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Salinity and Water Potential Sensor for Evaluation of Soil Water Quality

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SALINITY AND WATER POTENTIAL SENSOR FOR EVALUATION OF SOIL WATER QUALITY

by

Melvin Dee Campbell

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soils and Irrigation

UTAH STATE UNIVERSITY
Logan, Utah

1969

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I wish to acknowledge with appreciation the fellowship provided by The Federal Water Pollution Control Administration who made this past year of study possible.

I wish to express appreciation for the assistance of both Dr. R. J. Hanks whose encouragement and suggestions have given direction to this study and Diane F. Perkes who helped prepare the manuscript.

Melvin Dee Campbell
Melvin Dee Campbell

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ABSTRACT

Salinity and Water Potential Sensor for Evaluation of Soil Water Quality

by

Melvin D. Campbell, Master of Science
Utah State University, 1969

Major Professor: Dr. R. J. Hanks
Department: Soils and Meteorology

The objective of this study was to evaluate response times of a salinity sensor and a soil psychrometer. Influences of pressure, temperature and molar concentration changes were to be measured.

Salinity sensor response times ranged from 50 to 130 minutes during solution adsorption while desorption response times were perhaps ten times as long. Temperature affected both response times and equilibrium values, but pressure did not affect either.

Soil psychrometer response times ranged from from 40 to 80 minutes for either adsorption or desorption of solution. However, other factors probably related to indirectness of measurement made the soil psychrometer fail to reflect osmotic potential. Both pressure and temperature effects were significant.

Comparisons between hypothetical soil water infiltration times and sensor response times together with soil psychrometer failure led to the conclusion that the salinity sensor may be useful while the soil psychrometer would probably not be useful for return-flow water quality control.

(64 pages)

INTRODUCTION

Water Loss and Degradation

Perhaps twenty to seventy percent of the water diverted from a river for irrigation is lost to the intended user through at least one of the following:

1. evaporation
2. seepage from diversion structures
3. excess irrigation.

Concern is directed toward the latter two losses mentioned above because such water dissolves and suspends substances found in soils through which it passes.

Possibly as much as thirty percent of the water diverted from a river may return to that river as drainage water downstream, carrying additional dissolved solids. Such return water with its attendant increased salinity is less fit for downstream use than it would have been had it not been diverted. Thus, by diversion, water quality may be degraded by leaching of soil salts. Such leaching repeated along a water course may render a stream unfit for agricultural use. For example Thorne and Peterson (1954) reported a substantial increase in salinity of Colorado river water between Glenwood Springs, Colorado and Hoover Dam, 341 to 665 ppm, respectively.

Control of Loss and Degradation

At least two things could be done to improve water quality downstream: first, eliminate seepage and evaporative losses from diversion systems by using closed ducts to carry the water to farms; second, manage water application and drainage on the farm to optimize water and associated salt inflow and outflow. The second possibility for control will require the use of water and salt sensors.

Salinity measurement and control within the soil may be accomplished provided that adequate salinity sensors are available. A sensor must provide short response time capability and precision with accuracy reproducible and traceable to some accepted standard. Low cost over time would also be an essential quality. A few salinity sensors are available but they have not been widely used or tested, especially those that are capable of measuring salinity in place.

Water measurement and control in the soil will demand precision, accuracy, repeatability and traceability to an accepted standard, coupled with short response time. An irrigation method must be so chosen that application time can be carefully controlled. Instruments are available for measurement of soil water that have been widely used and tested.

Purpose and Limits of this Study

This investigation is intended to determine the equilibrium time characteristics of the Richards (1966) salinity sensor and the Rawlins and Dalton (1967) field psychrometer under varying temperatures, pressures and salt concentrations.

Preliminary tests with lysimeters showed that the two sensors gave variable results which made interpretation difficult. It was apparent that further knowledge of sensor characteristics was needed before results would be useful in the field.

The salinity sensor developed by Richards (1966)[1] will be tested in fixed temperature and fixed pressure environments using five salt concentrations which will exceed the salt range normally encountered in either water or soil. Equilibrium times will be measured following transfer of sensors from pure water to salt solution, and the reverse. Stress will be applied by pressure in a pressure plate, and equilibrium off-set effects will be measured.

The soil psychrometer developed by Rawlins and Dalton (1967)[2] will be subjected to at least two different temperatures and pressures for each salt concentration, and equilibrium time will be measured, first from pure water to solution and then reverse.

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[1] Manufactured by Soil Moisture Equipment Company of Santa Barbara, California.

[2] Manufactured in a modified form by E. C. Campbell of Logan, Utah.

REVIEW OF LITERATURE

Principles of Soil Systems

Use of thermodynamics for this study

According to Mahan (1964, p. 1), "Thermodynamics provides the most general and efficient methods for studying and understanding complex physical phenomena. . . ." The necessity of dealing with bulk matter in this study without access to tools other than those of thermodynamics makes their use not only desirable but essential. Mahan (1964, p. 1) states that, "The properties of matter which are so obvious to us are called Macroscopic properties, and they are, naturally, the first features we use to describe a physical situation." Thus, thermodynamics may well provide the most desirable tools to use for the sake of adequate description. However, during the course of this study, more than simple thermodynamics became necessary for adequate description of phenomena observed. Such description will appear in the discussion to follow. Nevertheless, thermodynamics will furnish the principle analytical tools for evaluating the operation of the soil psychrometers and salinity sensors. Such evaluation is the central purpose of this study.

Attention will center on the Gibbs free energy function as it relates to chemical potential, water potential and osmotic pressure.

No attempt will be made to establish a theoretical basis or justification for the mathematical material used. However, the work and conclusions of others will be drawn from, and their conclusions will be relied on as far as agreement appears unanimous.

Thermodynamic functions useful in soil systems analysis

Edlefsen and Anderson (1943, p. 31) state that, "Probably the most useful thermodynamic function, as far as the student of soil moisture is concerned, is free energy." However, chemical potential, μ, osmotic pressure, π, and water potential, Ψ, are probably just as important as free energy, G, in this paper.

Following is a tabulated set of equations showing relation of Gibbs free energy to other thermodynamic functions.

Definitions: w = work
q = heat
E = internal energy
G = Gibbs free energy
S = entropy
T = absolute temperature
V = volume
P = pressure

Relationships:

$$E = q + w$$
$$G = E + PV - TS$$
$$dG = -SdT + VdP$$
$$dS = \frac{dq(rev)}{T}$$

One must keep in mind that not all authors use the same symbols, even though equivalent relationships persist. While Moore (1962) used G for Gibbs free energy, Edlefsen and Anderson (1943) used f, and still others have used F. Nevertheless, equivalent mathematical and physical relationships appear to hold.

Relation of thermodynamic functions to each other

Slatyer (1967, p. 20) identified chemical potential, μ, in terms of pressure by "$\mu_i - \mu_i^o = RT \ln P_i/P_i^o$ where μ_i^o and P_i^o are the chemical potential and partial gas pressure, respectively, of the ith component in the pure phase at the reference temperature and pressure." But Moore (1962) shows that $\mu_i = \left(\frac{dG}{dn_i}\right)_{T,P,n_j}$ where G is Gibbs free energy and n_i is the number of moles of the ith component. He then shows that the total differential for Gibbs free energy, G, is $dG = -SdT + VdP + \Sigma\mu_i\, dn_i$.

According to Slatyer (1967, p. 21), water potential, Ψ, is related to chemical potential in the following way:

$$\Psi = \frac{(\mu_w - \mu_w^o)}{\overline{V}_w} \qquad (1.47)$$

where μ_w is ambient chemical potential of water, μ_w^o is chemical potential of water in the standard state and $\overline{V}$ is the partial molal volume of water. Then Slatyer (1967, p. 25) defines osmotic pressure, π, as "the equilibrium pressure difference ($P^{eq} - P^o$) . . . ." and shows the relation of π to pressure and water activity by $\pi = \frac{-RT}{\overline{V}} \ln a_w$, in which a_w is equivalent to P/P^o as shown above. This assumes that water vapor acts as an ideal gas.

Relation of thermodynamic functions to a system

Now that the relations of thermodynamic functions to each other have been shown, their relations to a system will be considered.

Perhaps two kinds of systems need to be distinguished. The first kind is a closed system in which no mass transfer can take place, but the closed system does not pertain to this study. The second is its complement, the open system, in which mass transfer can take place and commonly does.

Moore (1962, p. 98) observes that such an equation as $dG = -SdT + VdP + \sum\mu_i \, dn_i$ applies to an "open system" so that dn_i can be either added to or removed from the system. Further, he notes that at constant temperature and pressure "$dG = \sum\mu_i \, dn_i$" and states that such an equation will apply to each phase of a multiple phase system (Moore, 1962, p. 99). He says that adding or removing dn_i may occur simply between phases within a system.

Although equilibrium is required for the above equations to hold, successive measurements of sensor status will indicate when that equilibrium is being approached, and such measurements can indicate how rapidly the sensors respond to gradients imposed by non-equilibrium conditions. One might wish to discard thermodynamics here were it not for the fact that equilibrium conditions and the time required to establish them must be measured. The only known way to ascertain that equilibrium does in fact exist is to prove by successive measurements that there is no further tendency for a system to change with time. Equilibrium will exist only at the end points of measurement or not at all in this study.

The relation of thermodynamic functions to sensor operation

The soil psychrometer requires a constant temperature environment because it measures infinitesimal temperature depressions as a function of water vapor diffusion rate following equilibrium upset. The psychrometer operation will be discussed in detail later, but, at present, the dependence of the soil psychrometer response on constant temperature, constant pressure and constant molar composition of the liquid phase at equilibrium with its complementary vapor phase can scarcely be over stated.

The salinity sensor depends on constant composition of ions mobilized by external electromotive force, and the sensor cannot, therefore, demonstrate the status of a solution with which it is not in equilibrium. While temperature and pressure may affect the salinity sensor readings, mass transport of solute through the sensor will produce changes in the sensor conductivity.

The soil psychrometer, then, depends on dP, dT and dn_i while the salinity sensor depends principally on dn_i. These three incremental functions themselves depend on equilibrium for precise definition and cannot be defined precisely in this study because equilibrium will rarely or never be fully achieved.

Equilibrium considerations

Equilibrium is required by both types of sensors for precise system measurement. Mahan (1964, p. 7) suggests three criteria essential to equilibrium: "First, the mechanical properties of a system must be uniform and constant." "Second, the chemical composition of a system at equilibrium must be uniform, and there must be no net chemical reactions taking place." The third criterion is ". . . that the temperature of the system must be uniform and must be the same as the temperature of the surroundings."

Moore (1962, pp. 99-100), on the other hand, states the criteria in a slightly different way. He says that "for thermal equilibrium it is necessary that the temperatures of all the phases be the same." Furthermore, he states that "for mechanical equilibrium it is necessary that the pressures of all the phases be the same." Finally, "for any component $_i$ in the system, the value of the chemical potential μ_i must be the same in every phase, when the system is in equilibrium at constant T and P."

Such conditions as these six impose the necessity for energy transfer to occur so that temperature, pressure and composition may exist uniformly throughout a system.

Measurement requires equilibrium upset

While macroscopic equilibrium is essential for the use of the two types of sensors herein considered, microscopic upset of that equilibrium is essential for measurement of the system parameters by the sensors.

The soil psychrometer requires mass transfer of water vapor in response to a thermal upset induced by an electromotive force, which in turn causes thermally induced electromotive force generation in proportion to the rate of water vapor mass transfer.

The salinity sensor, on the other hand, does not require equilibrium upset for any other reason than to balance an alternating-current bridge. During this operation, none of the three free energy terms is upset significantly, although dn_i may be more than the other two.

Such equilibrium upset must be sufficiently small to be negligible by comparison with macrosystem conditions. That is, the time necessary for equilibrium to be re-established must be significantly less than the cycle time required by the parameter being measured, such as irrigation infiltration time into a root zone.

Water potential and salinity in soils

Water potential has been defined in various ways, but Slatyer and Taylor (1960, p. 922) have given a useful definition for our purpose. They say that ". . .water potential is the difference between the partial specific Gibbs free energy of water in the system under consideration and of free pure water at the same temperature (which is the reference state)." In other words water potential is a measure of the tenacity with which water is held by some other system compared to the tenacity of a system of pure free water at a given temperature.

Water potential is related to the problem of return flow water quality in at least two ways: first dissolved salts alter the osmotic potential of water in such a way that water transport for plant use may be altogether prevented even while sufficient water remains in the soil to percolate into ground water and thence to return flow water. Second, the water potential in a soil, which is due to soil matrix is the significant soil water restraining energy, and when that potential is high, water percolation is proportionally more probable than when potential is low. (Low water potential implies a value negative from zero while high water potential implies a value approaching zero from the negative side.) This statement is to imply that as P/P^o approaches unity, neglecting salinity effects, the hydraulic conductivity approaches a maximum value.

Salinity of soil water has usually been measured as conductivity of saturation extracts from field samples (Agricultural Handbook No. 60, 1954). Water has had conductivity tests as well as chemical analyses run to determine both quality and quantity of salt content. Perhaps the most significant influence salinity has, as far as this study is concerned, is return flow water degradation which manifests itself in crop yield reduction, suppression of germination at seed time and water potential reduction. The water potential reduction results from suppression of P so that the value of P/P^o is lowered.

Salinity and Water Potential Measurements

Methods and sensors

The most widely used method of measuring soil salinity is the measurement of electrical conductivity of a soil water paste or a water extract. These methods are destructive and are made under conditions much different from those found in the field. The Richards (1966) sensor was designed to be used under field conditions. Almost no information is available on the reliability or precautions necessary with the use of this sensor.

For the purposes of this study only those water potential sensors that measure the osmotic component will be considered. This restriction eliminates consideration of all water potential sensors except those based on measurement of vapor pressure. Richards and Ogata (1958) and Zollinger, Campbell and Taylor (1966) described early vapor pressure measuring instruments that required precise temperature control attainable only in the laboratory. Rawlins and Dalton (1967) later described a modification of these instruments that eliminated the need for precise temperature control and allowed field use of their instruments.

The salinity sensor

The Richards (1966) salinity sensor chosen for testing is shown in figure 1. It consists of two platinum screen electrodes separated about 1.0 mm and fired in place-on a

SOIL SALINITY SENSOR

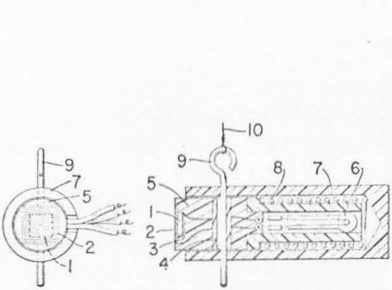

Fig. 1—Front and sectional views showing: (1) ceramic plate, (2) front screen electrode, (3) back electrode, (4) nylon tubing, (5) epoxy block, (6) thermistor, (7) outer Lucite case, (8) spring for holding the sensitive element against soil, (9) release pin, and (10) pull wire.

Source: Richards (1966, p. 333)

porous ceramic insulator. A thermistor is imbedded in an epoxy block with the ceramic plate so that the porous ceramic plate has an exposed surface for solution adsorption. The thermistor provides for temperature measurement. The two platinum screen electrodes have wires extending from their edges to connect to an alternating-current bridge for measurement.

Equilibrium of the sensor may be established by diffusion of solute into or out of the porous ceramic plate at one end of the sensor. The pores in the ceramic plate are small enough to maintain water saturation while soil water potential drops down to about a -15 bars water potential level in the surrounding soil. Thermodynamically, this means that a sort of diffusion pressure forces the sensor to undergo dn_i incremental composition change of solute until at the time of equilibrium, $dn_i = 0$.

The soil psychrometer

The soil psychrometer of Rawlins and Dalton (1967) consists of two chromel-P-constantan thermocouple junctions surrounded by a porous ceramic bulb. One of the junctions consists of two parts: first, the chromel-copper junction and second, the constantan-copper junction. The two copper wires that lead from this two-part junction extend outside of the psychrometer several feet. The type of soil psychrometer developed by Rawlins and Dalton (1967) is shown in figure 2, and figure 3 shows the electrical schematic for measurement of sensor output.

The soil psychrometer depends for operation on the Peltier effect by which the single-part junction temperature is depressed as a result of current flow in opposite the normal direction; such temperature depression forces condensation of water vapor from the microatmosphere surrounding the junction. After cooling the junction, differential voltage output by the two junctions is measured, and this voltage difference is related to the rate of water evaporation from the single-part junction, which is related to the water vapor concentration. The water vapor concentration at equilibrium with its liquid phase is an expression of the activity of that water. Thus, the energy status of the water in liquid phase may be deduced by comparisons between voltage readings over soil samples and those over standard molal sugar or salt solutions.

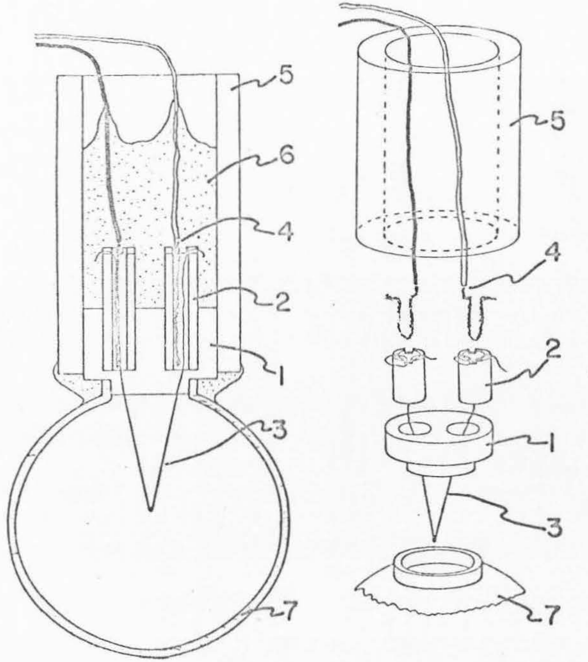

Figure 2. --Cross section and exploded view of th thermocouple psychrometer used for measuring soil water potential in situ.

Source: Rawlins and Dalton (1967, p. 299)

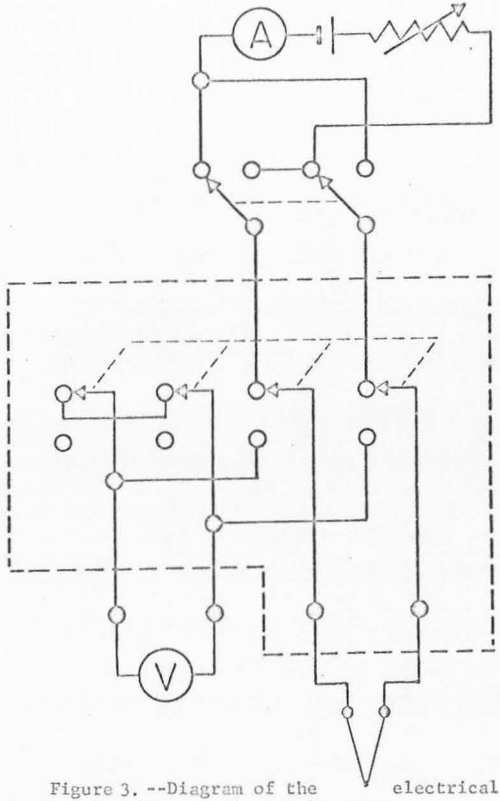

Figure 3.--Diagram of the electrical circuit for the thermocouple psychrometer.

Source: Rawlins and Dalton (1967, p. 299)

METHODS AND MATERIALS

Equilibrium Time Tests at Two Temperatures with Constant Pressure

The soil psychrometer

The main objective of this study was to determine the diffusion response time of the sensor to an abrupt change in salt concentration at the sensor face. Measurements were made with temperatures constant throughout the test. Two different temperature regimes were studied.

A controlled temperature water bath was set up inside a controlled temperature room. The bath was controlled to ±0.001C by a Hallikainen Thermotrol and monitored by both a thermistor bridge output to a Leeds & Northrup recorder and a Dymec Quartz Thermometer. Room temperature was 21.7 ±0.5C. Atmospheric pressure averaged 641.2 mm Hg during the tests.

Thermocouple differential voltages were measured by two systems: a 419-A Hewlett-Packard D. C. Null Voltmeter and a Leeds & Northrup D. C. Null Detector output to a Leeds & Northrup Speedomax H, Compact AZAR recorder.

Five solutions of $CaCl_2$ were prepared: 0.1m, 0.2m, 0.3m, 0.4m and 0.5m (molal). Erlenmeyer flasks with a capacity of 125 ml were filled with 100 g of each solution and suspended by a wood rack into the controlled temperature water bath. Five similar flasks with 100 g of distilled water were placed opposite the solution flasks in the bath, and all flasks were stoppered with rubber stoppers.

After the flask temperatures had reached bath temperature, soil psychrometers were placed in the contents of each flask and stoppers were reinstalled. Ten minutes after the psychrometers were installed in the flasks, measurements at ten-minute intervals were begun. When maximum or minimum readings had been repeated two or three times, the psychrometers were removed from their flasks and exchanged with their opposites; that is, those in pure water were placed in salt solutions and those in salt solutions were placed in pure water. Again readings were recorded at ten-minute intervals until maximum or minimum values were repeated.

Soil-water-salt and soil-water solutions were prepared and placed in 125 ml Erlenmeyer flasks, and the flasks were stoppered and suspended from the wood rack into the controlled temperature bath water. The soil-water-salt solution consisted of 70 g of 1.0 molal $Ca\,Cl_2$ solution mixed with 110 g of Millville silt loam soil to make a thin paste. The soil-water solution consisted of 63.01 g of distilled water mixed with 110 g of Millville silt loam soil to make a thin paste. Both solutions were prepared by adding soil to the liquid phase and then mixing the contents with a malt mixer.

A soil psychrometer was placed in each soil solution, and measurements were recorded, as before, at ten-minute intervals. After maximum and minimum measurements were repeated, the two psychrometers were exchanged and measurements recorded until maximum and minimum values were repeated.

The salinity sensor

The objective of this equilibrium time test was to measure sensor response time to salt concentration changes at two fixed external temperatures and constant pressure.

The soil-water-salt, soil-water and water-salt solutions described and used for the soil psychrometer tests were used for the salinity sensor tests in a similar way. An industrial Instrument, Inc., model RC-1B Conductivity Bridge was used to measure the sensor resistance. The two salinity sensors used in the tests were first brought to equilibrium in saline and non-saline solutions and then exchanged and monitored at ten-minute intervals until values were repeated on either of the two sensors. This procedure was followed at two temperatures while pressures remained constant.

Equilibrium Time Tests with Variable Pressure and Concentration

The soil psychrometer and salinity sensor

Various pressures were applied to both soil psychrometers and salinity sensors and the systems they were to measure so that pressure influence could be evaluated for each sensor.

A fifteen-bar pressure plate[3] was installed in a controlled temperature water bath. The porous plate was rinsed thoroughly with distilled water and then soaked in distilled water prior to placing it in the pressure chamber. Two soil psychrometers and two salinity sensors were placed inside the pressure chamber, and the lead wires from these four sensors were threaded through two 1/4 inch holes in the pressure chamber wall. The holes were sealed and the wires fastened in place by waterproof epoxy. The porous ceramic plate was removed from distilled water and installed quickly into the pressure chamber, and 40 ml of distilled water was poured over the plate to keep it moist during sample placement and chamber closure.

A soil-water-salt solution was mixed in a 125 ml Erlenmeyer flask using a malt mixer; 75.72 g of 0.1 molal $Ca\ Cl_2$ solution was mixed with 100 g of Millville silt loam soil. The soil-water-salt solution was divided with 25 ml going into a 50 ml beaker and the remainder into a ring container placed on top of the porous ceramic pressure plate.

One salinity sensor and one soil psychrometer were placed in solution in the 50 ml beaker, while the other soil psychrometer and salinity sensor were placed in the soil-water-salt solution contained by the ring on the porous pressure plate.

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[3] Manufactured by Soil Moisture Equipment Company of Santa Barbara, California.

The rubber seal ring and pressure chamber lid were set in place and fastened with the bolts provided, and the bolts were tightened alternately and evenly to insure against leaks.

Water was placed in the controlled temperature water bath to a depth of five or six inches above the top of the pressure chamber lid. Bath temperature was then brought to 24.993C, and equilibrium was established sufficiently well to obtain repeat readings with no change in thermocouple zero offset over a ten-minute interval. At this equilibrium point the sensor readings were recorded.

The pressure in the chamber was elevated from ambient atmospheric to 5.1 bars gage. Sensor measurements were recorded at ten-minute intervals until repeat readings were obtained or bi-directional variations between readings were apparent. Pressure was then reduced to 2.7 bars gage, 1.4 bars gage, 0.7 bar gage and 0.0 bar gage, and measurements at equilibrium were recorded for each pressure value. All measurements were made using the equipment previously described for that sensor except that noise level was sufficiently high that only the Hewlett-Packard D. C. Null Voltmeter was used for soil psychrometer output measurement. Throughout this phase of the test, the temperature of the bath was controlled to 24.993 ±0.001C.

RESULTS AND DISCUSSION

Equilibrium Time Tests at Two Temperatures with Constant Pressure

The soil psychrometer

The time vs sensor readings after an abrupt change in salt concentration are shown in figures 4 and 5. If the process of salt water movement into the sensor were simply a process of diffusion, a plot of sensor reading vs log time would yield a straight line (similar to infiltration of water into soil).

The curves shown in figure 4 appear to be sigmoid curves such as one might get from integrating the area under a skewed bell curve. Perhaps the sigmoid shape is the result of more than diffusion of solute to the interior wall of the porous ceramic bulb. For example, consider the case of a non-uniform, porous, ceramic cup. If one interior point of the cup were reached by the diffusing solution sooner than another interior point, then a gradient would be established between those two points through the vapor phase. If the sensor were placed centrally in that vapor path, the measurements of that sensor would be modified in such a way as to reflect the energy status of the vapor stream rather than the total interior space of the sensor. Such influence would be eliminated only by establishing equilibrium among the vapor sources.

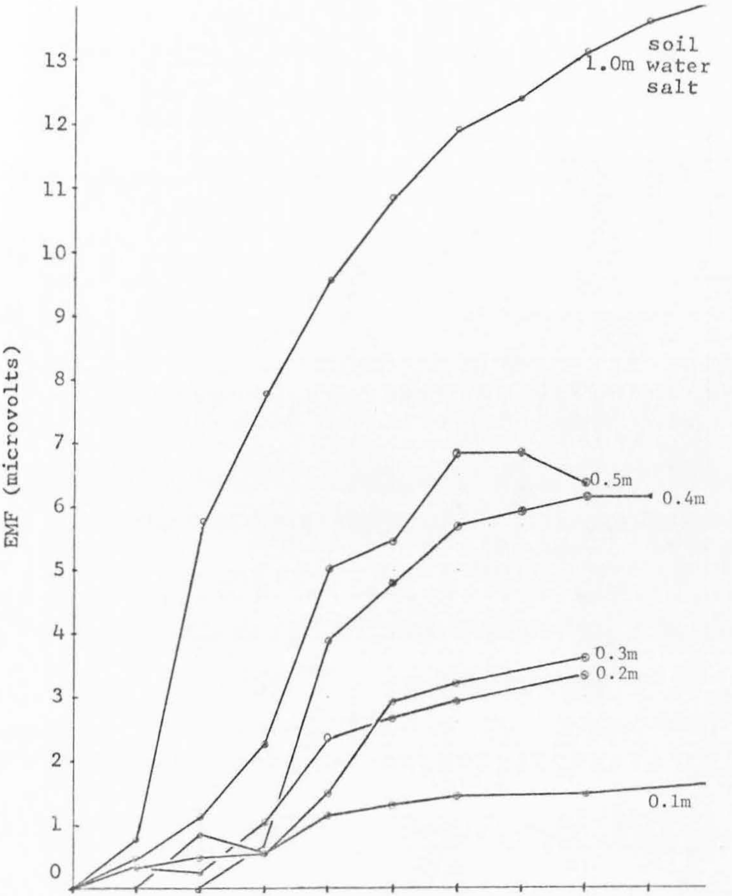

Figure 4. Soil psychrometer solution adsorption (EMF vs time).

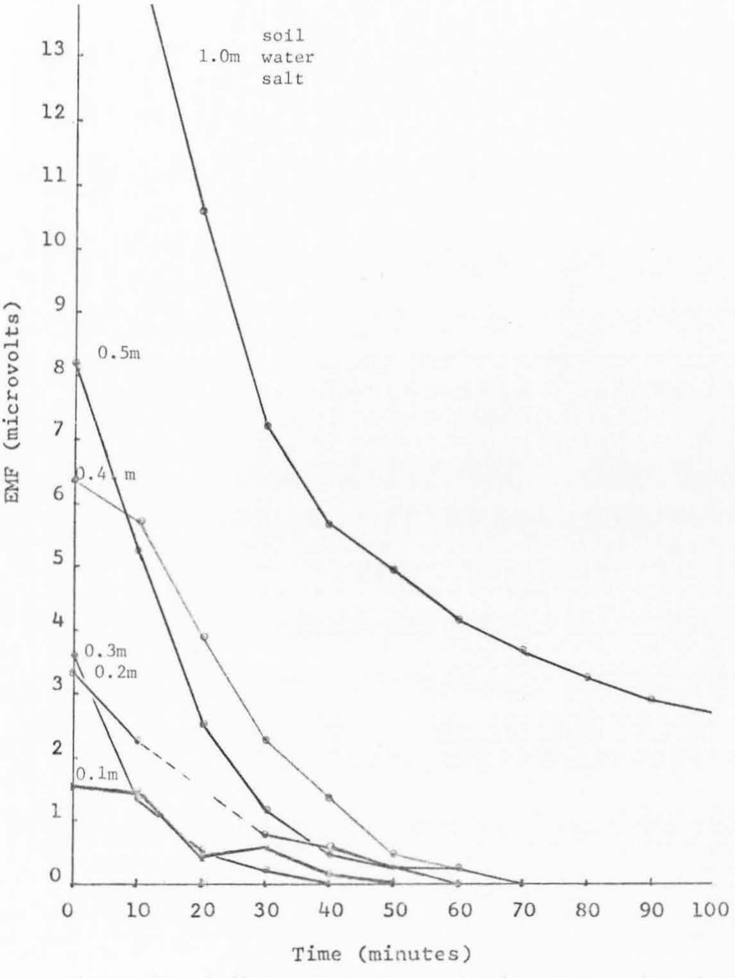

Figure 5. Soil psychrometer solution desorption (EMF vs time).

The curves in figure 4 all show a similar tendency, and the points along a curve may be considered in terms of curve slope at those points, that is, $\frac{dv}{dt}$, where v is voltage and t is time. If $\frac{dv}{dt}$ were a log function, the value $\left|\frac{dv}{dt}\right|$ would be constantly decreasing, but such is seen to be not the case. In fact, the slope variation indicates that some critical value is reached at the inflection point of the curves where maximum reaction does occur, but significance of this maximum rate is not known unless it represents the point of convergence of the pure water to solution and solution to pure water diffusion curves combined. If such were the case, the departure of the curves in figures 8 and 9 from straight lines could be explained by the fact that two phenomena each capable of log plot overlapped but not symmetrically.

A comparison of figures 4 and 5 indicates that the adsorption times to equilibrium were longer than desorption times, except in the case of the soil-water-salt solution. Why this is so is not known. Perhaps the influence of the double layer in the soil solution acted as a modifier of ion transport into the porous ceramic cup in such a way that diffusion times were nearly equal for both adsorption and desorption despite the persistance of the sigmoid shape in the adsorption curve.

The straightness of the desorption curve on semi-log

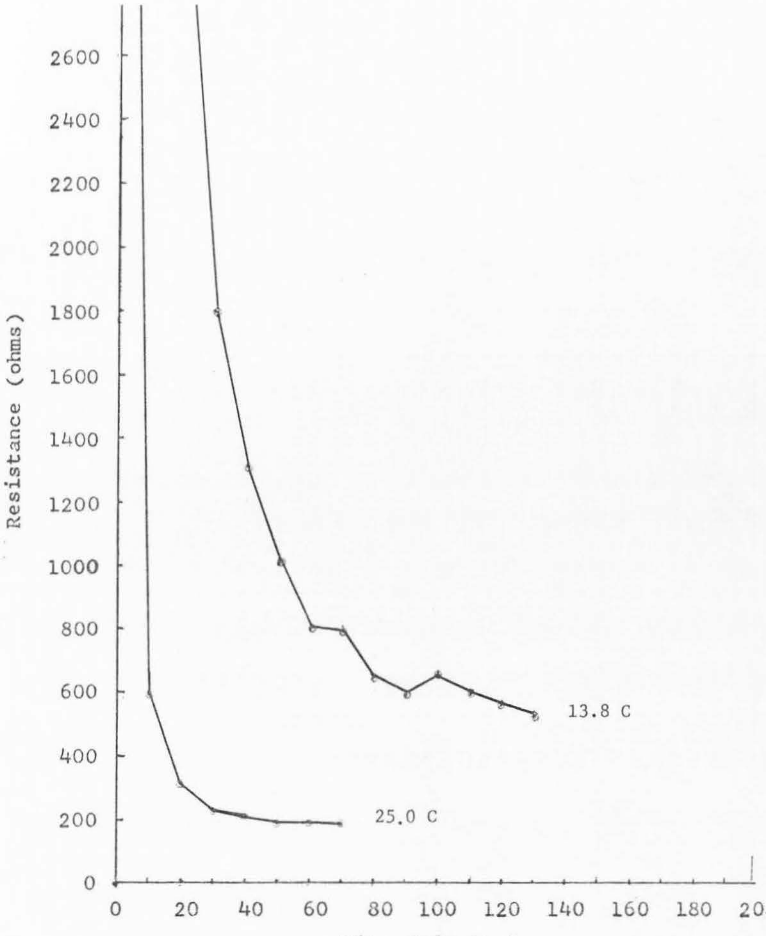

Figure 6. Salinity sensor solution adsorption (resistance vs time)

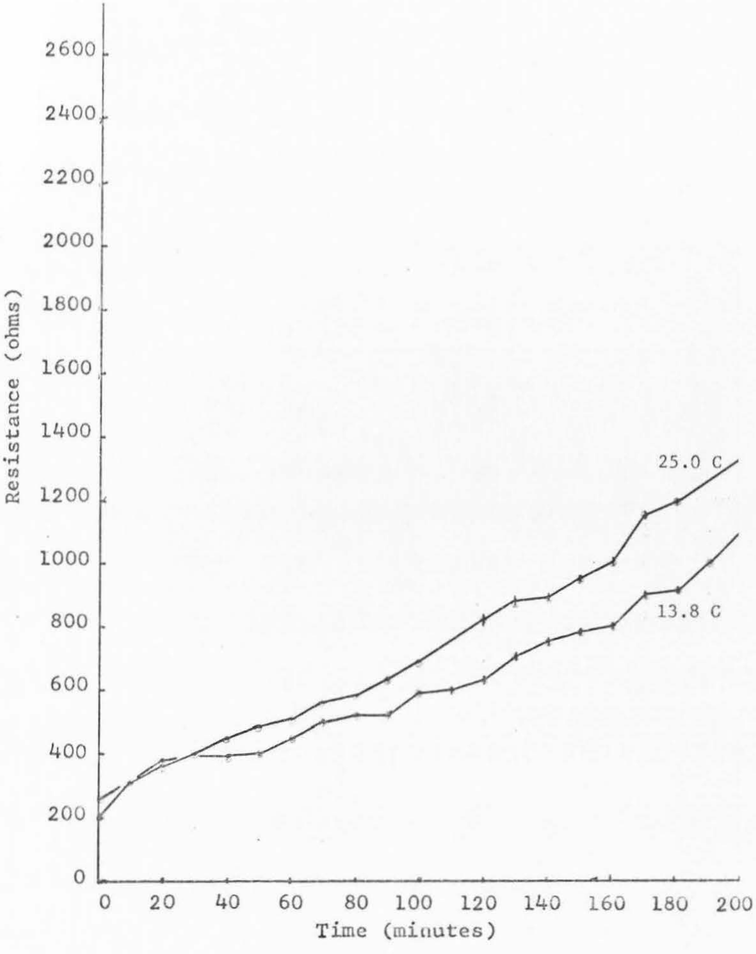

Figure 7. Salinity sensor solution desorption (resistance vs time)

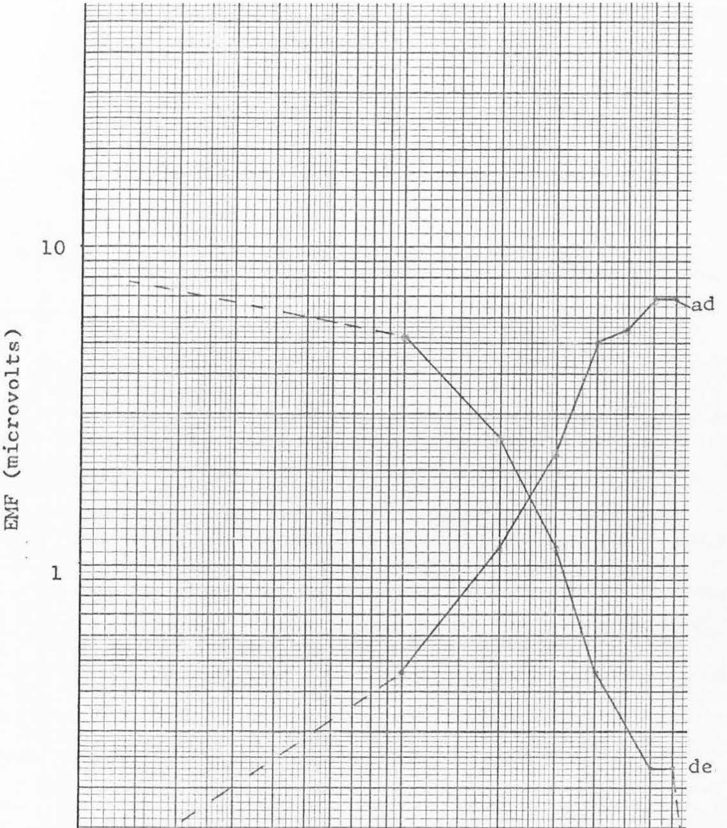

Figure 8. Soil psychrometer log-log plot of 0.5m solution adsorption and desorption (EMF vs time).

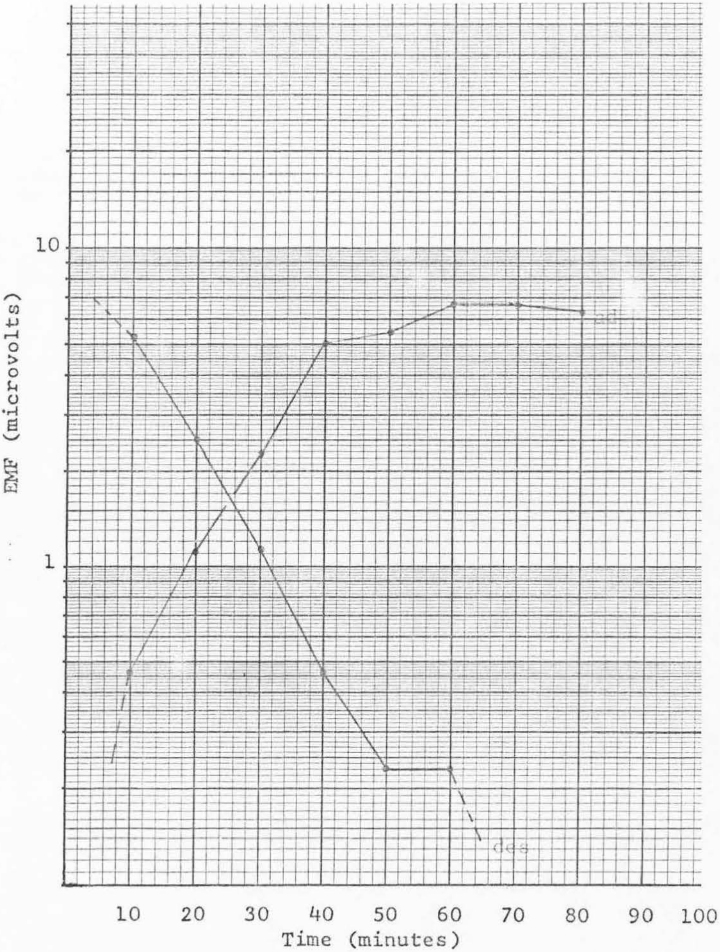

Figure 9. Soil psychrometer semi-log plot of 0.5m solution adsorption and desorption (EMF vs time)

paper shown in figure 9 is somewhat surprising, with only the slightest reverse sigmoid tendency.

Perhaps the logarithmic tendency of the desorption curve and the departure from logarithmic of the adsorption curve are related to the dominant influence of pure free water on the interior micro atmosphere of the soil psychrometer cup. That is, as long as pure free water remained anywhere on the interior wall of the porous cup, the influence of that pure free water was probably far greater on the micro atmosphere than its proportion of the total surface. If such were the case, the micro atmosphere would tend to be wetter with a consequent lower microvolt differential output. Apparently this is what happens. The influence of such a phenomenon will be discussed later.

The thermodynamic interpretation of the soil psychrometer data indicates that in the equation $dG = -SdT + VdP + \Sigma \mu_i \, dn_i$, one must look only at the last term because of its relation to ψ through P/P^o. However, if entropy is considered a driving force, perhaps it will be necessary to consider another term of this equation or perhaps another equation.

When the soil psychrometer function is considered in terms of thermodynamics, explanation is simplified. For example, if one introduces a porous ceramic cup saturated with pure free water into a salt solution and treats entropy as a driving force, the pure water in the cup will tend to become randomized as salt enters and simultaneously the free energy of the water will decrease and manifest itself in the form of reduced vapor pressure in proportion to the molar concentration of the solute present in the otherwise pure water at a given time. Since entropy cannot manifest itself in the presence of complete order except as a driving force or tendency, the influence of residual water, free from salt influence, on interior walls of the porous ceramic cup would dominate, and the differential voltage output would be low. The data collected support this hypothesis.

On the other hand, when a porous ceramic cup saturated with $Ca\ Cl_2$ solution is introduced into pure, free water, the entropy change of the pure, free water is assured by the solute present because there is no pure, free water to manifest its influence without energy input from surroundings. If all external dP, dV, dT and dn_i remain excluded from the system, the system entropy increases in proportion to the solute present. Consequently, the differential voltage output is not suppressed in a way contrary to the influence of normal solute diffusion, and a nearly straight line results if a semi-log plot of desorption is made. These conclusions justify both the use of the equation stated and the restriction of this treatment to the last term of that equation if Raoult's Law holds for $\psi = RT \ln P/P^o$. Raoult's Law states that $p = \frac{ni}{n_t} p^o$ or $\frac{P}{P^o} = \frac{ni}{n_t}$, in which n_t = total moles and the other symbols have the same meanings as before.

Uniformity of plot curvature prevents us from resorting to a straight line on the log plot of the desorption curve even though it approaches a straight line.

If the conductivity equation from Agricultural Handbook 60 (1954, p. 17) is used for calculating soil water energy depression with increased salt concentration and we assume a saturation extract which measures 4 m mhos cm^{-1}, the resulting osmotic pressure change predicted is $0.36 \times 4 = 1.44$ bars. If 0.1 molal Ca Cl_2 solution has an osmotic pressure of 4.42 bars and a proportional psychrometric desorption time is sought, the result will be about ten minutes. Such proportionality probably does not hold, however. This is evidenced by the desorption curve differences of time against voltage output which is proportional to solute concentration. In fact, a more probable equilibrium time requirement for desorption would be thirty minutes.

The salinity sensor

The salinity sensor adsorption-time curves in figure 6 differs from the desorption-time curves in figure 7. Diffusion of salt into the sensor was much more rapid than loss of salt from the sensor. This response was opposite that of the psychrometer, but probably such a difference was accountable to the fact that the salt itself was the component being measured whereas the salt effect upon the water and thence upon the water vapor was the route of

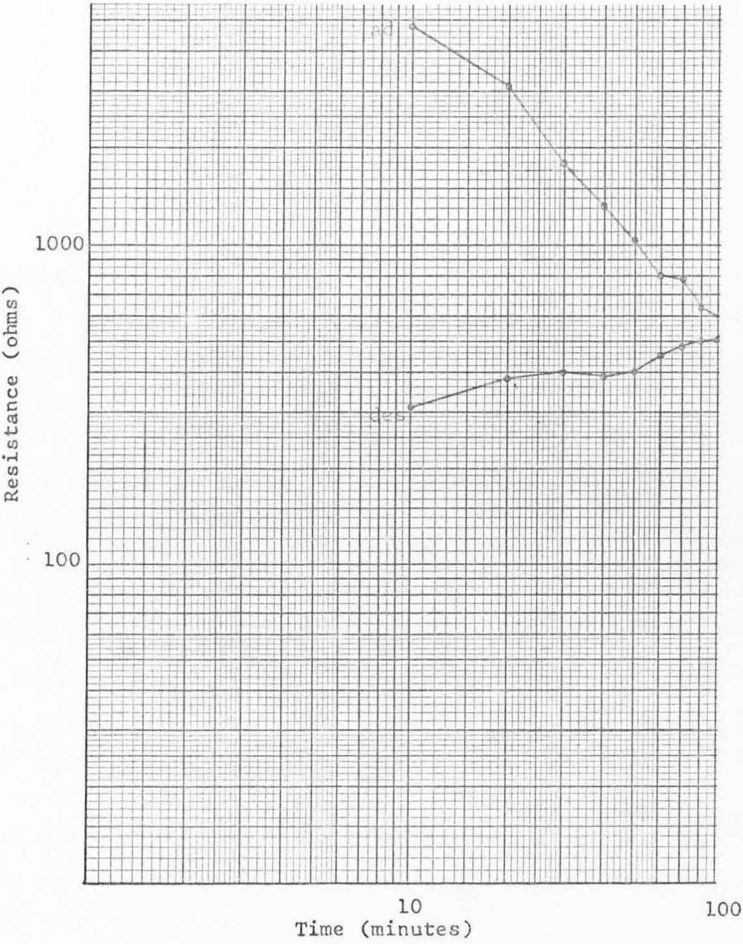

Figure 10. Salinity sensor log-log plot of 0.5m solution adsorption and desorption (resistance vs time)

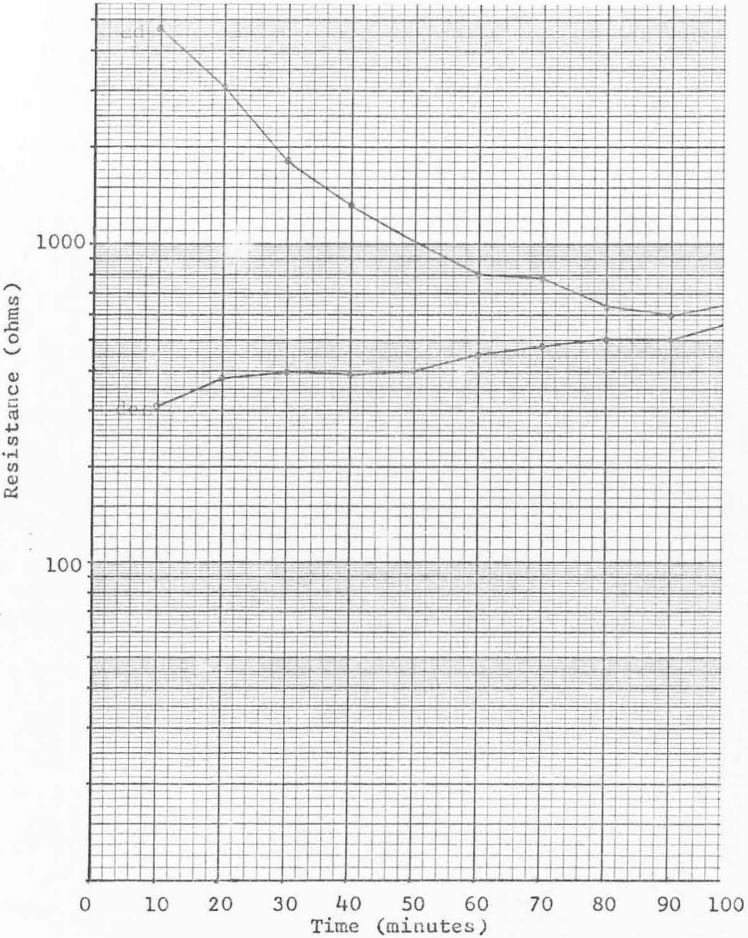

Figure 11. Salinity sensor semi-log plot of 0.5m solution adsorption and desorption (resistance vs time)

psychrometric measurement change. The salinity sensor apparently did not have an intermediate substance or phase influence because the logarithmic plot of data points yielded a nearly straight line, as shown in figures 10 and 11, for both adsorption and desorption.

Adsorption was more rapid in 25C water than in 13.8C water by nearly twice. This result was expected purely because of doubling of reaction rate for each 10C temperature rise.

Time lag of the sensors ranged from an adsorption time of 50 to 130 minutes while desorption from maximum conductivity of the sensor to a reading of 1000 ohms resistance ranged from 160 to 190 minutes, and 230 to 270 minutes were required to attain 1700 ohms resistance, depending on temperature.

Equilibrium Time Tests with Variable Pressure and Molar Concentration

The soil psychrometer

When pressure of 5.1 bars gage was applied to the soil-water-salt systems in which the soil psychrometers were immersed, their readings dropped from about 0.85 microvolt average to 0.05 microvolt average.

Such a large percentage change over such a narrow pressure change was somewhat surprising, and preliminary observations led to the assumption that the increased pressure had induced sensor failure. This assumption proved later to be in error. The search for an explanation to describe the consequence of the pressure change led to the hypothesis that if the macrosystem of thermodynamics were replaced by the microsystem of molecular dynamics, the consequence of such a pressure change might be explainable. On the basis of molecular kinetics an increase of pressure should increase the probability of colision by some constant raised to an exponential value. But all the while the partial vapor pressure should remain constant if in fact it were dependent on temperature only and temperature did not change. Naturally, such increased interference as that which would result from increased pressure would impede water vapor flow in the micro atmosphere surrounding the psychrometer thermocouple cold junction. If such were the case, then either increasing the gradient or increasing the cooling time of the thermocouple would yield a higher reading than that available by the ordinary cooling method. The gradient could not be increased because of I·R heating, so the cooling period was lengthened. The result was as postulated; the increased cooling time did yield values well above those available by the normal method. For example, whereas the 5 ma current for 15 seconds yielded values of 0.00 μv and 0.20 μv, the 5 ma current for 90 seconds yielded values of 0.12 μv and 0.36 μv, respectively. These results prompted the step-wise pressure reduction and measurement at each pressure step. The results appear in table 2 and figure 12.

While such results are restricted to pressures positive from 0.85 bar absolute to 5.1 bars gage, by far the greatest change is between 0.85 bar absolute and 0.7 bar gage. Such results prompt the conclusion that each sensor must be calibrated at that atmospheric pressure at which it will be used; otherwise the calibration may well be invalid.

The data on which figures 12 and 13 are based relate to equilibrium after extraction of some of the water from the sample on the porous ceramic plate. The differential voltage shift in the sample contained in the 50 ml beaker may be accountable to increased water activity which resulted in rapid vapor transfer into the solution. Such a conclusion could account for the 1.0 to 0.65 microvolt equilibrium value change of that solution. While this is possible, its probability is not known to me.

The salinity sensor

The results of the pressure influence on salinity sensor equilibrium are shown in table 4 and figure 13.

Perhaps the most prominant quality observable from these data is the nearly complete lack of change of the sensors. Even the plate sample from which water was extracted shows no influence on sensor resistance. Possibly this lack of indication is related to the comparitively slow desorption characteristics of the salinity sensors.

Table 1. Soil psychrometer EMF output during Ca Cl_2 solution adsorption from 7 concentrations

Elapsed Time (min.)	T=13.8C					Soil Water Salt	T=24.99C
	0.1m	0.2m	0.3m	0.4m	0.5m	1.0m	0.3m
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.0	0.32	0.32	0.0	0.46	0.78	0.0
20	0.86	0.25	0.50	0.68	1.14	5.68	2.22
30	0.59	1.03	0.57	3.88	2.28	7.75	5.55
40	1.17	2.32	1.51	4.78	5.02	9.55	7.20
50	1.32	2.67	2.94	5.70	5.47	10.83	6.64
60	1.46	2.94	3.21	5.92	6.84	11.88	7.20
70	---	---	---	6.15	6.84	12.40	
80	1.49	3.32	3.60	6.15	6.38	13.10	
90	---					13.59	
100	1.64					13.35	
110	1.52					13.35	
120						13.89	
130						13.89	

Table 2. Soil psychrometer EMF output during Ca Cl_2 solution desorption of 7 solutions

Elapsed Time (min.)			T=13.8C			Soil Water Salt	T=24.99C
	0.1m	0.2m	0.3m	0.4m	0.5m	1.0m	0.3m
0	1.55	3.32	3.60	6.37	8.20	16.3	7.20
10	1.44	2.26	1.35	5.70	5.24	14.4	4.15
20	0.42		0.50	3.88	2.50	10.59	2.22
30	0.57	0.77	0.21	2.28	1.14	7.22	1.39
40	0.14	0.57	0.0	1.37	0.46	5.68	0.28
50	0.0	0.27	0.0	0.46	0.23	4.91	0.0
60	0.0	0.0	0.0	0.23	0.23	4.13	0.0
70	0.0	---	---	0.0	0.0	3.62	
80		0.0	0.0	0.0	0.0	3.21	
90						3.87	
100						2.67	
110						2.40	
120						1.87	
130						1.87	

Table 3. Salinity sensor resistance during adsorption of solution.

Time (min.)	Resistance (ohms)	Time (min.)	Resistance (ohms)	Time (min.)	Resistance (ohms)
Sensor 1102 at 13.8C					
0		90	600	180	490
		100	650	190	460
				200	480
10	4800	110	600	210	470
20	3100	120	560	220	480
30	1800	130	500	230	460
40	1310	140	520	240	460
50	1010	150	540	250	
60	800	160	510	260	
70	790	170	530	270	
80	640				
Sensor 1106 at 25C					
0	6570	40	210		
10	590	50	195		
20	310	60	195		
30	230	70	190		

Table 4. Salinity sensor resistance during desorption of solution.

Time (min.)	Resistance (ohms)	Time (min.)	Resistance (ohms)	Time (min.)	Resistance (ohms)
		Sensor 1102 at 25C			
0	200	100	690	190	---
10	310	110	---	200	1330
20	360	120	820	210	1490
30	400	130	880	220	---
40	450	140	890	230	---
50	480	150	950	240	1800
60	505	160	1000	250	
70	560	170	1150	260	
80	580	180	1190	270	
90	630				
		Sensor 1106 at 13.8C			
0	300	100	570	190	1000
10	310	110	580	200	1100
20	380	120	610	210	1180
30	400	130	680	220	1250
40	390	140	730	230	1310
50	400	150	780	240	1470
60	450	160	800	250	1510
70	480	170	900	260	1590
80	500	180	910	270	1700
90	500				

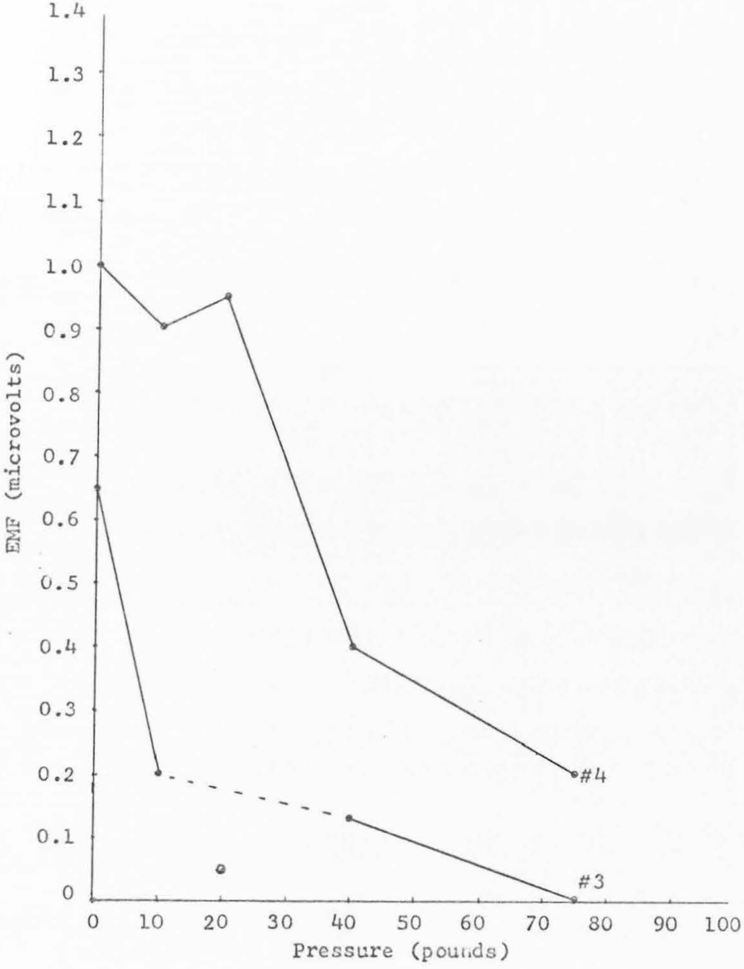

Figure 12. Soil psychrometer EMF vs pressure.

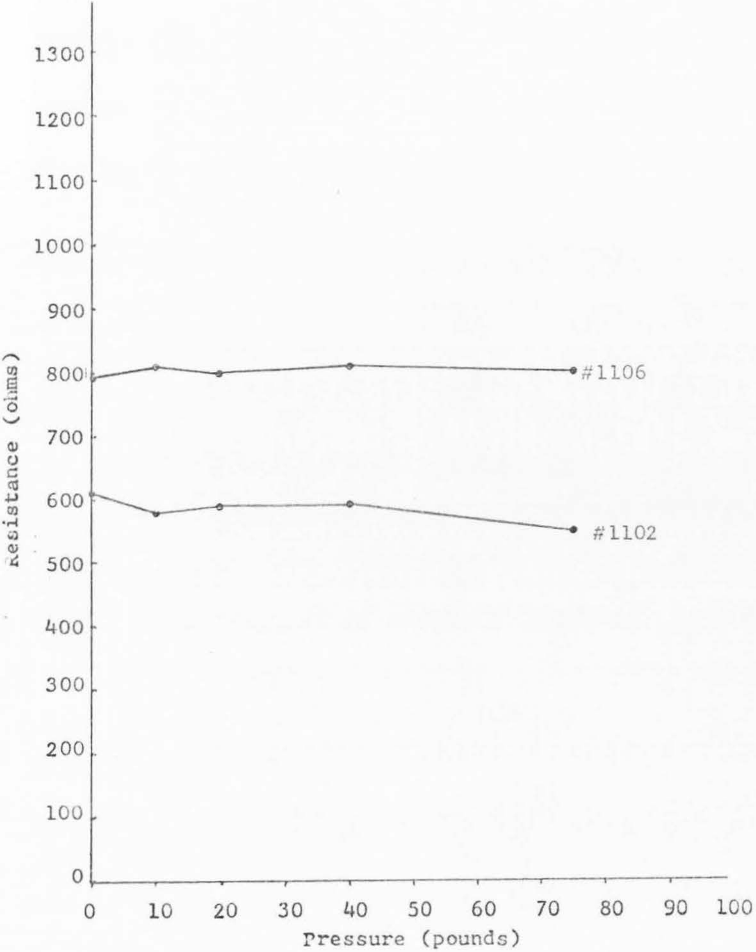

Figure 13. Salinity sensor resistance vs pressure.

Joint Sensor Function and Lysimeter Tests

Sensor function

Both salinity sensors and soil psychrometers respond to changes of temperature and molar concentration. However, the salinity sensor operates directly in response to salt whereas soil psychrometers respond to changes in vapor pressure. Thus the soil psychrometer is an indirect measurement device whereas the salinity sensor is a direct measurement device.

The directness of access to measurement probably influences the shape of the curves in figures 4, 5, 6 and 7. Furthermore, the departure of psychrometer curves from simple infiltration rate curves probably is the result of such indirectness of measurement.

If water infiltration rate for sand were 0.5 inch hour^{-1} into a root zone 4 feet deep and the water-holding capacity were 1 inch foot^{-1}, then 8 hours would be required to fill the root zone. If irrigation uniformity demanded that application time be 1/4 infiltration time, then application time would be 2 hours. If sensors were placed at 2-foot intervals to a depth of 6 feet, the first salinity sensor would reach equilibrium if salt adsorption prevailed, about the time water would reach the second sensor while the soil psychrometer would equilibrate in about 1/8 that time. Although desorption would not alter psychrometer performance significantly, it would prolong the equilibrium process for the salinity sensor far beyond the time required to fill the root zone. The water infiltration rate for clay would help relieve this problem because it is about 1/3 to 1/10 that of sand. The sensors would, therefore, have 3 to 10 times longer in clay than in sand for equilibrium to be established. Such hypothetical results indicate that response times of both salinity sensors and soil psychrometers are satisfactory for use in quality control of return-flow water. However, other characteristics of the soil psychrometer make it unsuitable.

Lysimeter tests

Lysimeter data collected between March 1, 1969 and May 4, 1969 are shown in tables 5 through 8. While these data do not represent an essential part of this experiment, they did show the need for these sensor tests. These data show time, depths and measurements for the lysimeter that was treated with 1000 g $CaCl_2$ on April 7, and again on April 9, 1969.

The measurements tabulated show that increased salt was present during both the water conductivity tests and the chloride ion tests beginning April 7, 1969. Furthermore, tabulations show that salt probably did not reach beyond the 16-inch depth.

The salinity sensors showed similar results at the

Table 5. Salinity sensor electrical conductivity vs time at given depths in the lysimeter (m mhos cm^{-1})

	Depth (inches)				
Time	6	16	26	36	Bottom
3-1-69	2.0	2.0	2.0	2.0	2.1
3-3	2.0	2.0	2.0	2.0	2.0
3-5	2.0	2.0	2.0	2.0	2.1
3-8	2.0	2.0	2.0	2.0	2.1
3-15	2.0	2.0	2.0	2.0	2.1
3-27	2.0	2.0	2.0	2.0	2.2
3-29	2.0	2.0	2.0	2.0	2.2
3-31	2.0	2.0	2.0	2.0	2.2
4-2-69	2.0	2.0	2.0	2.0	2.3
		Salt Added			
4-7	3.8	2.0	2.0	2.0	2.2
4-9	3.1	2.0	2.0	2.0	2.1
4-14	5.0	2.0	2.0	2.0	2.1
4-16	5.1	2.0	2.0	2.0	2.3
4-19	4.5	2.0	2.0	2.0	2.4
4-24	3.3	2.0	2.0	2.0	2.5
4-26	5.0	2.0	2.0	2.2	2.6
5-4-69	5.2	2.0	2.1	2.0	2.5

Table 6. Water sample extract electrical conductivity vs time at given depths in the lysimeter (m mhos cm^{-1})

Time	Depth (inches)				
	6	16	26	36	Bottom
3-1-69	0.58	0.92	---	---	1.28
3-3	0.78	1.01	---	---	1.30
3-5	0.97	0.97	---	---	1.21
3-8	0.92	1.12	---	---	1.21
3-15	1.42	1.57	---	---	1.36
3-27	0.63	0.95	---	---	1.16
3-29	0.82	0.83	---	---	0.81
3-31	0.62	0.82	---	---	1.19
4-2	0.68	0.99	---	---	0.94
		Salt Added			
4-7	2.56	1.18	---	---	1.22
4-9	2.70	1.19	---	---	1.11
4-14	6.00	1.20	---	---	1.50
4-16	6.20	1.30	---	---	1.33
4-19	4.50	1.05	---	---	1.40
4-24	4.22	0.90	1.05	1.90	1.22
4-26	4.26	1.18	0.92	1.01	0.89
5-4	2.90	1.20	1.28	1.55	1.28

Table 7. Chloride ion concentration vs time at given depths in the lysimeter (ppm)

Time	Depth (inches)				Bottom
	6	16	26	36	
3-1-69	2.49	1.51	---	---	1.51
3-3	---	1.0	---	---	1.0
3-5	---	---	---	---	6.47
3-8	---	1.42	---	---	1.0
3-15	1.42	5.05	---	---	6.21
3-27	0.71	4.26	---	---	0.71
3-29	1.35	4.35	---	---	4.90
3-31	1.0	0.18	---	---	3.90
4-2	1.0	3.37	---	---	3.37
		Salt Added			
4-7	78.9	---	---	---	9.60
4-9	747.0	28.8	---	---	6.84
4-14	---	---	---	---	12.3
4-16	1480.0	---	---	---	11.0
4-19	936.0	32.8	---	---	7.45
4-24	---	---	48.2	236	7.04
4-26	---	---	---	---	---
5-4	---	---	---	---	---

Table 8. Soil psychrometer EMF vs time at given depths in the lysimeter

Time	Depth (inches)				
	6	16	26	36	Bottom
3-1-69	5.1	2.2	1.2	---	---
3-3	5.0	2.3	1.2	---	---
3-5	---	---	0.8	---	0.3
3-10	4.2	---	---	---	---
3-27	---	---	---	---	---
4-7-69	0.4	0.2	0.2	---	---
4-9	---	0.8	0.6	0.6	0.4
4-14	0.4	0.4	0.6	---	---
4-19	0.6	0.2	---	---	---
4-25	---	0.1	0.3	1.2	0.4
4-26	0.3	---	0.5	---	0.3
4-28	0.6	0.1	0.7	0.3	0.5
5-3-69	0.5	0.2	0.5	0.3	0.6
7-9-69	2.25	---	0.5	0.25	0.5

16-inch level. The psychrometers did not register a definite change until nearly 90 days after the first salt application, and this change may have been the result of surface evaporation rather than salinity effect.

Such failure of the soil psychrometer may be explained by the hypothesis stated earlier in which pure water influence was said to predominate over saline solution influence. Thus the indirectness of measurement appears to have significant consequences on the soil psychrometer measurements.

SUMMARY AND CONCLUSIONS

The objective of this study was to evaluate the response times of the salinity sensor developed by Richards (1966) and the soil psychrometer developed by Rawlins and Dalton (1967). These response times were to be measured in such a way that not more than one term in the Gibbs free energy equation would vary during a test run. In this way the influence of changes of temperature, pressure and molar concentration could be measured independently.

Salinity sensor response time to equilibrium during salt adsorption ranged from 50 minutes at 25C to 130 minutes at 13.8C. Response time during desorption was not measured to equilibrium, but the time range from maximum sensor conductivity to 1000 ohms resistance was from 160 minutes at 25C to 190 minutes at 13.8C, and the time range to 1700 ohms resistance was from 230 minutes at 25C to 270 minutes at 13.8C. Maximum resistance readings were assumed to exist after 24 hours of equilibration even though equilibrium was not yet completely demonstrated. Pressure changes had little or no effect on the sensors.

Consideration of these response time requirements in the light of average water infiltration times into sand and clay prompts the conclusion that the salinity sensors tested may be useful instruments for quality control of of return-flow water.

Response times of the soil psychrometer ranged from 60 minutes at 25C to 80 minutes at 13.8C during adsorption of salt solution while desorption of salt solution, required from 40 minutes at 13.8C to 50 minutes at 25C. The longer desorption time at the higher temperature is probably related to the persistance of entropic influence caused by initial saturation of the sensor by saline solution. Such response times as these are acceptable for both sand and clay soils.

Pressure changes altered psychrometer outputs as much as 300 percent over a 0.7 bar range, and the greatest pressure effect occurred immediately above the average atmospheric pressure.

Preliminary lysimeter tests using the soil psychrometer indicated that salinity in the soil near the sensor did not influence the sensor with any degree of certainty during the 90 days following the application of salt. These preliminary lysimeter tests coupled with the response time tests of this study indicate that more testing must be done before conclusive results are obtained. But on the basis of these results the soil psychrometer is considered not suitable for use in quality control of return-flow water. This conclusion is based on the proposition that the method of sensor operation is not sufficiently direct to override the prominant influence of pure, free water which seems to mask the influence of salt, at least in a real soil system such as that in the lysimeter.

The following suggestions are offered with the hope of diminishing the problems encountered during this study:

1. Make the porous ceramic plate that holds the salinity sensor electrodes apart, thinner and more uniform to yield better repeatability and faster response time.
2. Test the soil psychrometer at the interface of a saline soil and a non-saline soil to establish the actual vs the theoretical influence of pure free water on measured water potential using various salt concentrations in the saline soil.

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