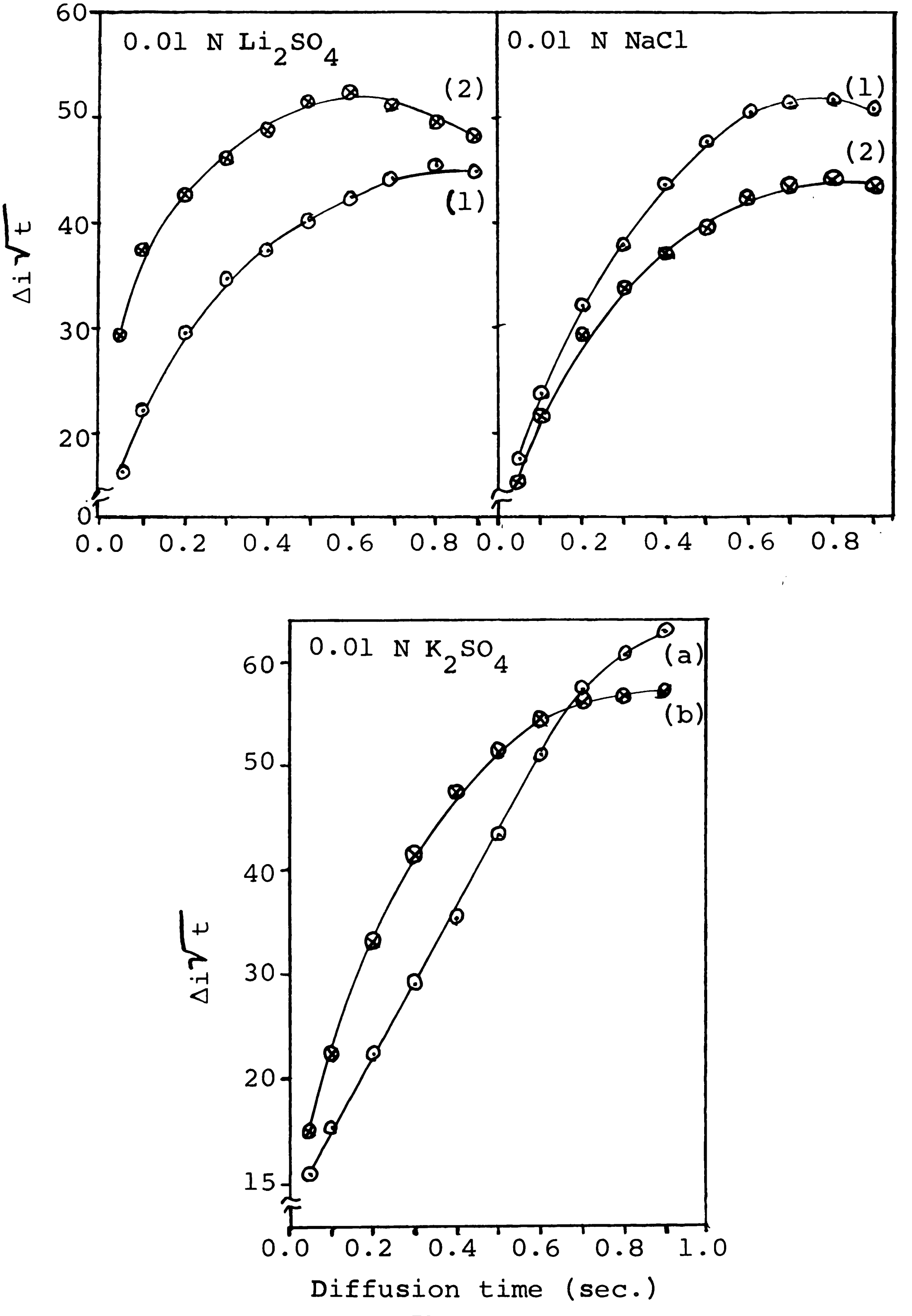


Figure 20. Variations in $\Delta i\sqrt{t}$ from 0.01 N $Li_2SO_4$, NaCl and $K_2SO_4$ using different electrode treatments.

For explanation of curves (1) and (2) see Figure 19. Curve (a) in $K_2SO_4$ was obtained after the electrode had been stored for on-half day at -1.0 volt in 0.01 N $K_2SO_4$. Curve (b) was obtained after the electrodes were exposed for one-half hour to $K_2SO_4$ in an "open circuit" state.

a higher value of $\Delta i\sqrt{t}$. The first two sets of data, curves (1) and (2), recorded from $MgSO_4$ were nearly the same and showed only a small influence from $Cl^-$ "poisoning." Measurements from KCl were obtained next. Exposure to KCl for one-half hour (curve 2) decreased the oxygen sensitivity of the electrodes. A re-run was then made in $MgSO_4$ (curve 3) to show that the decrease in sensitivity persisted in another salt prior to equilibration. Diffusion currents recorded from $Li_2SO_4$ increased after equilibration between the salt and the electrode. Subsequent measurements in NaCl decreased electrode sensitivity.

In summary, oxygen diffusion currents from $Na_2CO_3$, $Na_2SO_4$, $MgSO_4$, and $Li_2SO_4$ increased after electrodes stood in each respective salt for one-half hour. Exposure of electrodes to KCl in an open circuit position markedly decreased the oxygen sensitivity of electrodes. If some complex was formed between the ions in KCl and the platinum surface, then it appeared to dissolve when the electrodes were stored in different salts. The process was apparently one of alternately blocking and exposing potential active sites of oxygen reduction on the platinum surface.

In 0.01 N $Na_2CO_3$, which has a pH of about 11, the maximum value of $\Delta i\sqrt{t}$ was nearly the same as in neutral

salts. This indicated that the reduction mechanism involved the same number of electrons under conditions of both high and neutral pH at the applied voltage of -0.75 volt.

The maximum values of $\Delta i\sqrt{t}$ for six of the salt solutions in Figures 19 and 20 were used to calculate the oxygen concentrations given in Table 9 (equation 4, page 69). The concentrations ranged from 9.3 to 10.9 ppm. and averaged 9.58 ppm. These calculated concentrations were all slightly higher than the approximate known value of 9.0 ppm.

Table 9. Oxygen concentrations in bentonite suspensions and various salt solutions that were calculated with linear diffusion theory from maximum products of $\Delta i\sqrt{t}$ obtained at diffusion times of less than 1 second.

| Medium | ppm. $O_2$ | Medium | ppm. $O_2$ |
|---|---|---|---|
| Bentonite | 7.4 | 0.01 N $Na_2SO_4$ | 10.9 |
| 0.01 N KCl (known) | 9.0 | 0.01 N $MgSO_4$ | 9.7 |
| 0.01 N KCl (measured) | 9.2 | 0.01 N $Li_2SO_4$ | 9.6 |
| 0.01 N $Na_2CO_3$ | 10.2 | 0.01 N NaCl | 9.6 |

Diffusion data from 0.01 N $K_2SO_4$ was also reported in Figure 20, page 90. This salt was tried because KCl gave a maximum in $\Delta i\sqrt{t}$ at shorter diffusion times (Figure 19) than the other salt solutions studied. This response was attributed to faster charge build-up in the double layer.

It was thought that $K_2SO_4$ might produce a similar early maximum, because of the cation size, without "poisoning" the electrode surface.

In the preceding studies electrodes have been stored at -1.0 volt in 0.01 N KCl to increase their sensitivity to oxygen (page 38). If $K_2SO_4$ could substitute for KCl as a supporting electrolyte, then it might also be useful for storing electrodes at -1.0 volt to avoid $Cl^-$. As a result, the electrodes were stored at -1.0 volt in $K_2SO_4$ for one-half day prior to obtaining curve (a). Curve (b) was recorded after the same electrodes stood for one-half hour in $K_2SO_4$ with no applied voltage. In curve (a) oxygen diffusion currents were low at short diffusion times and products of $\Delta i\sqrt{t}$ never reached a maximum prior to one second. In curve (b) diffusion currents were higher at the shorter times. Some material that decreased the amount of oxygen reduced at shorter diffusion times, was apparently deposited on the electrode while the negative voltage was applied. After some equilibration between the salt and the electrode, the reduction current at shorter time increased, indicating that a precipitated material was dissolved from the electrode surfaces in the absence of -1.0 volt. The comparison between curve (a) and (b) suggested that if

sufficient time had been allowed for the electrode surface to equilibrate with the solution, a maximum in $\Delta i\sqrt{t}$ might have been obtained.

Studies in this section showed that sulfate salts may be useful as a supporting electrolyte for oxygen diffusion measurements at short times. No interaction between the ions in solution and the electrode surface was noted that decreased electrode sensitivity to oxygen when the electrodes were placed in these salts with no applied voltage. However, storage of electrodes at -1.0 volt in $K_2SO_4$ for three days decreased their sensitivity at shorter diffusion times. The application of negative voltage pulses would need to be short and infrequent to avoid interference from these electrolytes. Even though sulfate salts might be useful as supporting electrolytes, they cannot be used for storing electrodes at -1.0 volt for long times.

## General Discussion

### Calculation of Oxygen Concentration by Theoretical Means

In the theoretical section of this chapter it was proposed that diffusion to a cylindrical platinum electrode might contain a phase of linear diffusion at diffusion times between 0.1 and 1.0 second. Studies were conducted in bentonite and various salt solutions to determine if such a phase was present and to define the conditions under which such a phase appeared.

In early data, aerated bentonite suspensions produced maximum values of $\Delta i \sqrt{t}$ at about 0.6 second when currents were recorded from glass insulated platinum electrodes with mercury junctions (Figure 14, page 73). In more detailed readings at less than one second, this maximum appeared as a plateau (Figure 16, page 79). In variously oxygenated bentonite suspensions, the plateau shifted to shorter diffusion times (0.6 to 0.3 second) as the oxygen concentration decreased from 21 to 5%. The products of $\Delta i \sqrt{t}$ from air saturated 0.01 N KCl were very similar to data from bentonite suspensions except that higher currents were recorded from the pure salt, indicating that its $O_2$ concentration was higher.

Similar plots of $\Delta i \sqrt{t}$ were also obtained from a range of salts including $Na_2CO_3$, $Na_2SO_4$, $MgSO_4$, $Li_2SO_4$, NaCl and $K_2SO_4$ (Figures 19 and 20, pages 89 and 90). In each salt solution where the influence of $Cl^-$ was minimized, the maximum products of $\Delta i \sqrt{t}$ were similar.

The characteristic trends that appeared in $\Delta i \sqrt{t}$

with time from salt solutions and bentonite suspensions included the following phases: an increase from zero to about 0.5 second diffusion time, a maximum at 0.4 to 0.6 second, and then a decrease prior to 1.0 second. The initial rise in $\Delta i\sqrt{t}$ was produced by charging of the double layer next to the platinum surface. The maximum in $\Delta i\sqrt{t}$ probably represented a maximum rate of oxygen reduction. The declining products of $\Delta i\sqrt{t}$ that followed this maximum may have represented a phase of interference from reaction products that cause a decreased rate of oxygen diffusion and oxygen reduction.

It seems reasonable to assume that a short phase of linear diffusion occurred near the maximum in $\Delta i\sqrt{t}$. However, because oxygen was not reduced at a maximum rate from zero diffusion time, error would be expected in calculating dissolved oxygen concentrations from the maximum products of $\Delta i\sqrt{t}$. The diffusion currents measured during the maximum should be slightly higher under these conditions than would be predicted by linear diffusion theory if a maximum rate of oxygen reduction had been initiated at zero diffusion time. Concentrations that were calculated from the maximum products were all slightly higher than the approximate known dissolved oxygen concentrations as can be seen in Table 9, page 92. The fact that all the calculated values were consistently higher than the known values supported the interpretation that the phase of maximum $\Delta i\sqrt{t}$ represented a short phase of linear diffusion to the wire electrodes.

In summary, constant products of $\Delta i\sqrt{t}$ were found at the diffusion times suggested by theoretical considerations. These products from various salt solutions produced oxygen concentrations very near the known values for those salts. Both of these findings are strong recommendations for further examination of oxygen diffusion currents at short times.

At the same time, there are many unanswered questions in these studies that place reservations on the validity of the above findings. For example: before reproducible oxygen reduction currents could be recorded, an equilibrium concentration of chemisorbed oxygen had to form on the surface of electrodes. The condition of the electrode surface as influenced by prior treatment also affected the measured currents. This response can be assumed to reflect the initial chemisorbed oxygen on the electrode. Because a fairly uniform treatment was used on the electrodes during this phase of studies, the number of sites available for chemisorption of oxygen would always have been nearly the same. Therefore, the maximum products of $\Delta i \sqrt{t}$ may have been produced from the reduction of chemisorbed oxygen rather than from linear oxygen diffusion. No estimate of the influence of chemisorbed oxygen on diffusion measurements at short times could be made from these studies.

## Experimental Calibration of Electrodes

The average of four currents obtained in bentonite with Epon insulated electrodes produced a fairly linear plot with $O_2$ concentration that did not intersect zero current (Figure 10, page 61). The glass mounted platinum electrodes, with mercury junctions were three times more sensitive than the Epon electrodes and produced a better linear fit, but the curve they produced also did not intersect zero current at zero oxygen concentration (Figure 17, page 81). This response from both electrode types was traced to residual currents that were five to ten microamperes too low. Reducible substances, formed on the electrode in the presence of KCl, were not allowed to accumulate on the electrodes prior to recording residual currents as they were prior to recording total currents. This and other sources of variability influenced the reliability of all the recorded data.

The usefulness of bare stationary platinum wire electrodes for measurement of oxygen concentration is currently limited by electrode variability. The factors involved in altering electrode sensitivity must be clearly understood and controlled if reliable measurements are to be obtained from bare electrodes. Once the variability problem is overcome, an apparatus that would permit rapid electrode calibration would be useful. In the present study four electrodes were used for all diffusion data. Their calibration at four oxygen concentrations was a major task. With sufficient control of variability, the electrode number could be decreased and some of the difficulties of calibration overcome.

## Conclusions

The findings of the studies in this chapter are summarized as follows:

1. Epon insulated electrodes gave much higher residual currents than glass mounted electrodes. As a result they were unsatisfactory for oxygen diffusion measurements at short times.
2. Variability in diffusion currents resulted from:

   (a) "poisoning" of the platinum surface in 0.01

N KCl but not in bentonite suspensions that contained KCl; (b) sensitizing the electrodes with -1.0 volt applied for several hours; (c) inherent electrode variability, that appeared as "drifts" in sensitivity for groups of electrodes and changes in the sensitivity of individual electrodes within a group; and (d) not permitting electrodes to equilibrate with the media prior to recording both total and residual currents in the presence of reactive materials.

3. With glass insulated electrodes the highest oxygen reduction currents were produced at an applied voltage of -0.75 volt. Interference from other reactions appeared at -0.80 volt.
4. Glass mounted platinum electrodes with mercury junctions were three times more sensitive and produced a better linear relationship with oxygen concentration than Epon electrodes.
5. Characteristic trends in diffusion currents from less than one second indicated that the electrode process at short diffusion times was complex. However, the maximum products of $\Delta i \sqrt{t}$ were constant for a few tenths of a second immediately after the

electrode surface was fully charged. This appeared to represent a short phase of linear diffusion.

6. Oxygen concentrations calculated from the maximum products of $\Delta i\sqrt{t}$ with linear diffusion theory gave an average concentration of 9.58 ppm. $O_2$ for six salt solutions whose known concentrations are about 9.0 ppm. at 20°C. A concentration of 7.4 ppm. was calculated for aerated bentonite suspensions at 20°C.
7. The usefulness of bare stationary platinum wire electrodes for measuring oxygen concentrations is limited by electrode variability. Nonetheless, oxygen diffusion currents from glass insulated electrodes were linear with oxygen concentration. However, with four electrodes, the calibration at four oxygen concentrations is a lengthy procedure.

# CHAPTER V

# POLAROGRAMS FROM AN EMF APPLIED AS A TRIANGULAR WAVE

A rectified triangular or saw-tooth wave can be applied to electrode systems to record complete polarograms on single photographs using oscillographic polarography as described by Heyrovsky (11) and Davis and Seaborn (6). The triangular wave may be useful for charging the electrodes through a voltage range that will produce a maximum rate of oxygen reduction at short time. The equipment used with triangular charging waves has the advantage of avoiding the need for mechanical switching in the electrode circuit.

In this chapter the general nature of oxygen reduction currents from triangular waves was examined in bentonite suspensions and in 0.01 N KCl so that the usefulness of the technique for measuring short term oxygen reduction currents in soils could be assessed. The operating characteristics of the circuit and the gradual charging of the electrodes might be used to obtain oxygen reduction currents with a minimum influence of diffusion rate through the media.

The entire polarogram obtained with each reading might also be useful for examining factors that interfere with the sensitivity of platinum electrodes to oxygen.

## The Apparatus

The basic component parts of the apparatus for generating the signal and for recording the polarograms were essentially the same as in the study of short diffusion times (Figure 6, page 35). To convert the circuit from a direct current pulse polarograph to a polarograph using a triangular voltage signal, the switching mechanism and the voltage control box in Figure 6 were replaced by a direct couple to a rectified triangular wave from the low frequency function generator as shown in Figure 21. The rectifying network consisted of a diode in series with a 220Ω and a 390Ω resistor. The signal applied to the electrodes was tapped from the 220Ω resistor. By using such a low resistance in the signal generating circuit, the higher variable resistance in the electrode circuit did not influence the applied signal. The voltage divider was used to minimize distortion of the triangular wave due to diode lag.

The rectified triangular wave was then fed to the

signal routing box shown in Figure 6, page 35. The signal routing box allowed the electrode circuit to be (a) shorted through a small resistance with no signal applied, (b) coupled to the triangular wave so the platinum electrode was charged negatively and the reference cell charged positively, and (c) left in an open circuit position (as in previous experiments, page 37). A selector switch permitted one of three signals to be routed to the oscilloscope: (a) the current flowing to the platinum electrodes, (b) the voltage applied with the electrodes in the circuit, and (c) the rectified triangular wave with the electrodes removed from the circuit.

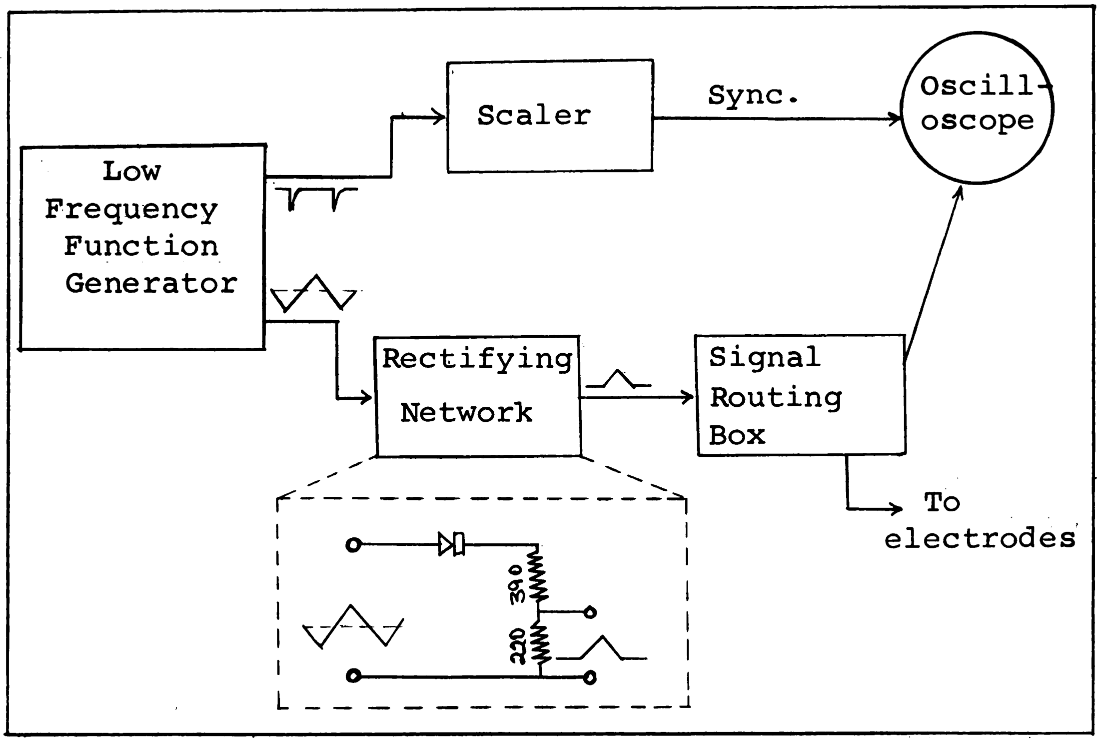


Figure 21. Simplified schematic diagram of the apparatus for applying a triangular wave to the electrodes and automatically presenting the polarogram on an oscilloscope.

Figure 22 shows the main rectified signal output of the generator and the synchronizing pulse which was fed to a scaler. This was used to trigger the scope trace so the polarogram would be presented automatically. In this study only an occasional signal was applied to the electrodes so a scaler was used to count the number of cycles that elapsed between circuit closures. The scaler was also used to detect the beginning of each triangular wave and aided in photographing the polarograms.

The rectified triangular wave, which was controlled by the function generator, was variable in both frequency and amplitude. Because variable signals were used throughout the studies of this section, certain notations were adopted so the variable properties of the applied signals could be easily identified. Figure 22 shows that the peak applied voltage was designated "$E_{Max}$". "Rise time" was chosen to designate the interval of time which elapsed while the platinum electrode was being driven negatively (Rise time = seconds per cycle/4). The differential rate of voltage change per unit time was designated dE/dt. Signals with rise times of 0.25, 0.5, 1.5, and 2.5 seconds were used. They represent cycle times of 1, 2, 6 and 10 seconds respectively.

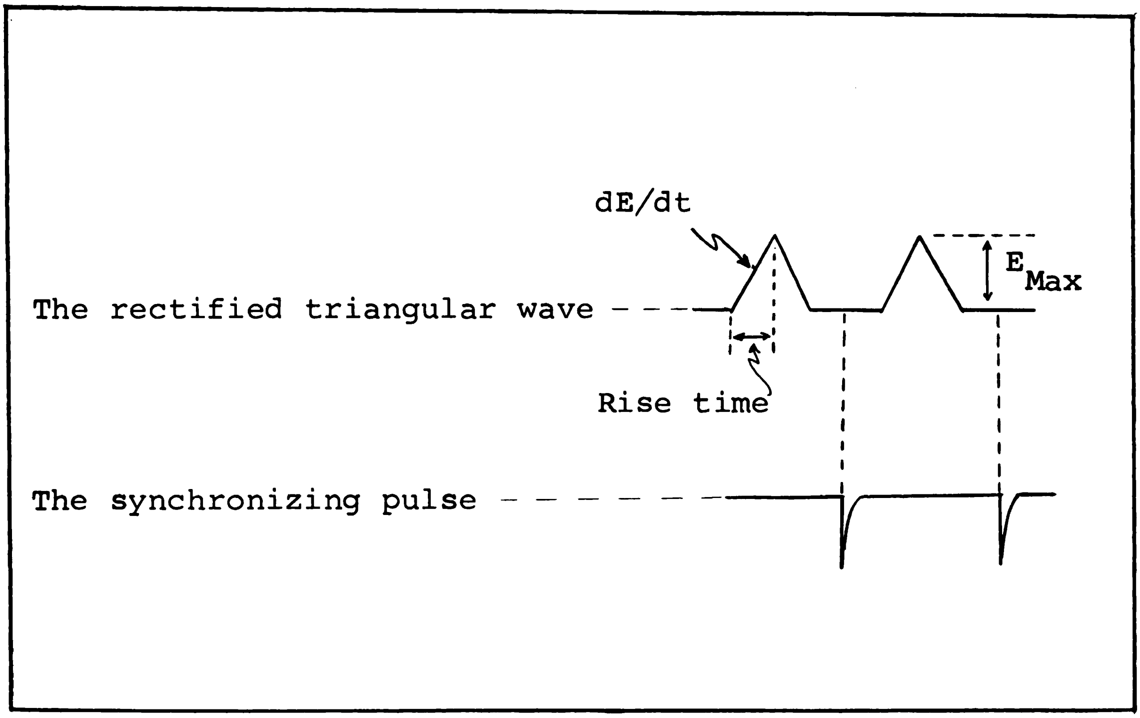


Figure 22: The wave forms from the function generator.

Epon insulated platinum electroeds (Figure 7, page 39) were used for all the data of this section. This study was conducted prior to discovering the difficulties with leakage currents and the fusion resistance in these electrodes.

## General Procedure

Polarograms were recorded photographically using a polaroid camera that had variable lens positions so that several curves could be recorded on each photograph (Figure 23).

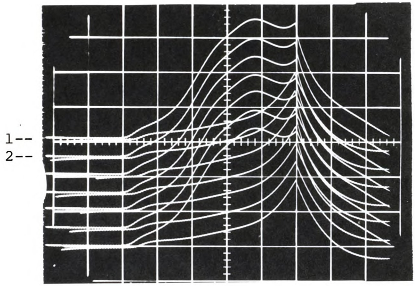


Figure 23. Polarograms recorded to obtain oxygen reduction currents.

The higher curves were taken from air saturated bentonite and the lower ones from $N_2$ saturated bentonite.

The seven pairs of curves were obtained at 50 cycle intervals with a signal of 1 second rise time.

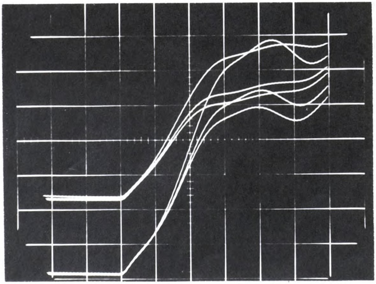


Figure 24. The current-time curves from three successive cycles of a triangular wave applied to an electrode.

The top three curves were from 3% bentonite in distilled water and the bottom three from 3% bentonite in 0.01 N KCl.

Residual currents were recorded for each total current polarogram. Oxygen reduction currents could then be calculated by measuring the difference directly. Difference measurements were made at the $O_2$ maximum when it was present. When the $O_2$ maximum was absent, measurements were made at the point of maximum difference in distance between the two curves. A 1000Ω resistor was used across the terminals of the oscilloscope so that current could be read directly as microamperes. Resistance in series with the electrodes will not disrupt electrode behavior when using a charging wave as it will with the application of a direct current voltage. If a sufficiently slow charging wave is used, the oxygen maximum should appear on the polarogram when the voltage becomes sufficiently low at the platinum surface to reduce oxygen. Unless one desired to know the half-wave potential, a shift of the $O_2$ maximum to higher or lower total voltages was not important.

Two types of liquid media were used in this study. Bentonite suspensions were 3% Na-bentonite in 0.01 N KCl. A pure solution of 0.01 N KCl was also used because of its known oxygen content.

Rectified triangular waves with different rise times were used to obtain reduction currents at a range of effective diffusion times. At the time these studies were run it was felt that oxygen adsorbed on the electrode surface might adversely affect the relationship between oxygen reduction currents and dissolved oxygen concentrations. Therefore, a range of effective diffusion times was studied so that adsorbed oxygen effects might be detected.

## Rest Period Required between Triangular Waves

When successive triangular waves were applied to a platinum electrode, a diffusion sphere was established around the platinum tip. The photograph in Figure 24 shows three successive cycles of a signal with a rise time of 1 second and $E_{Max} = -1.0$ volt. The first cycle represents the reduction current from a platinum electrode in equilibrium with the media, the second and third cycles were lower in amplitude because oxygen was not being replenished at the same rate that it had been reduced.

A study was conducted to determine how many cycles needed to be removed between each applied triangular wave before the initial reduction current could be reproduced without moving the electrode in the medium. Two calibrated platinum electrodes (page118) that were producing similar polarograms were used to obtain a sequence of curves from both air saturated and oxygen free bentonite. One electrode was positioned in each medium. Various numbers of cycles ranging from 5 to 100 were removed from signals with three different rise times, 0.5, 1.0, and 1.5 seconds.

The sequence of polarograms given in Figure 23 show how the data in Table 10 were obtained. A signal of four seconds per cycle and 1 second rise time at 50 cycle intervals was applied to the electrodes. In the first pair of curves, labeled (1), the first triangular wave was applied to the electrode in the air saturated bentonite. Then by changing the electrode selector switch, the second wave was applied to the electrode in oxygen free medium. While the electrodes were in an open circuit position, the incoming signals were counted with the scaler until the proper number of cycles had elapsed. The second pair of polarograms were then recorded. In the photograph given in Figure 23, where 50 cycles of a 4 seconds per cycle signal were omitted between each of the applied triangular waves, oxygen was reduced during about 2 of the 4 seconds of signal length. Then the electrodes were allowed to "rest" for 200 seconds and the second pair of curves were obtained.

The oxygen reduction currents recorded in this study are summarized in Table 10 and plotted in Figure 25. Constant

Table 10. Oxygen reduction currents from polarograms obtained in aerated bentonite suspensions.

| Cycle applied to the electrodes | | Oxygen reduction current in microamperes<br>Signal applied [rise time (sec.)][a] | | |
|---|---|---|---|---|
| Frequency | Number | 0.5 | 1 | 1.5 |
| Every 5th cycle | 1 | | 55.5 | 45.6 |
| | 6 | | 49.3 | 40.2 |
| | 11 | | 46.1 | 38.7 |
| | 16 | | 45.0 | 37.6 |
| | 21 | | 43.0 | 36.5 |
| | 26 | | 43.0 | 36.0 |
| | 31 | | | 35.0 |
| Every 10th cycle | 1 | 70.6 | | |
| | 11 | 67.9 | | |
| | 21 | 65.2 | | |
| | 31 | 63.2 | | |
| | 41 | 61.4 | | |
| | 51 | 61.4 | | |
| | 61 | 60.6 | | |
| Every 20th cycle | 1 | | 55.7 | 45.6 |
| | 21 | | 53.3 | 44.5 |
| | 41 | | 53.1 | 44.0 |
| | 61 | | ---- | 43.5 |
| | 81 | | 51.9 | 42.8 |
| | 101 | | 51.3 | 42.8 |
| | 121 | | 50.9 | |
| Every 50th cycle | 1 | 74.4 | 55.7 | 46.4 |
| | 51 | 72.6 | 55.7 | 45.3 |
| | 101 | 72.4 | 55.7 | 45.9 |
| | 151 | 71.6 | 55.1 | 45.3 |
| | 201 | 71.6 | 55.1 | 45.3 |
| | 251 | 71.4 | 55.1 | 45.3 |
| | 301 | | 55.1 | |
| Every 100th cycle | 1 | 73.9 | | |
| | 101 | 73.9 | | |
| | 201 | 73.9 | | |
| | 301 | 73.9 | | |
| | 401 | 73.9 | | |
| | 501 | 73.9 | | |

[a] A triangular wave with $E_{Max} = -1.0$ volt was used with Epon insulated electrodes.

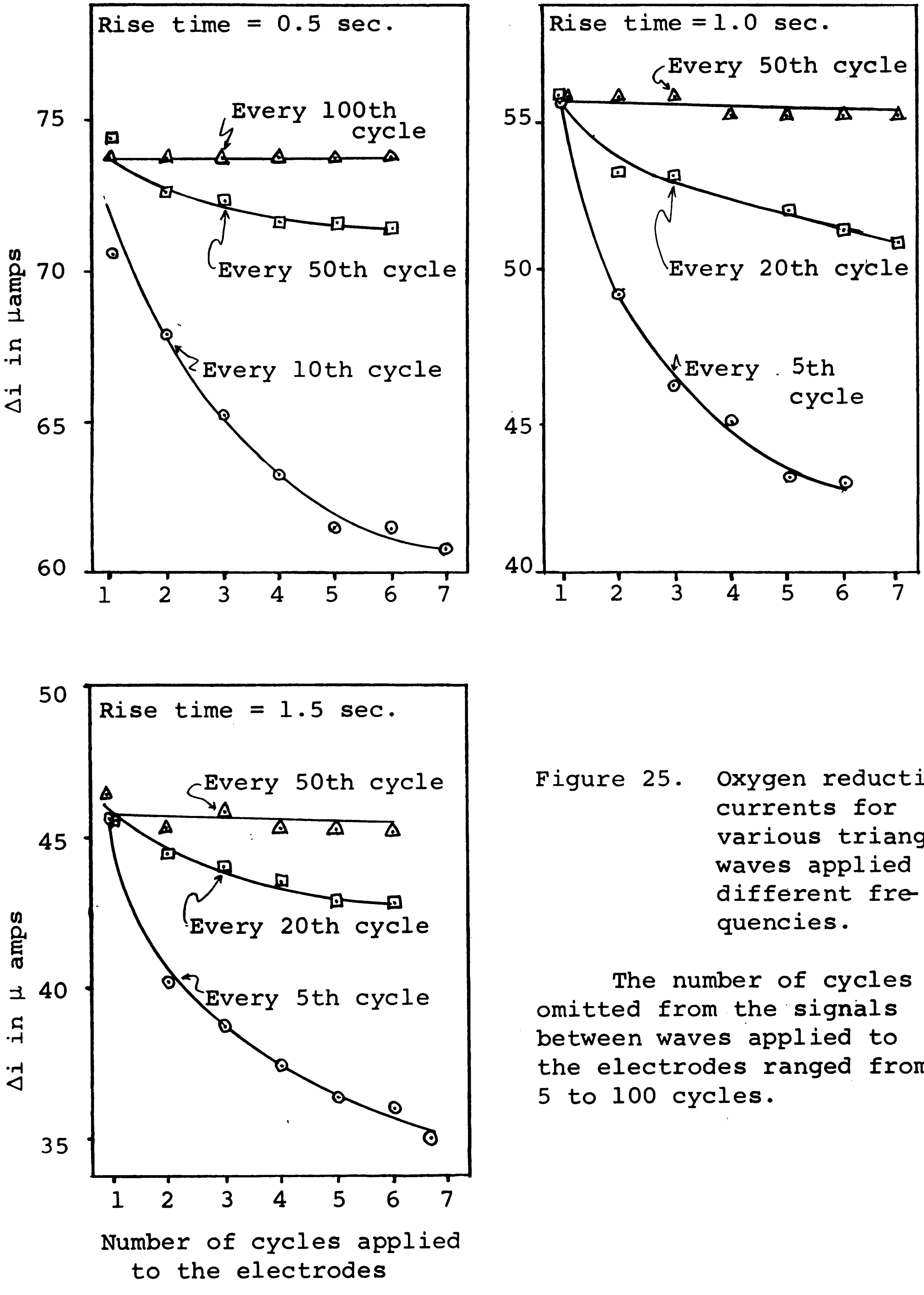


Figure 25. Oxygen reduction currents for various triangular waves applied at different frequencies.

The number of cycles omitted from the signals between waves applied to the electrodes ranged from 5 to 100 cycles.

current values were obtained when 50 cycles were removed from the signals with 1 and 1.5 second rise times, and when 100 cycles were removed from the triangular wave with 0.5 second rise time. In each case the ratio of voltage off to voltage on time was greater than 100:1 before equilibrium oxygen reduction currents were obtained with repeated cycles. This ratio agreed with that determined in preliminary studies using a pulsing technique.

The numerical values in Table 10 represent single readings of the difference in current between two electrodes. Very good agreement was obtained between the oxygen reduction current of the initial cycles and the equilibrium Δi values in all cases. Only one value showed as much as 5% variability. That was the current from the first cycle of the 0.5 second rise time triangular wave where every 10th cycle was omitted. The initial and equilibrium Δi values increased with decreasing rise time. At rise time of 1.5, 1 and 0.5 they were 45.3, 55.1, and 73.9 respectively. The increased current resulted because measurements at the oxygen maxima were made at shorter and shorter effective diffusion times as the signal rise time decreased. The corresponding approximate diffusion times at the point of measurement were about 2/3 of the rise time.

## Oxygen Concentration Studies

Polarograms were obtained from suspensions of bentonite and from 0.01 N KCl that had been oxygenated with 5, 10, 15, and 21% $O_2$. Triangular waves with rise times of 1.5, 1.0, 0.5, and 0.25 seconds were applied with $E_{Max}$ adjusted between -1.0 to -1.5 volts. Two electrodes were used to obtain $\Delta i$ values by the difference method. One electrode was placed in the medium containing oxygen and the other was placed in the $N_2$ saturated suspension. This method allowed readings to be recorded more rapidly than with one electrode because cross contamination was avoided.

Two sequences of readings from bentonite were included in Figure 26 to demonstrate the kind of results that were obtained in this section. The oxygen reduction currents were recorded at two different rise times, 0.5 and 1.5 seconds (Figure 26a). The $\Delta i$ values for the faster signal were naturally higher than those obtained with the longer rise time because they were obtained at a shorter effective diffusion time. A similar trend was obtained with rise times of 1.0 and 0.25 seconds.

In the second sequence reported for bentonite in 0.01 N KCl (Figure 26b) for a triangular wave with a rise time of 0.5 seconds, electrode sensitivity to oxygen

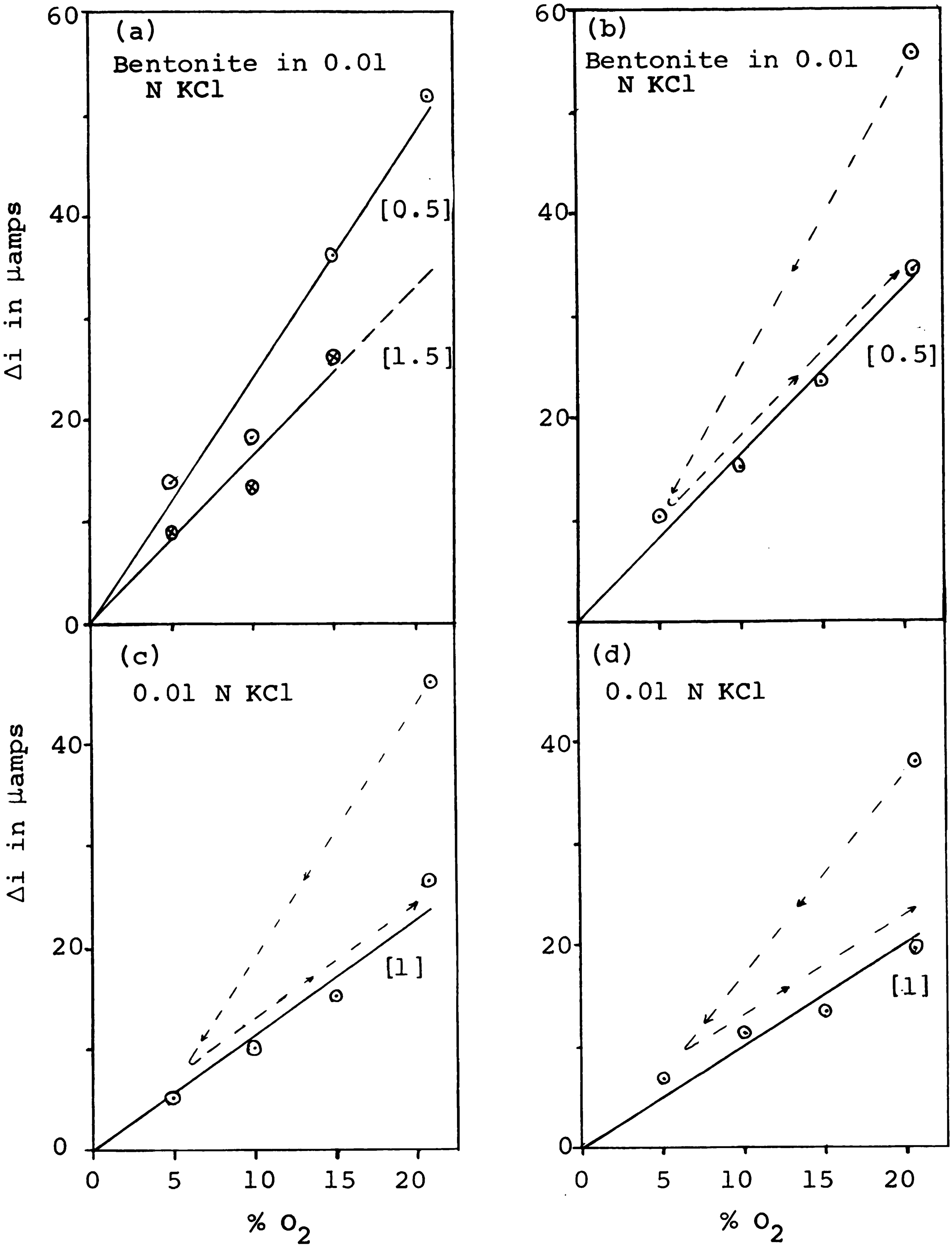


Figure 26. Oxygen reduction currents with oxygen concentration using triangular waves.

The dashed arrows indicate the order in which the readings were made within a single sequence. Two electrodes were used for the data in a, b, and c. One was positioned in oxygen containing media and the other was positioned in $N_2$ saturated media. For the data in d, one electrode was used entirely. From two to six equilibrium oxygen reduction currents were averaged for each point. The rise time of the applied signal in seconds is given with each curve.

decreased markedly after the first group of readings. A set of equilibrium oxygen reduction currents was obtained from 21% $O_2$ bentonite at the beginning of the sequence. Currents were then recorded from bentonite suspensions that contained equilibrium concentrations of $O_2$ from 5, 10, 15, and 21% oxygen in mixed gases. These were made in order from low to high concentrations as indicated by the dashed arrows in Figure 26. Prior to the first reading in 21% $O_2$ bentonite, the electrodes had been stored in distilled water. The result was that the initial $\Delta i$ value was not reproduced by a similar set of readings in 21% $O_2$ bentonite at the end of the sequence, because of the "poisoning" from KCl previously reported. It was not known why the second sequence of readings from bentonite showed systematic variation while the first group did not. In the previous chapter, "poisoning" was not observed from bentonite in KCl but only in KCl alone. Between the individual readings in bentonite in Figure 26b, the electrodes may have been placed in 0.01 N KCl by mistake rather than in distilled water.

Similar data from a triangular wave of one second rise time showed a more severe "poisoning" trend than that reported for the 0.5 second rise time signal in Figure 26b. With the longer rise time, only a small difference in

average $\Delta i$ was obtained between 10 and 15% $O_2$ suspensions. This response was similar to that from measurements in oxygenated 0.01 N KCl in Figure 18, page 85.

Two sequences of readings were then obtained from 0.01 N KCl to determine if "poisoning" from KCl was responsible for the depressed sensitivity. The data of Figure 26d were obtained by using only one electrode that was moved from nitrogen saturated to oxygen containing KCl. In contrast, those of Figure 26c were obtained by using two different calibrated electrodes with one in each media. Both sequences produced the same trend that was observed in the second bentonite sequence. Each group of readings was recorded on separate days, and the electrodes had been stored in distilled water for 12 or more hours prior to each sequence. Therefore, any soluble material that might have been formed on the electrode surfaces while they were in the salt solutions would have been dissolved between each of the four sets of readings.

The very marked decrease in electrode sensitivity, produced by exposing the platinum electrodes to KCl, suggested that a complex involving the platinum surface and the electrolyte was formed which decreased the number of sites that had been active in oxygen reduction. The

same phenomena appeared in the data of the previous chapter (page 91).

## Electrode Calibration

The technique used for obtaining oxygen reduction currents with two different electrodes, one in $O_2$ containing media and another in $N_2$ saturated media (the two electrode difference method), required some means of electrode calibration. Successive triangular waves were applied to the electrodes in air saturated bentonite and the resulting current-time curves were recorded photographically. Electrodes were paired by selecting those that gave similar total current values at the oxygen maximum of successive polarograms.

A sample of the data obtained from electrode calibration is given in Table 11. Total currents from two separate sets of calibration polarograms are given for electrodes 10, 11, 12, and 13. The duplicate readings from electrode 11, obtained on the same day, agreed well with one another but they were higher than readings from electrodes 10, 12, and 13. The amplitudes of cycle 2 through 6 for the latter electrodes showed good agreement on the first day but varied some when the calibration was repeated one day later. Amplitudes for the first cycle from electrodes 10, 12, and 13 ranged from 34.5 to 44.5. Similar data for other calibrated electrodes fell within the same range but no clear pattern of variability was apparent.

Table 11. Total currents from polarograms obtained in bentonite in 0.01 N KCl for electrode calibration.

| Electrode number | Total current at the oxygen maximum in μamperes[a] | | | | | |
|---|---|---|---|---|---|---|
| | Cycle number | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 10 | 44.5[b] | 28.6 | 23.4 | 19.1 | 18.0 | 17.0 |
| | 42.5[c] | 30.7 | 26.0 | ---- | ---- | ---- |
| 11 | 48.8[b] | 32.8 | 26.5 | 22.3 | 19.1 | 18.0 |
| | 47.8[b] | 31.8 | 25.5 | 21.2 | 20.2 | 18.1 |
| 12 | 42.5[b] | 29.7 | 23.4 | 19.1 | 17.0 | 15.9 |
| | 42.5[c] | 32.8 | 28.6 | ---- | ---- | ---- |
| 13 | 39.2[b] | 27.5 | 22.3 | 19.1 | 17.0 | 15.9 |
| | 34.5[c] | 26.0 | 22.3 | ---- | ---- | ---- |

[a] Successive cycles of a triangular wave with a rise time of 1.5 seconds and an $E_{Max} = -1.0$ volt were applied to the electrodes.

[b] Polarograms were recorded on the same day.

[c] Polarograms were recorded one day after (a).

In the preceding data the total current at the oxygen maximum was different for each electrode. The total current was also different for the same electrode from one calibration to the next. Therefore, the reliability of the two-electrode difference method should be questioned. Both methods were used in the data in Figure 26, on page 115. Only one electrode was used for the data presented in Figure 26d, but the "two-electrode difference method" was used with the data in Figure 26c. In both cases, electrode sensitivity to oxygen decreased and electrode variability was approximately equal. In data not reported, residual current curves for individual electrodes varied as much as currents obtained from different electrodes. Therefore with frequent calibration, difference measurements using two electrodes should produce reliable oxygen reduction currents. This method was of interest because cross-contamination between samples was avoided and also because future measurements might be made by recording only the difference currents. Standard oscilloscope units are available for obtaining this type of data.

## Potential of the Method

If electrode variability can be overcome then the use of a rectified triangular wave might prove to be the only method for obtaining oxygen reduction currents from soils which can be used for estimation of dissolved oxygen

concentrations. This is based upon several observations that were made in Chapter IV on diffusion curves at short times and in Chapter VI, on oxygen concentration studies in soils that follows immediately. The product of $\Delta i\sqrt{t}$ was observed to increase to a maximum value at about 0.6 second in pure salt solutions and in suspensions of bentonite. In soils where either no salt was added or samples were adjusted to 20 cm. moisture tension, oxygen reduction never proceeded at a maximum rate at short diffusion times as indicated by the absence of a plateau in $\Delta i\sqrt{t}$. This difference in response was interpreted to reflect the rate at which the double layer next to the electrode surface became charged. In addition to the kind of media, the electrode construction and the applied voltage also influenced the rate of charge build-up.

In order to make valid measures of dissolved oxygen, the electrode surface must be charged so that oxygen reduction occurs at a maximum rate. The polarograms given in Figure 23 on page 107 show that a maximum value of $\Delta i$ was obtained in each set of polarograms. This maximum resulted when the electrode double layer was sufficiently charged to reduce oxygen at a maximum rate. The factors which interfere with the rate of charge build-up when using a direct current pulse, such as series resistance, current leakage and the magnitude of the applied voltage, are cancelled out with the triangular wave. If a sufficiently high maximum voltage and a sufficiently slow signal are applied, then a maximum rate of oxygen reduction should always be observed unless the surface conditions of the electrode, rather than the surface charge, is limiting.

If the problem of charge deficiency at the electrode surface in soils can be overcome with a traingular wave, then the technique should be useful in estimating dissolved oxygen concentrations in soils when used with experimental calibration.

## Conclusions

The studies of this chapter demonstrated that the rest period between applied triangular waves needed to be about one hundred times longer than the period of oxygen reduction to avoid forming an oxygen deficit around the electrode. Calibration of electrodes in variously oxygenated bentonite suspensions and KCl solutions produced linear plots of $\Delta i$ vs % $O_2$ after equilibrium was established between the platinum surface and ions in solution.

# CHAPTER VI

# OXYGEN CONCENTRATION STUDIES IN SOILS

## Measurements in Samples of Variously Oxygenated Aggregates

Studies were conducted in variously oxygenated Brookston aggregate systems to see if soils would produce diffusion currents at short times that would be at all comparable to those from bentonite suspensions (Figures 16 and 17 on pages 79 and 81). Oxygen diffusion currents at less than one second were recorded by applying a direct current square wave of -0.75 volt to glass insulated platinum electrodes.

Measurements were made in two kinds of soil systems. One system contained aggregates 2 to 4 mm. in diameter and was moistened with an electrolyte, 0.01 N KCl. The other contained aggregates 0.5 to 2 mm. in diameter and was moistened with only distilled water. Samples of both the air-dry aggregates (2-4 mm. in diameter) and the appropriate liquids were equilibrated with $N_2$, and 5, 10, 15 and 20% $O_2$. Manifolds were placed on sintered glass filtration funnels

and the containers were also purged with the appropriate gas. The dry aggregates were then placed in the funnels to about a 2 inch depth and saturated with the appropriate gas saturated liquids. Gas was flushed through the manifold for about 10 minutes prior to recording diffusion curves from each sample with all four electrodes.

The method of recording diffusion currents from these soil samples allowed equilibrium to be established between oxygen containing samples and the electrodes but not between the nitrogen saturated samples and the electrodes. In both cases the electrodes were first inserted just below the soil surface and two -0.75 volt pulses were applied. They were then repositioned to about 0.75 inch below the surface. In oxygenated samples the electrodes were allowed to equilibrate in this new position for five minutes. In nitrogen saturated samples residual currents were recorded very shortly after the electrodes were repositioned. This procedure duplicates as closely as possible that used with the measurements in bentonite suspensions reported in Figure 16, page 79.

Diffusion curves were recorded from both saturated aggregates and aggregates adjusted to 20 cm. tension after 3 hours drainage. Calculations for $\Delta i\sqrt{t}$ were made from

the average of 4 electrode readings. Average diffusion currents that were selected from plots of $\Delta i\sqrt{t}$ were plotted with $O_2$ concentration. The corresponding diffusion currents for individual electrodes are found in the appendix, Tables 15, 16, 17, and 18 on pages 154 through 161.

Graphs of the data from aggregates that had been wet with 0.01 N KCl are given in Figure 27. In saturated systems the products of $\Delta i\sqrt{t}$ were maximum at 0.2 to 0.3 second. These compare roughly to the maxima from bentonite at 0.2 to 0.8 second diffusion time. The currents, that were measured in soils which had been equilibrated with 10% $O_2$, were higher than currents from 15% $O_2$ samples because of variability. Values for $\Delta i$ at 0.3 second diffusion time in saturated samples were plotted with $O_2$ concentration at the bottom left of Figure 27. All the points, except the 15% current, fell near a straight line that intersected zero. This indicated that reactive materials other than oxygen which form reducible substances on electrode surfaces did not accumulate during five minutes of equilibration in this soil.

When the tension was increased to 20 cm., quite a different response was observed in the product of $\Delta i\sqrt{t}$. The products from 5 and 10% $O_2$ were fairly constant up to

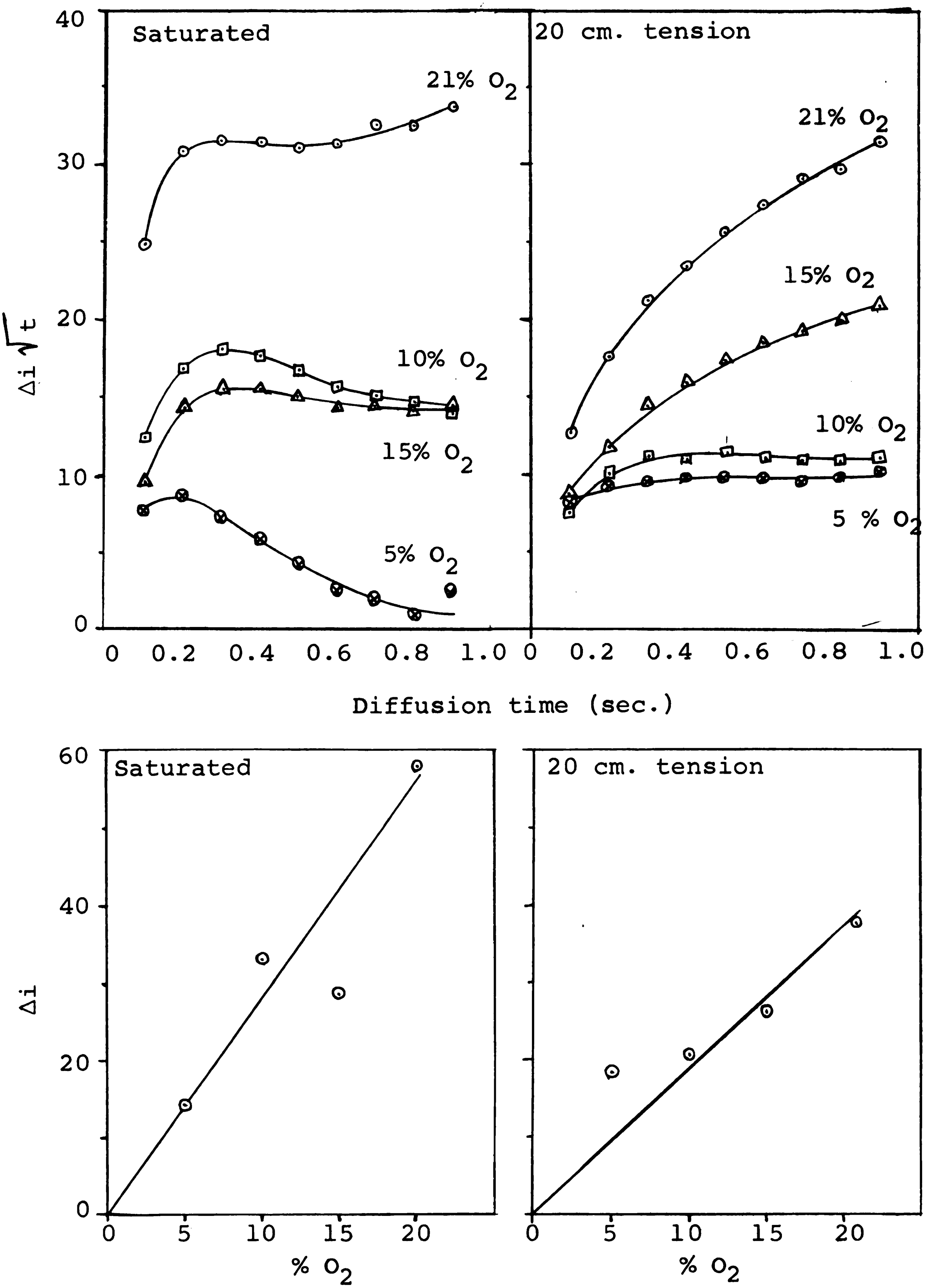


Figure 27. The influence of oxygen concentration on diffusion currents from soils moistened with 0.01 N KCl.

Readings from Brookston aggregates (2-4 mm. in diameter) were obtained from glass insulated platinum electrodes. Diffusion currents from 0.3 second were plotted with oxygen concentration in the lower graphs. Detailed data for these figures appear in the appendix, Tables 15 and 16, pages 154 through 157.

one second, but those from 15 and 20% $O_2$ samples increased over the range of diffusion times studied. A plot of $\Delta i$ with $O_2$ concentration for the samples at 20 cm. moisture tension gave a fairly straight line except for the 5% concentration.

In the absence of supporting electrolyte, no maximum in the product of $\Delta i\sqrt{t}$ appeared for either the saturated aggregates or aggregates adjusted to 20 cm. moisture tension. In the saturated samples $\Delta i\sqrt{t}$ increased slightly up to one second in the 5 and 10% $O_2$ samples (Figure 28). The increase in $\Delta i\sqrt{t}$ with time was considerably larger at higher oxygen concentrations. This response was similar to that observed in the data of Figure 27 for samples wet with KCl and adjusted to 20 cm. tension. The relationship between 0.5 second diffusion currents and oxygen concentration was fairly linear in the saturated samples except that the current from 15% $O_2$ soil was high.

When the aggregates that contained no added salt were drained to 20 cm. tension, the diffusion currents in 5, 10 and 15% $O_2$ soils were much higher than in saturated samples. The currents from 21% $O_2$ soil fell off badly. This response is reflected in the plot of $\Delta i$ at 0.5 second diffusion time with percent oxygen. Currents were

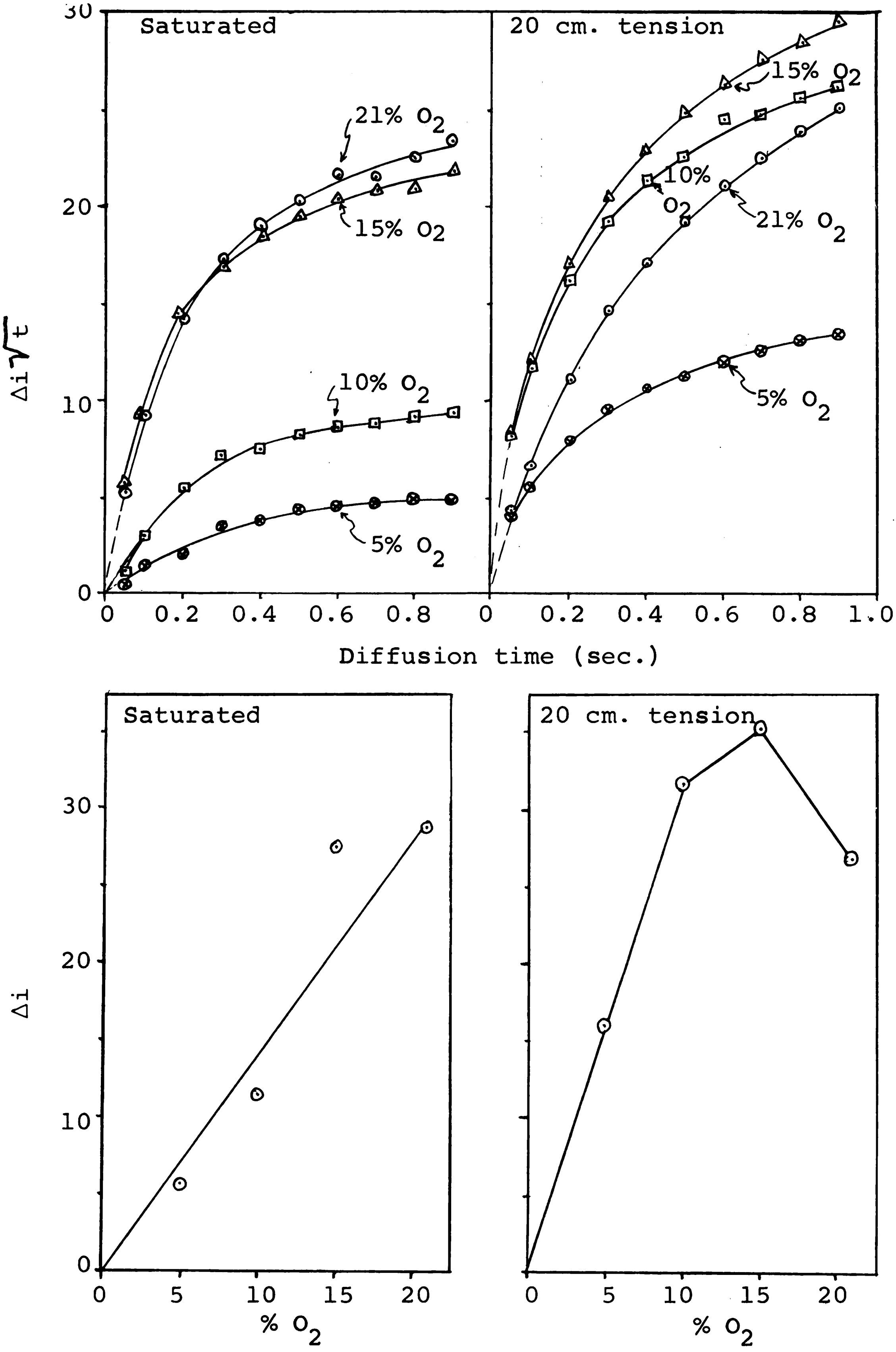


Figure 28. The influence of oxygen concentration on diffusion currents from soils moistened with distilled water.

Readings from Brookston aggregates (0.5-2 mm. in diameter) were obtained from glass insulated platinum electrodes. Diffusion currents from 0.5 second were plotted with oxygen concentration in the lower graphs. Detailed data for these figures appear in the appendix, Tables 17 and 18, pages 158 through 161.

lower in 21% $O_2$ soils than in soils equilibrated with either 10 or 15% $O_2$.

The absence of a maximum in $\Delta i\sqrt{t}$ at less than one second and the gradual increase in $\Delta i\sqrt{t}$ up to 1 second indicated that the double layer of the electrode was charged slowly in soils that were either adjusted to 20 cm. tension or contained no added electrolyte. This response was similar to that from measurements in bentonite suspensions with Epon insulated electrodes (Figure 11, page 63). In that case, current "leakage" and junction resistance probably hindered charge build-up. On the other hand, in the soils systems (Figures 27 and 28) charge accumulation was probably slowed by a moderate resistance through the soil matrix at low electrolyte concentration or at slight moisture tensions.

A slow rate of charge build-up in the double layer can also be used to explain the very low diffusion currents in Figure 28 that were obtained from aggregates equilibrated with 21% $O_2$ and adjusted to 20 cm. tension with no added salt. Similar results were obtained from bentonite suspension during the phase of charge accumulation at less than 0.3 seconds (Figure 16, page 79). No relationship between diffusion currents and oxygen concentration were found in bentonite during this charging period. In soil samples where

no salt had been added, this charging period was undoubtedly extended to longer diffusion times, especially where tensions were adjusted to 20 cm.

## Measurements in Single Aggregates

One of the goals of this study was to be able to measure oxygen concentrations within microenvironments where oxygen may limit the aerobic metabolism of both soil microorganisms and plant roots. A short-term incubation was conducted using aggregates from a virgin Brookston clay loam with an organic matter content of about 8%. Aggregates were collected in a field moist state and separated into 3 sizes; large (3 to 5 cm. in diameter), medium (2 to 3.5 cm. in diameter) and small (1 to 2.5 cm. in diameter). The aggregates were placed on several layers of saturated blotter paper in containers convered with polyethylene. Half of the aggregates were incubated with 5% dextrose in 0.01 N KCl and half with 0.01 N KCl alone. The KCl had been added to provide a sufficient concentration of supporting electrolyte so that the electrode surface would be charged rapidly at short diffusion times.

A special small electrode was made from 28 gauge platinum wire (0.321 mm. diameter) cut to 2 millimeters length and mounted in Epon adhesive. The electrode was mounted on a stable, screwdriven platform with a millimeter scale positioned below it. Diffusion curves were usually recorded in triplicate (sometimes more) at -0.65 volt applied after 10 and 30 hours incubation at a series of depths from 0 to 10 or 12 mm. in 2 mm. increments. Duplicate diffusion curves were recorded from air saturated 0.01 N KCl both before and after each sequence of readings to serve as a reference for electrode sensitivity. The readings from KCl were obtained rapidly to prevent loss of oxygen sensitivity.

The average corrected diffusion currents were analyzed for constant products of $\Delta i\sqrt{t}$ over the diffusion times of 1 to 9 seconds. The data obtained from large aggregates incubated with dextrose for 10 hours are in Table 12. This was given to show a sample of the data that were obtained from all the aggregates and to show that the trend in $\Delta i\sqrt{t}$ was similar to that of Figure 9a on page 49 for larger Epon insulated electrodes. At positions where oxygen was abundant, $\Delta i\sqrt{t}$ increased with diffusion time (0-2 mm. and 8-10 mm. depths) and either remained constant or decreased at positions of low oxygen concentration (2-4, 4-6 and 6-8 mm. depths).

Curves of 5 second oxygen diffusion currents with

Table 12. Oxygen diffusion currents inside large aggregates after 10 hours incubation with 5% dextrose.

| Diffusion time (sec.) | Depth in aggregates (mm.)[b] | | | | | | | | | | Standard[c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0-2 | | 2-4 | | 4-6 | | 6-8 | | 8-10 | | 21% $O_2$ in 0.01 N KCl | |
| | $\Delta i$[a] | $\Delta i \sqrt{t}$ | $\Delta i$ | $\Delta i \sqrt{t}$ | $\Delta i$ | $\Delta i \sqrt{t}$ | $\Delta i$ | $\Delta i \sqrt{t}$ | $\Delta i$ | $\Delta i \sqrt{t}$ | $\Delta i$ | $\Delta i \sqrt{t}$ |
| 1 | 3.47 | 3.47 | 0.80 | 0.80 | 0.78 | 0.78 | 0.96 | 0.96 | 2.00 | 2.00 | 5.60 | 5.60 |
| 2 | 2.78 | 3.95 | 0.49 | 0.69 | 0.54 | 0.76 | 0.76 | 1.08 | 1.47 | 2.09 | 4.37 | 6.21 |
| 3 | 2.48 | 4.31 | 0.31 | 0.54 | 0.42 | 0.73 | 0.62 | 1.08 | 1.37 | 2.38 | 3.86 | 6.72 |
| 4 | 2.39 | 4.78 | 0.29 | 0.58 | 0.40 | 0.80 | 0.62 | 1.24 | 1.33 | 2.66 | 3.44 | 6.88 |
| 5 | 2.31 | 5.17 | 0.29 | 0.65 | 0.38 | 0.85 | 0.58 | 1.58 | 1.24 | 2.78 | 3.18 | 7.11 |
| 6 | 2.27 | 5.58 | 0.27 | 0.66 | 0.36 | 0.88 | 0.58 | 1.42 | 1.25 | 3.07 | 3.04 | 7.48 |
| 7 | 2.24 | 5.93 | 0.24 | 0.63 | 0.38 | 1.01 | 0.55 | 1.46 | 1.22 | 3.23 | 2.89 | 7.65 |
| 8 | 2.17 | 6.16 | 0.20 | 0.57 | 0.31 | 0.88 | 0.55 | 1.56 | 1.15 | 3.26 | 2.82 | 8.01 |
| 9 | 2.02 | 6.06 | 0.09 | 0.27 | 0.18 | 0.54 | 0.38 | 1.14 | 1.02 | 3.06 | 2.71 | 8.13 |

[a] The current in microamperes was obtained from Epon insulated platinum electrodes with tips from 28 ga. wire (0.321 mm. diameter) cut to 2 mm. length. Aggregates were moistened with 5% dextrose in 0.01 N KCl.

[b] Each current value is the average of four duplicate readings with the same electrode.

[c] These standard diffusion currents from aerated 0.01 N KCl were recorded at the end of the run.

depth for each aggregate size are given in Figure 29. The current measured in 0.01 N KCl is represented by the dashed line at 3 to 3.5 microamperes. These were the average of readings taken both before and after each sequence was recorded. Some of the diffusion currents measured at shallow depths in aggregates wet with 0.01 N KCl only, exceeded the currents recorded from the standard salt solution. The standard currents were not compared to air saturated diffusion currents in aggregates because instrumental difficulties were encountered when they were to be recorded.

Because only crude calibration was attempted by recording diffusion currents from 0.01 N KCl, the measured currents could only be interpreted relatively. In the large aggregates where the microbial activity was stimulated by dextrose, the oxygen concentration was greatly decreased at 2-4 mm. below the aggregate surface after 10 hours incubation. After 30 hours incubation the estimated oxygen concentration at 2-4 mm. was low in the large aggregates incubated both with and without dextrose. In the larger aggregates under conditions of oxygen stress, the oxygen concentration seemed to increase in the center of the aggregates, indicating that oxygen may have been consumed primarily in the surface layers. The lower diffusion

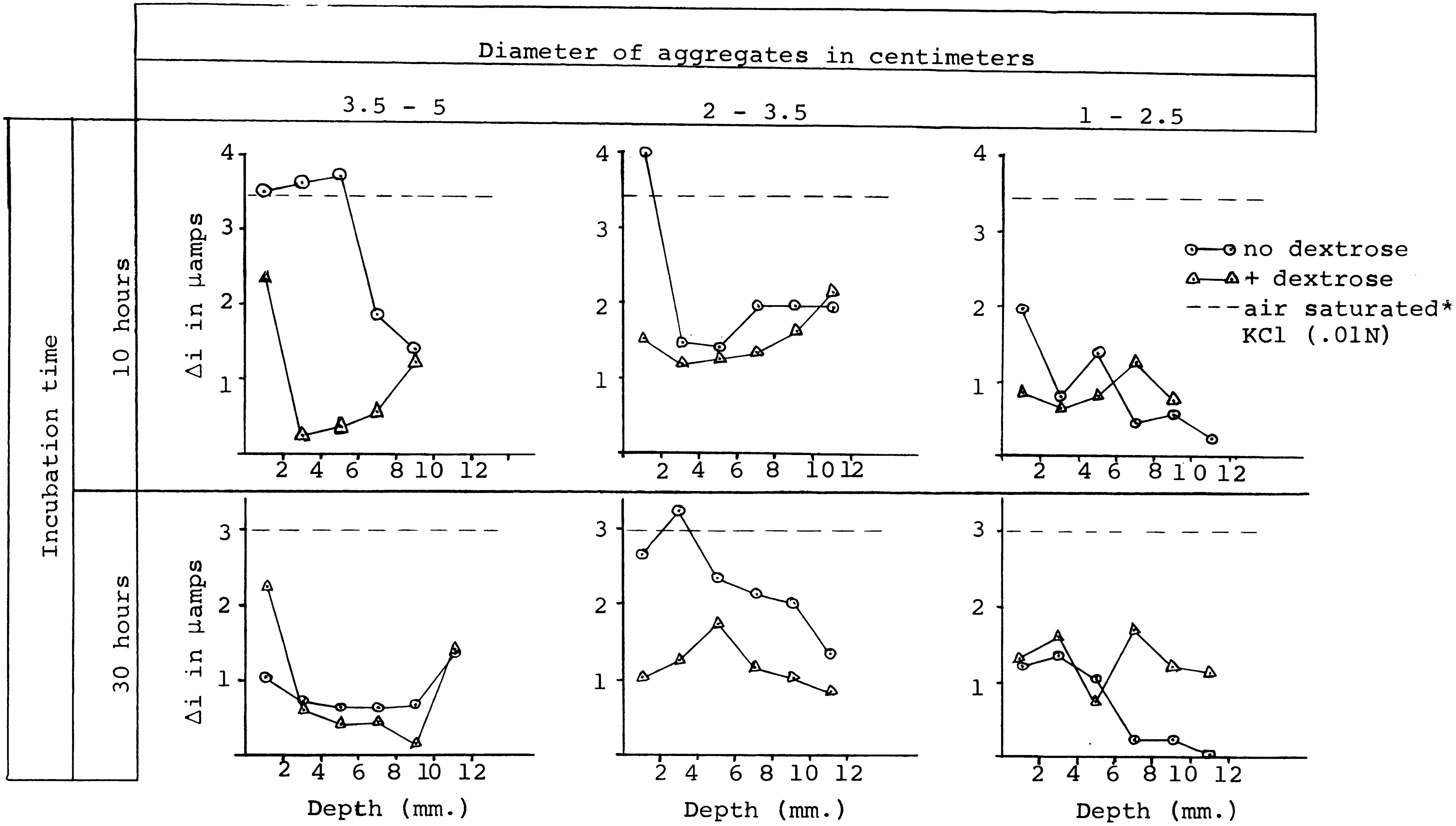


Figure 29. Profiles of estimated oxygen concentration in aggregates of three sizes at two incubation times.

*The currents are 5 second diffusion currents and the average of four readings with the same electrode. The standard currents from KCl are the average of currents from the beginning and the end of each incubation sequence.

currents recorded for the smaller aggregates may have resulted from slightly lower moisture tensions. All aggregates were laying directly on saturated blotter paper so those of smaller diameter would have been at a slightly higher moisture content than the larger aggregates.

## Conclusions

The measurement of diffusion currents from soils at short diffusion times showed that when either no salt was added or samples were adjusted to 20 cm. moisture tension oxygen reduction did not proceed at a maximum rate as indicated by the absence of a plateau in $\Delta i \sqrt{t}$. This response was attributed to a slow rate of charge accumulation in the double layer next to the platinum surface. The short term oxygen reduction currents from soils clearly indicated that a new development was necessary before diffusion currents from soils could be interpreted theoretically using linear diffusion theory or before diffusion currents from soils measured at short times could be calibrated against dissolved oxygen concentrations. Relative measures of oxygen concentration in aggregates incubated with 0.5% dextrose in 0.01 N KCl showed that the oxygen concentration was reduced to very low values at only 3 mm.

below the aggregate surface after 10 hours of incubation. Those incubated without dextrose gave similar low oxygen concentrations after 30 hours of incubation.

The study of relative oxygen concentrations in aggregates demonstrated the use that could be made of quantitative estimations of oxygen concentrations. It also showed that changes in oxygen concentration could be detected even with the rather crude method employed. A large number of very interesting studies on the oxygen relationships within aggregates could be conducted if the method were refined.

# CHAPTER VII

## SUMMARY

The estimation of dissolved oxygen concentrations with solid, stationary, platinum, wire electrodes was attempted using oscillographic polarography. Studies were conducted both by calibrating electrodes in media equilibrated with gases of known oxygen concentration and by calculating dissolved oxygen concentrations with linear diffusion theory from measured diffusion currents. With the latter technique it was assumed that linear diffusion occurred for path lengths that were short compared to the electrode radius.

A square wave with an amplitude of -0.75 volt was applied to the electrodes to obtain diffusion currents from zero to 30 seconds diffusion time. Currents from less than one second were recorded primarily for calculation with linear diffusion theory but were also used for experimental calibration of electrodes in media with controlled oxygen concentrations. A rectified triangular wave was also applied to calibrate the reduction currents from electrodes with polarograms for applied voltages between zero and -1.0 volt.

These methods were tested in 0.01 N KCl, in 3% bentonite made up in 0.01 N KCl, and in samples of soil aggregates. Each of these were adjusted to various oxygen tensions with gases of known oxygen concentration. Measurements were also made in several other air saturated salt solutions and in single aggregates that had been incubated with and without dextrose.

The diffusion currents that were recorded were greatly influenced by the rate of potential build-up at the electrode surface. The rate of charge accumulation was influenced by the following factors.

1. Electrode construction. Epon insulated electrodes produced high residual or "leakage currents" but those from glass insulated electrodes were low. The rate of double layer charge appeared to be slowed by the resistance of fused junctions as compared to mercury junctions.
2. The nature of the media. In liquid samples charge build-up occurred rapidly when glass insulated electrodes with mercury junctions were used. The rate of charge accumulation was slow in soils that had higher resistances. This was found in all unsaturated soils and in saturated soils at low ionic strength.

3. The amplitude of the applied square wave. The application of more negative voltages down to -0.75 volt increased diffusion currents at short diffusion times, but interfering reactions seemed to occur at -0.80 volt.

Variability was prevalent in all the diffusion current data that were recorded. In some cases variability was found to be systematic while in others it was erratic, but in most instances the observed variations could be placed into one of the following groups.

1. Electrode sensitivity decreased when the electrodes were in the presence of certain electrolytes. This was observed with the electrodes "open circuited" in KCl and NaCl. Storage of electrodes at -1.0 volt in $K_2SO_4$ also decreased electrode sensitivity. Equilibrating these electrodes in water after storage in other salt solutions increased their sensitivities again.
2. Storage of both "old" and "new" electrodes at -1.0 volt in 0.01 N KCl increased sensitivity.
3. The time that was allowed for equilibration between electrode surfaces and the media was important in

both samples containing oxygen and samples that were oxygen free. This was true particularly where small concentrations of reducible materials formed on the electrode surface from equilibration with the electrolyte.

4. Unexplained inherent variability was also prevalent. This appeared as "drifts" in the oxygen sensitivity of groups of electrodes and also as changes in the sensitivity of individual electrodes within a group.

Diffusion currents from less than one second indicated that the electrode process at short diffusion times was complex. In both aerated bentonite suspensions and salt solutions, the products of $\Delta i\sqrt{t}$ increased to a maximum while the double layer was charging at short diffusion times. It remained constant for a few tenths of a second and then decreased before one second. The plateau of maximum values shifted to shorter times with lower oxygen concentrations in bentonite suspensions. These constant maximum values of $\Delta i\sqrt{t}$ appeared to represent a short phase of linear diffusion to the platinum wire electrode.

Linear diffusion theory was used to calculate the oxygen concentrations from maximum products of $\Delta i\sqrt{t}$. In six aerated, dilute salt solutions the calculated concentrations

averaged 9.58 ppm. and ranged from 9.3 to 10.9 ppm. All the calculated concentrations were slightly higher than the approximate known concentrations of 9.0 ppm. at 20°C. These trends suggest that additional studies involving the theoretical analysis of diffusion curves at short times are justified.

Bare stationary platinum wire electrodes were successfully calibrated at various oxygen concentrations in suspensions of bentonite made up in 0.01 N KCl but not in KCl alone. In bentonite suspensions Epon insulated electrodes produced a linear relationship between oxygen concentration and one second diffusion currents but sensitivities were low. The diffusion currents at 0.5 seconds from glass insulated electrodes with mercury junctions also gave a linear relationship with the oxygen concentrations of bentonite suspensions. However, these electrodes produced currents that were three times higher than those from Epon insulated electrodes. Measurements were successfully made in aerated 0.01 N KCl but continued exposure of the electrodes to this salt solution produced erratic currents at other oxygen concentrations. This was attributed to "poisoning" of the electrode surface by a complex that formed between the electrolyte and the platinum. This complex apparently did not form

when clay was present with the salt.

Measurements in soils at various oxygen concentrations with glass insulated electrodes produced relatively low diffusion currents that reflected a slow rate of charge accumulation in the double layer of the electrodes. Maximum products of $\Delta i\sqrt{t}$ did not appear and the diffusion currents at less than one second showed little correlation with oxygen concentration. This response was observed at 20 cm. tension in the presence of added electrolyte and at both saturation and 20 cm. tension when no electrolyte was added. The double layer of the electrodes must be charged faster in soils before realistic diffusion currents can be obtained at these short diffusion times from soil systems.

Rectified triangular waves with rise times ranging from 0.5 to 1.5 seconds and a maximum voltage of -1.0 volt were used with Epon insulated electrodes. Calibration of these electrodes in media of controlled oxygen concentration was accomplished in both bentonite suspensions and 0.01 N KCl. In 0.01 N KCl, oxygen reduction currents were linear with oxygen concentration only after chemical equilibrium was established between the electrolyte and the electrode surface. Periodic application of the rectified triangular wave to electrodes demonstrated that oxygen reduction currents

declined during successive pulses unless the voltage off time was one hundred times greater than the period of oxygen reduction.

Relative measurements of oxygen concentration with depth were made using miniature Epon insulated electrodes in aggregates that had been incubated both with 0.5% dextrose in 0.01 N KCl and with 0.01 N KCl alone at moisture tensions below 5 cm. In aggregates 3 to 5 cm. in diameter, oxygen concentrations were reduced to very low values at 3 mm. below the aggregate surface after 10 hours incubation with dextrose and after 30 hours incubation with no added dextrose. This study demonstrated that abrupt changes in oxygen concentration were detected in incubated aggregates. A number of interesting studies of this type could be conducted with more quantitative methods using glass mounted electrodes.

In the calibration studies mentioned before, quantitative measurement of oxygen concentration was accomplished in liquid media but not in soils. The higher resistance of soils apparently limited the rate of charge accumulation in the double layer. The simple direct current pulse cannot be used to overcome this difficulty. However, a capacitive pulse can be added to the leading edge of the square wave to hasten the rate of charge accumulation. This modified

wave might cause sufficient charge to be accumulated so that a maximum rate of oxygen reduction would appear at less than one second in soils.

The rectified triangular wave might also be used to overcome the slow rate of charge accumulation in soils. The problem of series resistance should be minimized because, with the triangular wave, the oxygen maximum appears in the polarogram only when the voltage is sufficiently negative to reduce oxygen rapidly. By adjusting the peak voltage and the signal rise time the maximum should be observed in all cases. This technique could be especially useful for measurements in soils by calibration at controlled oxygen concentrations.

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# APPENDIX

Table 13. Oxygen diffusion currents for variously oxygenated 3% bentonite suspensions in 0.01 N KCl.

| | | Oxygen diffusion current in microamperes[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | | |
| $\%O_2$ | Diffusion time (sec.) | I | II | III | IV | Average $\Delta i$ | $\Delta i \sqrt{t}$ |
| 21 | 0.05 | 28.7 | 14.1 | 27.8 | 24.1 | 23.7 | 7.5 |
| | 0.1 | 43.5 | 27.8 | 43.5 | 35.3 | 37.5 | 11.3 |
| | 0.2 | 56.6 | 50.1 | 60.1 | 50.7 | 54.4 | 24.3 |
| | 0.3 | 59.0 | 59.8 | 66.2 | 55.5 | 60.1 | 33.7 |
| | 0.4 | 52.9 | 64.9 | 64.8 | 57.9 | 59.9 | 37.8 |
| | 0.5 | 46.1 | 64.8 | 60.1 | 53.1 | 56.0 | 39.5 |
| | 0.6 | 40.1 | 61.2 | 54.4 | 48.7 | 51.1 | 39.6 |
| | 0.7 | 35.9 | 57.5 | 50.1 | 43.5 | 46.8 | 39.1 |
| | 0.8 | 33.3 | 53.5 | 45.0 | 40.3 | 43.0 | 38.5 |
| | 0.9 | 30.5 | 49.6 | 41.6 | 37.0 | 37.2 | 35.2 |
| 15 | 0.05 | 58.3 | 32.3 | ---- | 26.0 | 38.9 | 8.7 |
| | 0.1 | 60.3 | 42.4 | 37.9 | 42.2 | 45.7 | 14.4 |
| | 0.2 | 52.7 | 55.8 | 52.8 | 60.0 | 55.3 | 24.7 |
| | 0.3 | 44.0 | 53.4 | 54.5 | 57.0 | 52.2 | 28.7 |
| | 0.4 | 37.4 | 46.4 | 50.4 | 50.3 | 46.1 | 29.2 |
| | 0.5 | 33.1 | 44.1 | 45.6 | 43.2 | 41.5 | 29.3 |
| | 0.6 | 28.9 | 39.4 | 40.7 | 38.1 | 36.8 | 28.5 |
| | 0.7 | 26.1 | 35.9 | 36.6 | 34.2 | 33.2 | 27.7 |
| | 0.8 | 23.7 | 32.7 | 30.7 | 29.6 | 29.2 | 26.1 |
| | 0.9 | 22.4 | 30.0 | 30.1 | 27.4 | 27.5 | 26.0 |

[a] These were obtained from measurements with platinum electrodes mounted in glass with mercury junctions using an applied voltage of -0.75.

Table 13. Continued.

| | | Oxygen diffusion current in microamperes[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | | |
| % $O_2$ | Diffusion time (sec.) | I | II | III | IV | Average $\Delta i$ | $\Delta i \sqrt{t}$ |
| 10 | 0.05 | 49.0 | ---- | ---- | ---- | 49.0 | 11.0 |
| | 0.1 | 53.7 | 54.6 | 41.6 | 37.9 | 46.9 | 14.8 |
| | 0.2 | 48.5 | 58.5 | 43.3 | 40.3 | 47.64 | 21.3 |
| | 0.3 | 39.6 | 54.8 | 40.7 | 37.7 | 43.2 | 23.7 |
| | 0.4 | 31.6 | 47.2 | 37.4 | 33.5 | 37.4 | 23.7 |
| | 0.5 | 26.5 | 40.7 | 32.2 | 29.0 | 32.1 | 22.7 |
| | 0.6 | 22.6 | 35.2 | 27.9 | 24.2 | 27.5 | 21.3 |
| | 0.7 | 20.0 | 30.3 | 23.7 | 20.9 | 23.7 | 19.9 |
| | 0.8 | 18.1 | 26.3 | 20.9 | 18.5 | 21.0 | 18.7 |
| | 0.9 | 16.8 | 23.1 | 19.2 | 16.7 | 19.0 | 18.0 |
| 5 | 0.05 | 28.3 | ---- | ---- | ---- | 28.3 | 6.3 |
| | 0.1 | 34.4 | ---- | 40.3 | 28.5 | 34.4 | 10.9 |
| | 0.2 | 33.3 | 32.4 | 36.1 | 26.6 | 32.1 | 14.4 |
| | 0.3 | 24.8 | 29.6 | 30.0 | 25.2 | 27.4 | 15.0 |
| | 0.4 | 19.4 | 28.9 | 26.5 | 21.7 | 24.1 | 15.2 |
| | 0.5 | 14.6 | 26.6 | 21.8 | 18.3 | 20.4 | 14.4 |
| | 0.6 | 11.7 | 23.3 | 17.9 | 15.2 | 17.0 | 13.2 |
| | 0.7 | 10.0 | 18.9 | 16.7 | 12.8 | 14.6 | 12.2 |
| | 0.8 | 8.9 | 19.1 | 11.8 | 10.7 | 12.0 | 10.8 |
| | 0.9 | 8.1 | 17.0 | 10.7 | 9.6 | 11.4 | 10.8 |

Table 14. Oxygen diffusion currents from aerated $MgSO_4$ and $Li_2SO_4$.

| 0.01 N Salt | Diffusion time (sec.) | Oxygen diffusion current in microamperes: Electrode number 7 | 8 | 9 | 10 | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
|---|---|---|---|---|---|---|---|
| $MgSO_4$ | 0.05 | 82.7 | 70.2 | 83.2 | 89.2 | 81.3 | 18.2 |
| | 0.1 | 83.6 | 69.3 | 79.5 | 85.9 | 79.5 | 25.1 |
| | 0.2 | 84.1 | 68.4 | 78.1 | 81.3 | 78.0 | 34.9 |
| | 0.3 | 83.2 | 68.4 | 76.2 | 79.0 | 76.7 | 42.0 |
| | 0.4 | 81.8 | 66.1 | 72.5 | 78.5 | 74.7 | 47.2 |
| | 0.5 | 78.5 | 62.4 | 68.4 | 75.3 | 71.2 | 50.3 |
| | 0.6 | 73.0 | 58.2 | 63.3 | 72.1 | 66.7 | 51.7 |
| | 0.7 | 67.0 | 56.4 | 57.8 | 67.5 | 62.2 | 52.0 |
| | 0.8 | 60.5 | 46.7 | 51.7 | 61.9 | 55.2 | 49.4 |
| | 0.9 | 54.5 | 41.1 | 46.7 | 55.9 | 49.6 | 47.0 |
| $Li_2SO_4$ | 0.05 | 118.7 | 123.8 | 139.5 | 148.8 | 132.7 | 29.7 |
| | 0.1 | 107.2 | 110.0 | 125.7 | 130.3 | 118.3 | 37.4 |
| | 0.2 | 88.7 | 91.9 | 99.8 | 102.6 | 95.8 | 42.8 |
| | 0.3 | 82.2 | 82.2 | 83.6 | 87.8 | 84.0 | 46.0 |
| | 0.4 | 79.0 | 72.5 | 77.6 | 79.5 | 77.2 | 48.8 |
| | 0.5 | 74.4 | 67.9 | 73.0 | 73.5 | 72.2 | 51.1 |
| | 0.6 | 69.3 | 62.4 | 69.3 | 68.4 | 67.4 | 52.2 |
| | 0.7 | 63.8 | 56.8 | 64.2 | 61.0 | 61.5 | 51.4 |
| | 0.8 | 56.8 | 51.3 | 59.1 | 55.4 | 55.7 | 49.8 |
| | 0.9 | 51.3 | 46.7 | 54.5 | 50.8 | 50.8 | 48.2 |

Electrode had equilibrated with the salts. Glass insulated platinum wire electrodes with mercury junctions were used.

Table 15. Oxygen diffusion currents for variously oxygenated Brookston aggregates saturated with 0.01 N KCl.

| $\%O_2$ | Diffusion time (sec.) | Oxygen diffusion current in microamperes: Electrode number 7 | 8 | 9 | 10 | Average $\Delta i$ | $\Delta i \sqrt{t}$ |
|---|---|---|---|---|---|---|---|
| 21% | 0.1 | 68.4 | 63.8 | 119.9 | 62.9 | 78.8 | 24.9 |
| | 0.2 | 58.8 | 52.8 | 100.7 | 63.8 | 69.0 | 30.9 |
| | 0.3 | 49.0 | 46.2 | 78.8 | 56.9 | 57.7 | 31.6 |
| | 0.4 | 42.5 | 41.6 | 63.4 | 50.4 | 49.5 | 31.3 |
| | 0.5 | 38.8 | 38.8 | 52.8 | 43.9 | 43.6 | 30.8 |
| | 0.6 | 36.0 | 36.9 | 46.2 | 42.5 | 40.4 | 31.3 |
| | 0.7 | 35.1 | 35.1 | 42.1 | 41.6 | 38.5 | 32.2 |
| | 0.8 | 30.9 | 34.2 | 40.2 | 40.2 | 36.4 | 32.5 |
| | 0.9 | 30.8 | 34.2 | 37.8 | 39.3 | 35.8 | 34.0 |
| 15% | 0.1 | 32.2 | 32.4 | 27.8 | 25.0 | 29.4 | 9.3 |
| | 0.2 | 30.0 | 32.0 | 32.0 | 32.7 | 31.7 | 14.2 |
| | 0.3 | 24.4 | 30.5 | 28.7 | 29.2 | 28.3 | 15.5 |
| | 0.4 | 20.4 | 26.8 | 25.0 | 25.0 | 24.3 | 15.4 |
| | 0.5 | 17.4 | 24.4 | 22.0 | 20.0 | 21.0 | 14.9 |
| | 0.6 | 14.8 | 20.9 | 19.6 | 16.8 | 18.0 | 14.0 |
| | 0.7 | 14.2 | 20.9 | 17.4 | 17.2 | 17.4 | 14.6 |
| | 0.8 | 11.5 | 20.2 | 17.2 | 13.5 | 15.6 | 14.0 |
| | 0.9 | 11.1 | 19.6 | 16.8 | 12.4 | 15.3 | 14.5 |

Aggregates were 2 to 4 mm. in diameter. Glass insulated platinum wire electrodes with mercury junctions were used at -0.75 volt.

Table 15. Continued.

| $\%O_2$ | Diffusion time (sec.) | Oxygen diffusion current in microamperes | | | | | $\Delta i \sqrt{t}$ |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | Average $\Delta i$ | |
| | | 7 | 8 | 9 | 10 | | |
| 10% | 0.1 | 41.6 | 35.1 | 37.3 | 43.4 | 39.4 | 12.4 |
| | 0.2 | 37.4 | 36.5 | 34.6 | 40.2 | 37.2 | 16.6 |
| | 0.3 | 31.4 | 34.6 | 28.6 | 36.0 | 32.7 | 17.9 |
| | 0.4 | 26.3 | 30.0 | 25.0 | 28.6 | 27.5 | 17.4 |
| | 0.5 | 21.2 | 27.7 | 20.4 | 23.1 | 23.1 | 16.3 |
| | 0.6 | 17.6 | 25.8 | 18.4 | 18.0 | 20.0 | 15.5 |
| | 0.7 | 16.2 | 23.5 | 15.3 | 15.3 | 17.6 | 14.7 |
| | 0.8 | 14.9 | 21.2 | 14.8 | 14.8 | 16.0 | 14.3 |
| | 0.9 | 11.5 | 21.2 | 14.3 | 14.3 | 14.9 | 14.1 |
| 5% | 0.1 | 40.2 | 31.9 | 16.6 | 8.8 | 24.4 | 7.7 |
| | 0.2 | 24.5 | 20.3 | 17.1 | 13.8 | 18.9 | 8.5 |
| | 0.3 | 16.2 | 14.3 | 10.8 | 12.5 | 13.5 | 7.4 |
| | 0.4 | 10.2 | 10.6 | 7.9 | 8.3 | 9.3 | 5.9 |
| | 0.5 | 6.0 | 8.3 | 4.2 | 3.7 | 5.6 | 3.9 |
| | 0.6 | 4.2 | 6.5 | 2.8 | 0.9 | 3.6 | 2.8 |
| | 0.7 | 3.2 | 5.1 | 0.9 | 0.0 | 2.3 | 1.9 |
| | 0.8 | 0.5 | 3.7 | 0.0 | 0.0 | 1.1 | 0.9 |
| | 0.9 | 0.0 | 4.2 | 0.4 | 0.0 | 1.1 | 1.0 |

Table 16. Oxygen diffusion currents for variously oxygenated Brookston aggregates at 20 cm. tension with 0.01 N KCl.

| $\%O_2$ | Diffusion time (sec.) | Oxygen diffusion current in microamperes | | | | | |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
| | | 7 | 8 | 9 | 10 | | |
| 21% | 0.1 | 42.0 | 40.1 | 45.8 | 31.8 | 39.9 | 12.6 |
| | 0.2 | 42.0 | 42.6 | 43.1 | 30.8 | 39.6 | 17.7 |
| | 0.3 | 40.7 | 41.9 | 40.4 | 31.8 | 38.7 | 21.2 |
| | 0.4 | 38.3 | 39.5 | 37.8 | 30.8 | 36.6 | 23.1 |
| | 0.5 | 37.9 | 38.8 | 36.3 | 31.6 | 36.2 | 25.6 |
| | 0.6 | 36.5 | 37.6 | 34.6 | 32.5 | 35.3 | 27.4 |
| | 0.7 | 35.3 | 36.0 | 32.6 | 32.0 | 35.0 | 29.3 |
| | 0.8 | 34.1 | 35.1 | 31.6 | 31.7 | 33.1 | 29.6 |
| | 0.9 | 34.1 | 35.7 | 30.7 | 31.5 | 33.0 | 31.3 |
| 15% | 0.1 | 27.4 | 25.0 | 25.8 | 27.8 | 27.5 | 8.7 |
| | 0.2 | 27.1 | 29.9 | 25.4 | 23.8 | 26.6 | 11.9 |
| | 0.3 | 26.6 | 30.9 | 23.1 | 23.8 | 26.1 | 14.3 |
| | 0.4 | 25.5 | 29.6 | 21.1 | 22.7 | 24.7 | 15.6 |
| | 0.5 | 25.2 | 30.7 | 19.4 | 22.4 | 24.4 | 17.3 |
| | 0.6 | 24.5 | 29.7 | 18.0 | 22.6 | 23.7 | 18.4 |
| | 0.7 | 23.5 | 28.6 | 16.6 | 22.8 | 22.9 | 19.2 |
| | 0.8 | 22.6 | 28.9 | 15.1 | 22.5 | 22.3 | 19.9 |
| | 0.9 | 22.5 | 28.6 | 15.2 | 22.2 | 22.1 | 21.0 |

Aggregates were 2 to 4 mm. in diameter. Glass insulated platinum wire electrodes with mercury junctions were used at -0.75 volt.

Table 16. Continued.

| $\%O_2$ | Diffusion time (sec.) | Oxygen diffusion current in microamperes |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  | Electrode number |  |  |  | Average $\Delta i$ | $\Delta i \sqrt{t}$ |
|  |  | 7 | 8 | 9 | 10 |  |  |
| 10% | 0.1 | 16.3 | 10.8 | 21.0 | 50.8 | 24.7 | 7.8 |
|  | 0.2 | 20.9 | 7.8 | 23.0 | 38.0 | 22.4 | 10.0 |
|  | 0.3 | 20.9 | 6.3 | 25.7 | 29.2 | 20.5 | 11.3 |
|  | 0.4 | 20.3 | 4.9 | 20.9 | 23.0 | 17.3 | 10.9 |
|  | 0.5 | 20.8 | 4.4 | 20.0 | 18.4 | 15.9 | 11.2 |
|  | 0.6 | 20.2 | 3.3 | 18.0 | 16.1 | 14.4 | 11.2 |
|  | 0.7 | 20.0 | 2.4 | 17.0 | 13.2 | 13.2 | 11.0 |
|  | 0.8 | 19.3 | 2.0 | 15.9 | 11.4 | 12.2 | 10.9 |
|  | 0.9 | 19.1 | 3.0 | 15.0 | 9.5 | 11.7 | 11.1 |
| 5% | 0.1 | 38.6 | 12.8 | 31.0 | ---- | 27.5 | 8.7 |
|  | 0.2 | 26.9 | 18.4 | 21.3 | ---- | 22.2 | 9.9 |
|  | 0.3 | 18.7 | 18.3 | 17.1 | ---- | 18.0 | 10.0 |
|  | 0.4 | 13.2 | 17.8 | 15.4 | ---- | 15.5 | 7.8 |
|  | 0.5 | 11.5 | 17.0 | 13.9 | ---- | 14.1 | 10.0 |
|  | 0.6 | 10.4 | 15.7 | 12.5 | ---- | 12.9 | 10.0 |
|  | 0.7 | 8.9 | 14.6 | 9.9 | ---- | 11.1 | 9.3 |
|  | 0.8 | 8.3 | 14.4 | 11.1 | ---- | 11.3 | 10.1 |
|  | 0.9 | 8.6 | 14.0 | 10.9 | ---- | 11.2 | 10.6 |

Table 17. Oxygen diffusion currents for variously oxygenated Brookston aggregates saturated with distilled water.

| | | Oxygen diffusion current in microamperes | | | | | |
|---|---|---|---|---|---|---|---|
| | Diffusion | Electrode number | | | | | |
| %$O_2$ | time (sec.) | 7 | 8 | 9 | 10 | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
| 21% | 0.05 | 27.8 | 17.8 | 22.8 | 25.0 | 23.3 | 5.2 |
| | 0.1 | 30.5 | 21.3 | 30.0 | 32.6 | 28.6 | 9.0 |
| | 0.2 | 32.4 | 25.7 | 33.5 | 35.0 | 31.6 | 14.1 |
| | 0.3 | 31.2 | 25.7 | 33.1 | 34.8 | 31.5 | 17.2 |
| | 0.4 | 30.2 | 23.9 | 32.4 | 33.3 | 29.9 | 18.9 |
| | 0.5 | 29.1 | 22.2 | 31.5 | 32.2 | 28.7 | 20.3 |
| | 0.6 | 27.4 | 21.6 | 31.3 | 30.7 | 27.8 | 21.5 |
| | 0.7 | 23.5 | 20.4 | 29.2 | 29.6 | 25.7 | 21.5 |
| | 0.8 | 24.2 | 19.1 | 29.0 | 28.1 | 25.1 | 22.5 |
| | 0.9 | 23.1 | 18.5 | 28.7 | 27.8 | 24.5 | 23.3 |
| 15% | 0.05 | 14.4 | 13.9 | 32.9 | 40.3 | 25.4 | 5.7 |
| | 0.1 | 21.3 | 17.4 | 34.6 | 44.2 | 29.4 | 9.3 |
| | 0.2 | 24.4 | 21.8 | 36.5 | 44.0 | 31.7 | 14.2 |
| | 0.3 | 25.2 | 21.8 | 35.2 | 41.6 | 30.9 | 17.0 |
| | 0.4 | 24.4 | 19.6 | 33.7 | 38.5 | 29.0 | 18.4 |
| | 0.5 | 23.7 | 18.5 | 32.6 | 35.5 | 27.6 | 19.5 |
| | 0.6 | 22.9 | 17.8 | 31.5 | 33.3 | 26.4 | 20.4 |
| | 0.7 | 22.0 | 16.5 | 29.6 | 31.3 | 24.8 | 20.8 |
| | 0.8 | 20.7 | 15.7 | 28.1 | 29.1 | 23.4 | 20.9 |
| | 0.9 | 20.0 | 15.2 | 27.8 | 29.0 | 23.0 | 21.8 |

Aggregates were 0.5 to 2 mm. in diameter. Glass insulated platinum wire electrodes with mercury junctions were used at -0.75 volt.

Table 17. Continued.

| %$O_2$ | Diffusion time (sec.) | Oxygen diffusion current in microamperes | | | | | |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | | |
| | | 7 | 8 | 9 | 10 | Average $\Delta i$ | $\Delta i \sqrt{t}$ |
| 10% | 0.05 | 0.0 | 0.0 | 10.7 | 9.6 | 5.1 | 1.1 |
| | 0.1 | 3.9 | 0.0 | 16.8 | 15.4 | 9.0 | 2.9 |
| | 0.2 | 6.8 | 4.6 | 20.0 | 16.5 | 12.0 | 5.4 |
| | 0.3 | 6.9 | 8.7 | 19.4 | 16.3 | 12.8 | 7.0 |
| | 0.4 | 6.3 | 6.5 | 19.6 | 15.0 | 11.8 | 7.5 |
| | 0.5 | 6.9 | 6.7 | 18.5 | 13.9 | 11.5 | 8.1 |
| | 0.6 | 6.1 | 7.0 | 18.7 | 13.5 | 11.3 | 8.8 |
| | 0.7 | 5.7 | 6.3 | 17.0 | 13.1 | 10.5 | 8.8 |
| | 0.8 | 5.2 | 6.1 | 16.7 | 12.8 | 10.2 | 9.1 |
| | 0.9 | 4.6 | 5.4 | 16.7 | 13.0 | 9.9 | 9.4 |
| 5% | 0.05 | 0.0 | 0.0 | 4.8 | 2.0 | 1.7 | 0.4 |
| | 0.1 | 1.9 | 0.0 | 11.8 | 3.7 | 4.3 | 1.4 |
| | 0.2 | 4.3 | 1.9 | 10.9 | 4.3 | 5.3 | 2.4 |
| | 0.3 | 5.0 | 3.5 | 10.9 | 4.6 | 6.0 | 3.3 |
| | 0.4 | 4.4 | 3.3 | 10.9 | 5.2 | 6.0 | 3.8 |
| | 0.5 | 5.2 | 3.3 | 10.7 | 4.4 | 5.9 | 4.2 |
| | 0.6 | 5.0 | 3.3 | 10.6 | 4.3 | 5.8 | 4.5 |
| | 0.7 | 5.0 | 3.5 | 10.0 | 4.6 | 5.8 | 4.8 |
| | 0.8 | 4.3 | 2.8 | 10.2 | 5.0 | 5.5 | 5.0 |
| | 0.9 | 3.5 | 2.2 | 10.2 | 5.0 | 5.2 | 5.0 |

Table 18. Oxygen diffusion currents for variously oxygenated Brookston aggregates at 20 cm. tension with distilled water.

| $\%O_2$ | Diffusion time (sec.) | Oxygen diffusion current in microamperes | | | | | |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | | |
| | | 7 | 8 | 9 | 10 | Average $\Delta i$ | $\Delta i \sqrt{t}$ |
| 21% | 0.05 | 20.4 | 34.2 | 0.0 | 18.5 | 18.3 | 4.1 |
| | 0.1 | 22.8 | 33.8 | 3.1 | 25.7 | 21.4 | 6.8 |
| | 0.2 | 25.7 | 33.7 | 11.1 | 29.1 | 24.9 | 11.1 |
| | 0.3 | 27.9 | 34.0 | 14.6 | 29.6 | 26.6 | 14.6 |
| | 0.4 | 29.1 | 33.5 | 16.5 | 29.8 | 27.2 | 17.2 |
| | 0.5 | 30.0 | 32.2 | 17.0 | 29.0 | 27.1 | 19.1 |
| | 0.6 | 30.0 | 31.8 | 18.1 | 28.9 | 27.2 | 21.1 |
| | 0.7 | 29.6 | 32.0 | 19.1 | 27.8 | 27.1 | 22.7 |
| | 0.8 | 29.4 | 31.3 | 18.7 | 27.4 | 26.7 | 23.9 |
| | 0.9 | 29.2 | 30.3 | 18.5 | 27.6 | 26.4 | 25.1 |
| 15% | 0.05 | 17.8 | 38.5 | 30.9 | 59.6 | 36.7 | 8.2 |
| | 0.1 | 24.4 | 41.8 | 31.6 | 54.2 | 38.0 | 12.0 |
| | 0.2 | 29.8 | 40.2 | 32.8 | 50.1 | 38.2 | 17.1 |
| | 0.3 | 30.3 | 37.0 | 33.3 | 47.5 | 37.0 | 20.5 |
| | 0.4 | 30.9 | 35.5 | 33.1 | 45.7 | 36.3 | 23.0 |
| | 0.5 | 30.1 | 33.5 | 33.3 | 43.3 | 35.1 | 24.8 |
| | 0.6 | 29.8 | 32.2 | 32.6 | 41.4 | 34.0 | 26.3 |
| | 0.7 | 29.4 | 30.5 | 31.6 | 40.3 | 33.0 | 27.6 |
| | 0.8 | 28.1 | 30.0 | 30.9 | 38.5 | 31.9 | 28.5 |
| | 0.9 | 28.1 | 30.3 | 29.6 | 36.4 | 31.1 | 29.5 |

Aggregates were 0.5 to 2 mm. in diameter. Glass insulated platinum wire electrodes with mercury junctions were used at -0.75 volt.

Table 18. Continued.

| | | Oxygen diffusion current in microamperes | | | | | |
|---|---|---|---|---|---|---|---|
| | | Electrode number | | | | | |
| %$O_2$ | Diffusion time (sec.) | 7 | 8 | 9 | 10 | Average $\Delta i$ | $\Delta i\sqrt{t}$ |
| 10% | 0.05 | 24.2 | 22.6 | 44.0 | 53.7 | 36.1 | 8.1 |
| | 0.1 | 29.8 | 25.3 | 43.7 | 49.4 | 37.0 | 11.7 |
| | 0.2 | 33.1 | 25.4 | 42.2 | 44.4 | 36.3 | 16.2 |
| | 0.3 | 34.7 | 23.7 | 40.9 | 41.4 | 35.2 | 19.3 |
| | 0.4 | 32.9 | 22.4 | 39.2 | 41.1 | 33.9 | 21.4 |
| | 0.5 | 32.2 | 20.5 | 38.7 | 36.4 | 32.0 | 22.6 |
| | 0.6 | 31.8 | 21.8 | 37.6 | 34.8 | 31.5 | 24.4 |
| | 0.7 | 30.5 | 18.7 | 35.5 | 33.3 | 29.5 | 24.7 |
| | 0.8 | 29.8 | 17.6 | 34.6 | 31.5 | 28.4 | 25.3 |
| | 0.9 | 29.1 | 18.0 | 32.9 | 30.0 | 27.5 | 26.1 |
| 5% | 0.05 | 6.7 | 11.5 | 17.2 | 37.4 | 18.2 | 4.1 |
| | 0.1 | 11.3 | 11.1 | 16.3 | 32.7 | 17.9 | 5.6 |
| | 0.2 | 16.3 | 10.6 | 16.3 | 28.1 | 17.8 | 8.0 |
| | 0.3 | 17.6 | 9.3 | 16.8 | 25.3 | 17.3 | 9.5 |
| | 0.4 | 18.1 | 9.3 | 16.5 | 23.5 | 16.8 | 10.6 |
| | 0.5 | 17.6 | 8.0 | 17.0 | 21.5 | 16.0 | 11.3 |
| | 0.6 | 17.2 | 8.0 | 16.5 | 20.4 | 15.5 | 12.0 |
| | 0.7 | 17.0 | 7.8 | 15.7 | 19.8 | 15.1 | 12.6 |
| | 0.8 | 16.3 | 7.8 | 15.7 | 18.5 | 14.6 | 13.0 |
| | 0.9 | 15.7 | 8.0 | 14.8 | 18.3 | 14.2 | 13.5 |

Table 19. Summary of diffusion data from incubated aggregates using $\Delta i$ for 5 sec. of diffusion time. Epon insulated electrodes were used with -0.65 volt applied.

| Time Incubated | Depth in Aggregates (mm.) | $\Delta i$ ($\mu$amps) | | | | | |
|---|---|---|---|---|---|---|---|
| | | large aggregates | | medium aggregates | | smaller aggregates | |
| | | no dextrose | dextrose | no dextrose | dextrose | no dextrose | dextrose |
| About 10 hours | 0-2 | 3.51 | 2.31 | 4.00 | 1.53 | 1.98 | .84 |
| | 2-4 | 3.62 | .29 | 1.49 | 1.20 | .80 | .62 |
| | 4-6 | 3.73 | .38 | 1.40 | 1.29 | 1.38 | .80 |
| | 6-8 | 1.84 | .58 | 1.98 | 1.35 | .44 | 1.24 |
| | 8-10 | 1.40 | 1.24 | 1.98 | 1.67 | .58 | .73 |
| | 10-12 | ---- | ---- | 1.89 | 2.51 | .22 | ---- |
| After 30 hours | 0-2 | 1.07 | 2.27 | 2.63 | 1.01 | 1.27 | 1.30 |
| | 2-4 | .72 | .63 | 3.29 | 1.27 | 1.36 | 1.63 |
| | 4-6 | .67 | .41 | 2.36 | 1.74 | 1.07 | 1.23 |
| | 6-8 | .63 | .45 | 2.12 | 1.18 | .23 | 1.70 |
| | 8-10 | .70 | .19 | 2.02 | 1.01 | .25 | 1.21 |
| | 10-12 | 1.32 | 1.38 | 1.34 | .83 | .00 | 1.14 |