Operating characteristics and calibration of thermocouple psychrometers at low temperatures and potentials near zero

by Roy Madsen Degn

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Soils
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Abstract:
It was possible to obtain thermocouple psychrometer readings at -2 bars water potential in soil samples at temperatures as low as -20° C. Below -2 bars water potential the psychrometers worked well, -20° C seemed to be the low temperature limit for satisfactory operation. Under ideal conditions, water potential as high as -0.5 bar could be read from a single psychrometer at +20° C; this was not possible at lower temperatures. Correction factors for temperatures from -20° to +40° C were developed from data tabulated from standard psychrometric theory.

Hydrophobic coatings on thermocouple wires of four psychrometers stabilized readings, but made cooling rates and periods more critical.

Water potential in frozen soils comes to equilibrium with freezing potential (Ψi, the potential of the soil ice subsystem) which is a function of temperature alone, and can be calculated by the equation Ψi RT/V ln (Pi°/pw°), using the saturation vapor pressure over supercooled water and the saturation vapor pressure over ice at the temperature of interest, as obtained from standard water vapor pressure tables.

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A thesis submitted in partial fulfillment
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Soils

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ABSTRACT

It was possible to obtain thermocouple psychrometer readings at -2 bars water potential in soil samples at temperatures as low as -20° C. Below -2 bars water potential the psychrometers worked well, -20° C seemed to be the low temperature limit for satisfactory operation. Under ideal conditions, water potential as high as -0.5 bar could be read from a single psychrometer at +20° C; this was not possible at lower temperatures. Correction factors for temperatures from -20° to +40° C were developed from data tabulated from standard psychrometric theory.

Hydrophobic coatings on thermocouple wires of four psychrometers stabilized readings, but made cooling rates and periods more critical.

Water potential in frozen soils comes to equilibrium with freezing potential (ψ_i, the potential of the soil ice subsystem) which is a function of temperature alone, and can be calculated by the equation

$$\psi_i = RT/\overline{V} \ln (p_i{}^\circ / p_w{}^\circ),$$

using the saturation vapor pressure over supercooled water and the saturation vapor pressure over ice at the temperature of interest, as obtained from standard water vapor pressure tables.

INTRODUCTION

Scientists have continually searched for improved means of describing and measuring water status in plant and soil systems. Thermodynamics has long been recognized as a convenient means of describing the water relationships within these systems. Soil Water Potential is defined as, "The amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water, at a specified elevation and at atmospheric pressure, to the soil water (at the point under consideration)." This potential may be identified with the partial specific Gibbs free energy of the soil water with respect to pure free water at the same temperature (26). Application of the well known thermodynamic principles to plant and soil systems was delayed because of the difficulty encountered in accurately measuring the small vapor pressure differences between pure, free water and water in these systems. The development of the thermocouple psychrometer provided a convenient means of measuring the potential arising from these vapor pressure differences by measuring the thermoelectric EMF (Electromotive Force) in a dry junction and wet junction thermocouple circuit.

The commercial thermocouple psychrometers currently available to researchers are compact, reasonably priced, and quite uniform. They work best when the soil water content is below the optimum for plant growth, and they work best at soil temperatures above 10° C. Soil water potential nearer zero than -2 bars is difficult to determine with psychrometers currently available.

In 1951, Spanner (29) published the first report on successful operation of a thermocouple psychrometer for measuring "suction pressure." He placed a sample chamber in a water bath with precise temperature control (±0.0001° C). This chamber contained a test solution or plant tissue and a bismuth-tin alloy-bismuth thermocouple. Peltier cooling was used to deposit a water film on the thermocouple junction by condensation, thereby creating a wet bulb. The output was the electromotive force (EMF) caused by the temperature gradient between the wet junction and the dry junction, which was at the temperature of the water bath. Spanner read this EMF as the ballistic throw of a galvanometer.

In 1958, Monteith and Owen (19) described a Peltier-cooled thermocouple psychrometer based on Spanner's design, but modified by: (a) using commercially available 0.0152-cm Chromel and constantan wires for the thermocouple junction, instead of bismuth-tin alloy and bismuth wires that had to be hand drawn; and (b) reading the steady state thermocouple EMF developed by wet bulb-temperature depression (EMF plateau), instead of Spanner's ballistic throw. Monteith and Owen used a sample chamber and a constant temperature bath controlled to ±0.0004° C.

In 1958, Richards and Ogata (27) succeeded in measuring "water-binding forces" in soil as well as plant tissues. The Richards-Ogata psychrometer used a thermocouple that was fabricated by soldering a Chromel P wire to one side of a small silver ring, and a constantan wire to the opposite side. The Richards-Ogata psychrometer also used a water bath with precise temperature control. The psychrometer was placed in the water bath in much the same manner as the Spanner instrument, but a water droplet was placed on the silver ring before the psychrometer was placed in the sample chamber. The temperature of the bath was taken as the dry bulb temperature, and the wet loop (wet bulb) temperature was read from the thermocouple junction. Steady state conditions were reached in 10 to 30 minutes.

In 1964, Spanner (30) published a thermodynamics textbook using biological examples and problems. In 1968, Low, Hoekstra, and Anderson (17, 18) published papers on the thermodynamics of soil water systems. I used these publications extensively to check the theory I used in preparing this paper.

In 1966, Rawlins (22) published a detailed discussion of thermocouple psychrometric theory, describing both the Spanner and the Richards-Ogata psychrometers in terms of the mathematics of diffusion and conduction. This paper became the basis for new designs and further refinement of the mathematical description of thermocouple psychrometers. Peck (20) published a discussion on heat and water flux in psychrometers in 1968 and a discussion on sample effects (21) in 1969.

A real breakthrough in thermocouple psychrometry came in 1967 when Rawlins and Dalton (24) succeeded in using Peltier-cooled thermocouple psychrometers, without precise temperature control, to measure "soil water potential." Using Chromel P-constantan junctions enclosed in porous ceramic covers, Rawlins and Dalton investigated temperature effects on relative humidity, temperature effects on the psychrometers, and the effects of heat and water flux through the walls of the ceramic enclosures. Most of the temperature effects on the psychrometer and its associated circuitry were canceled by subtracting the EMF before cooling, from the EMF after cooling was complete. This was done by applying a bucking EMF to balance or cancel the dry bulb EMF before the cooling current was applied. Temperature effects on relative humidity were accounted for by correction factors. To maintain a water potential difference of less than 0.1 bar between the chamber and the sample, the minimum water conductivity through the porous ceramic enclosure was 4 $\mu g/cm^2$ per hour for each °C change in temperature per hour. According to Rawlins and Dalton, soil temperatures during these tests varied as much as 4° C per day without affecting psychrometer sensitivity. The 4° C per day temperature-change rate is approximately the same as the 0.001° C temperature-control requirement for 0.1-bar sensitivity established by Spanner (29). With a 20-second cooling period, as used by Rawlins and Dalton, 0.001° C divided by 0.333 minute, or 0.003° C per minute, would be an allowable rate of temperature change.

By 1968, Rawlins, Gardner, and Dalton (25) had determined water potential in soil and plant tissues with thermocouple psychrometers without precise temperature control. Soil water potential was measured with a psychrometer previously described by Rawlins and Dalton (24). Leaf water potential was measured with a similar psychrometer mounted in a Teflon test tube that was lined with a freshly picked, rinsed leaf.

In 1968, Campbell, Trull, and Gardner (7) developed a technique for making large, uniformly welded bead junctions on Chromel P-constantan wires which were not only more uniform and durable, but also displayed longer and more stable EMF plateaus than either the soldered junctions previously used, or the smaller welded junctions furnished by wire manufacturers.

Hsieh and Hungate (11) succeeded in producing a temperature-compensated thermocouple psychrometer that gave satisfactory results in rapidly changing temperature regimes. Brown (3) reported that psychrometers with fine-mesh stainless steel covers responded faster under dry conditions than psychrometers with porous ceramic covers. Van Haveren (31, 32) collected thermocouple psychrometer data in snowbanks and frozen soil. Van Haveren calibrated his psychrometers by projecting a curve from data taken above freezing. He did not report data from frozen soil systems but did present data from snowbanks which he used to determine water vapor pressure gradients within the snowpacks.

Several excellent review papers have been published recently on the construction and use of devices for measuring water potential. Among the more useful papers dealing with thermocouple psychrometry are those of Brown (3), Brown and Van Haveren (4), Lopushinsky (16), Rawlins (23), Scotter (28), and Wiebe et al. (34, 35).

OBJECTIVE

This project was undertaken to find the practical limits of operation of commercially available thermocouple psychrometers with respect to direct measurement of soil water potential in cold soil at temperatures above and below freezing, and in wet soil at potentials near zero. Measurements of soil water potential at low temperatures are important in studies of water movement in frozen soils, between frozen and unfrozen soils, and between frozen or unfrozen soil under a snowpack.

THEORY

At the freezing point, no sharp discontinuities are apparent in the temperature versus water vapor-pressure curve, below the freezing point, however, two curves emerge--one for supercooled water and another for ice. The thermocouple psychrometer measures water potential related to vapor pressure ratios as wet bulb-temperature, or ice bulb-temperature, depression (ΔT); therefore, it should be possible to extend the readings into frozen systems.

Because no measuring device functions perfectly, and because almost any variable physical property will deviate from ideal behavior, calibration procedures are necessary to relate thermocouple psychrometer output to the measured parameter. For example, the calibration curve relating EMF to water potential (ψ) is essentially linear for a thermocouple psychrometer. The curve deviates from linearity as "noise" enters the circuit, as the temperature versus thermocouple-EMF curve deviates from linearity, and as heat and water vapor fluxes influence wet bulb-temperature depression (Rawlins 22; Peck 20, 21). Within the limits of ideal behavior, the thermocouple EMF (microvolt signal) is determined by the wet bulb-temperature depression (ΔT), which is, in turn, related to the energy dissipation rate. Psychrometers respond to latent heat loss by measuring the degree of evaporative cooling. The thermocouple psychrometer responds to changes in the Gibbs free energy:

$$G - G^\circ = \Delta G = \int_{p^\circ}^{p} \frac{RT}{p}\, dp = RT \ln \frac{p}{p^\circ} \qquad [1]$$

where G = Gibbs free energy,

R = the universal gas constant,

T = temperature in degrees Kelvin,

ln = natural log,

p = vapor pressure of water in the system,

p° = vapor pressure of pure free water at the same temperature as the water in the system.

This energy-vapor pressure ratio relationship is similar for the usual expressions of potential energy of physical systems; it varies only with the constants used to express each property in the conventional units associated with it. These potentials are related to each other by their common theoretical equivalents to the right side of equation [2], which is often found in the literature in connection with discussions of water potential in soil and plant systems when equation [1] is divided by the partial molal volume of water, the energy function can be expressed as pressure:

$$\psi_\pi = (RT/\overline{V}) \ln a = -\pi \qquad [2]$$

where ψ_π = osmotic potential,

$\overline{V}$ = partial molal volume of water = 18.016 cm^3/Mole,

a = activity = $p/p°$,

π = osmotic pressure.

For comparison, measurements are usually corrected to standard conditions of 25° C and 1 standard atmosphere of barometric pressure.

The definitions of water potential components used in this paper are those given in the "Glossary of Soil Science Terms" published by the Soil Science Society of America (26).

Ψ_t (total water potential) is the sum of ψ_π (osmotic potential), ψ_g (gravitational potential), and ψ_m (matric or capillary potential). Equation [2] expresses ψ_t, the potential measured by thermocouple psychrometers because ψ_g and ψ_m affect soil water vapor pressure also. The relationship described in equation [2] is used to calibrate transducers such as thermocouple psychrometers. Equation [2] is also used to determine relative humidity or activity from colligative property measurements.

By inserting the proper constants, equation [2] reduces to the following:

$$\psi_\pi = \frac{(8.3143 \times 10^7 \text{ ergs Mole}^{-1}\ °K^{-1})\ (298.16\ °K)}{18.016 \text{ cm}^3 \text{ Mole}^{-1}} \ln a$$

$$= (137.60 \times 10^7 \text{ ergs cm}^{-3}) \ln a$$

$$= (137.60 \times 10^7 \text{ (dyne cm) cm}^{-3}) \ln a$$

$$= 1.376 \; (\ln a) \text{ bars} \qquad [3]$$

$$(1 \text{ bar} = 10 \;\; \text{dyne cm}^{-2})$$

Total water potential is a function of water content and temperature, as well as soil or plant matrices, and solution concentrations. At temperatures below freezing, a freezing potential (ψ_i) predominates and essentially controls the water potential of the soil water system (Low et al. 17, 18).

According to Hoekstra (10), Anderson and Hoekstra (1), and Low et al. (17, 18), the drying force of freezing soil arises because water migrates to the ice lenses that start to form in large pores, or soil voids. The ice lenses are made up of pure, normal hexagonal ice at the water potential of pure, normal ice. Liquid water, as well as water vapor, moves into or out of the solid phase until the water potential of the soil equals that of the ice. Therefore, according to Low et al. (17, 18) and Hoekstra (10, water potential of ice is a function of temperature alone,

$$\psi_i = RT/\overline{V}_i \ln (p_i^\circ/p_w^\circ), \qquad [4]$$

where all the symbols are the same as in equation [1] and [2] and in addition,

p_i° = the saturation vapor pressure of pure, normal ice at temperature T,

p_w° = the saturation vapor pressure of supercooled water at temperature T, and

ψ_i = the freezing potential, or water potential due to freezing.

Water potential decreases (becomes more negative) rapidly as the temperature falls below freezing; for example, the potential developed by freezing at -5° C is calculated at -60.8 bars by the use of equation [4].

Direct measurement of ψ_i by psychrometry would require that the wet bulb be covered with supercooled water instead of ice, as no potential would be apparent otherwise. ψ_i is most easily determined by calculation with equation [4] from temperature-vapor pressure data available in many standard tables.

Matric potential (ψ_m) can be thought of as expressing a definite thickness of liquid water film in a soil at a given temperature. Anderson and Tice (2) suggest that liquid soil water content is a function of ψ_m and the specific surface, and that liquid water content of a frozen soil can be determined if the specific surface and temperature of the soil (hence, soil water potential) are known.

The concept that ψ_i dominates a partly frozen soil system has been accepted by several prominent scientist. For example, Harlan, Banner, and Frieze (9) reported work with gypsum blocks, supporting the theory presented by Hoekstra (10) that ψ_i dominates a freezing soil system. Cary and Mayland (8) reported work on soil water and salt movement, taking Hoekstra's (10) viewpoint into account.

EXPERIMENTAL METHODS AND PROCEDURES

Eight commercial (Wescor[2]) thermocouple psychrometers were selected at random for this experiment. A microvolt meter, designed to read thermocouple psychrometers by the method given by Rawlins and Dalton (24), was used to detect the microvolt signal from these transducers. A new cooling switch was fabricated and incorporated into the measuring system, so that a laboratory timer could be used to determine the precise cooling period; a variable resistor was incorporated to determine the precise cooling rate, and a milliammeter was incorporated to monitor the cooling rate. A switch was added so the cooling current could be reversed to briefly provide heat for drying the thermocouple junctions. A recorder was used to read the thermocouples at -2 bars water potential, but it was not needed at -10 bars.

Soil samples were extracted to -2 and -10 bars water potential in pressure plate apparatus. Campbell and Gardner (6) found that very little change in matric potential occurred from the slight change in bulk density that probably resulted from repacking the soil around the thermocouple psychrometers.

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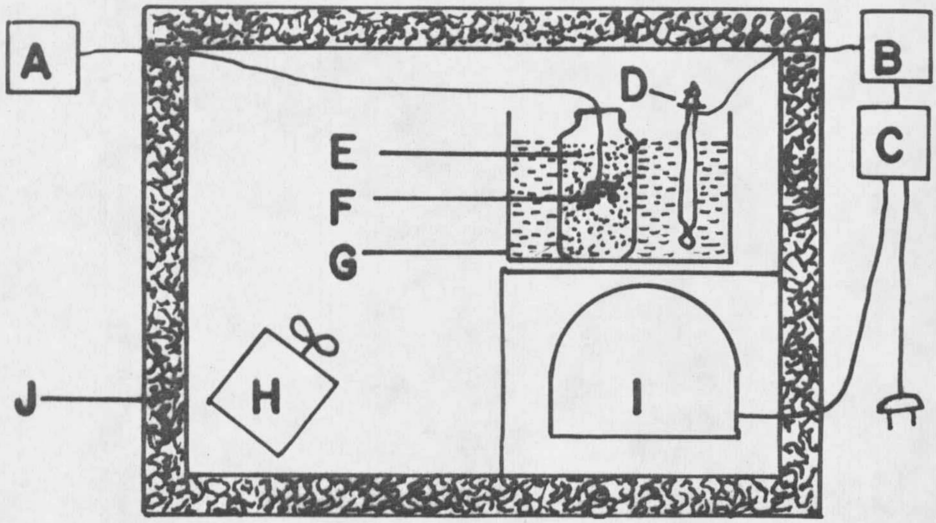
[2] Trade and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment by the USDA of the product listed.

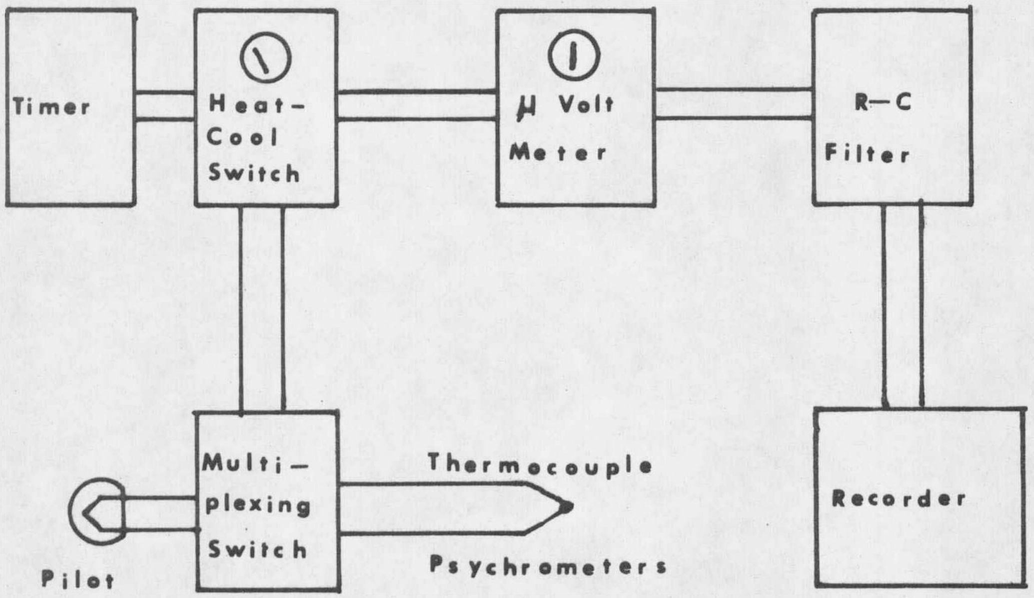
Several configurations of the experimental setup were tried. The most successful arrangement is shown in Figures 1, 2, and 3. Figure 1 shows a 2.3-kg soil sample placed in a mason jar with eight thermocouple psychrometers (three unmodified units, two with fine-mesh stainless steel covers and Vaseline-coated thermocouple wires, two with fine-mesh stainless steel covers and Teflon-coated wires, and one with a fine-mesh stainless steel cover and uncoated wires). The eight psychrometers were placed, approximately 4 mm apart, in a small circle at the center of the jar, with soil carefully packed around each psychrometer. The soil sample was packed to bulk density of 1.4 gm/cm^3. The jar was closed with a mason lid, and the psychrometer leads were brought out through a 2.5-cm diameter hole in the metal lid. Vaseline was placed around the wires to provide a vapor-tight seal between the wires and the lid. The jar was placed in an ethylene glycol water bath in a 0.14 m^3 home freezer. The refrigeration system was controlled by a mercury thermoregulator-actuated relay, which switched the compressor off and on. When the mercury bulb was submerged in the liquid bath, the thermoregulator performed with the proper cycle for the refrigeration system.

Whenever psychrometer leads were handled by hand, it took them up to 2 minutes to attain thermal equilibrium. Therefore, the psychrometers were multiplexed through a 3-level wafer switch. Positive thermocouple leads were soldered to the first wafer; negative leads, to the second wafer; and the third wafer was used for a pilot light display to identify the psychrometer being cooled or read.



A	Multiplexing Switch
B	Thermoregulator Relay
C	Power Relay
D	Mercury Thermoregulator
E	2.3 Kg Soil Sample
F	Psychrometers
G	Liquid Bath
H	Fan
I	Compressor
J	0.14 M^3 Freezer

Fig. I Cold Chamber



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R—C Filter

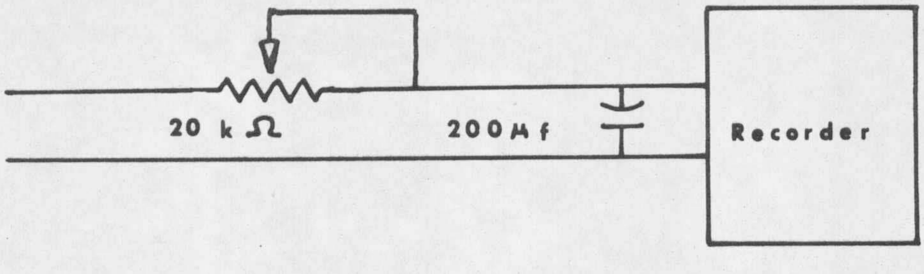
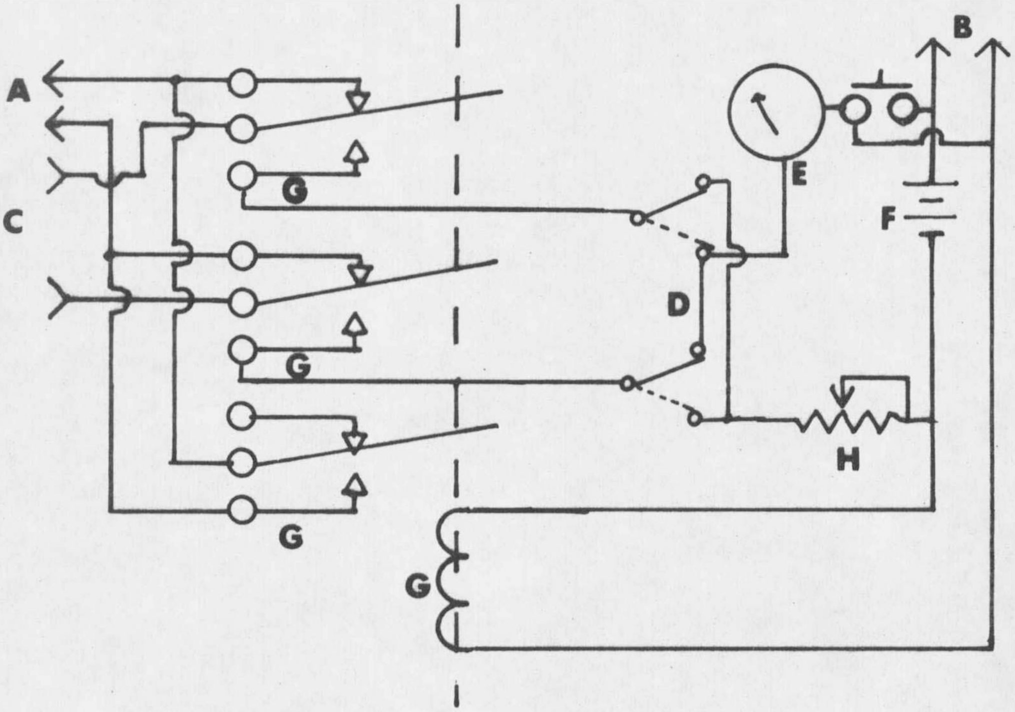


Fig. 2 Block Diagram of Reading Circuit



A	To μ Voltmeter
B	To Timer
C	From Psychrometers
D	DPDT Switch
E	Miliammeter
F	12 Volt Battery
G	3PDT Relay
H	10 kOhm Pot.

Fig. 3 Heat—Cool Switch

The instrumentation used to read the thermocouple psychrometers at -2 bars water potential is shown in Figure 2. All of the diagram blocks represent commercial laboratory instruments, except for the heat-cool switch shown in Figure 3, the wafer switch described in the previous paragraph, and the R-C filter shown in Figure 2.

A diagram of the heat-cool switch is shown in Figure 3. Precise control of cooling time and rate was needed at -2 bars water potential; therefore, a gold-plated relay, controlled by a commercial laboratory timer, was used to switch the cooling current which was monitored with a milliammeter. The switch proved reliable.

RESULTS AND DISCUSSION

Instrumentation Problems and Solutions: A great deal of difficulty was experienced in obtaining readings at -2 bars, or greater, water potential, under any circumstances. At -2 bars, much faster response was observed from psychrometers with fine-mesh stainless steel covers than from those with ceramic covers, as suggested by Brown (3). Meter deflection was observable from 5 to 10 minutes after packing the stainless steel-covered psychrometers in the soil samples, while the first meter deflection observable after packing the ceramic-covered units varied from 30 minutes to 12 hours. Coating the thermocouple wires with Teflon or Vaseline seemed to improve repeatability (reduce standard deviations). Korven and Taylor (14) reported that coating the thermocouple wires and junction with plastic spray improved stability by reducing oxidation, no change in calibration was reported.

It was found that the ceramic covers did not function as inert covers, either physically or chemically. Color changes on the ceramic covers were noted after 24 hours in standard sucrose test solutions, and after 2 weeks in field use. Jackson (12) reported effects from sodium salts used to disperse the clay for casting porous ceramics. One very clean psychrometer, with the cover removed, was placed in a test tube containing approximately 1 ml of NaCl test solution at 0.5 bar water potential. This psychrometer was readable at room temperature, but no valid readings could be obtained with standard ceramic-covered psychrometers in soil samples or test solutions at greater than -2 bars water potential. Brown (3) reported that fine-mesh stainless steel covers permitted faster response to changing water potential than did less porous ceramic covers, especially at water potentials low enough to break continuity of the water film between soil particles and the psychrometer cover. Of the psychrometers packed in the 2.3-kg soil sample, those with fine-mesh stainless steel covers were superior to those with ceramic covers in reaching equilibrium with the soil at both soil water potentials. Stainless steel conducted heat 50 to 100 times more rapidly than porous ceramic, and offered 2.5×10^9 times less resistance to the passage of soil water; therefore, it seems reasonable to assume that a psychrometer covered with fine-mesh stainless steel would reach temperature and vapor-pressure equilibrium with the soil much more rapidly than one covered with ceramic. By virtue of its thermal conductivity, 50 to 100 times that of soil, a fine-mesh stainless steel cover should reduce temperature gradients across the sample volume; the mean system temperature should be the mean temperature of the soil in contact with the cover.

In order to measure EMF plateaus at -2 bars water potential, the entire thermocouple psychrometer, including cover, wires, junction, electrical connections, and base, had to be extremely clean. A ceramic-covered psychrometer that had previously been calibrated in NaCl solutions could not be cleaned sufficiently so that its calibrations could be checked in sucrose solutions; however, a ceramic-covered psychrometer could be cleaned sufficiently for measuring soil water potential, by dipping it intact in dilute hydrochloric acid for 2 to 5 seconds; next, rinsing it vigorously under a stream of distilled water, while at the same time rotating it slowly so that each side of the porous cover was subjected to a 500-mm vacuum; then soaking it in distilled water for 24 to 48 hours; and finally, agitating it in an ultrasonic cleaner for a total of about 30 minutes during three or four periods. A psychrometer with a fine-mesh stainless steel cover could be cleaned simply by soaking it in distilled water, then agitating it in an ultrasonic cleaner, and finally, rinsing it in distilled water. Occasionally, the thermocouple wires and junction were so contaminated that psychrometers could not be cleaned intact. When contamination seemed evident, the psychrometer cover was removed, and the thermocouple wires and junction were inspected under a 50X microscope. Under the microscope, foreign matter was plainly evident in the form of crystals, often as large as the 0.025-mm diameter wire. It was found that this foreign matter could best be removed by dipping the wires and junction in 3 to 4 normal hydrochloric acid for 1 or 2 seconds, followed immediately by vigorous rinsing under a stream of distilled water, with a final rinse of acetone. The thermocouple junction, after such cleaning, was very smooth, and almost as reflective as a good mirror.

In order to determine possible reasons for wire and junction contamination, five new psychrometers were chosen at random and disassembled. It was found that the wires in two of the five psychrometers touched the side of the ceramic cover, wires in another had probably touched the end of the cover, and the junction in another was not as smooth as usual. It was evident that contamination could easily occur where the thermocouple actually touched the protective cover.

Special Reading Techniques: The effect of exposing a psychrometer to a saline soil or saline test solution is illustrated in Figure 4. These results are similar to those published by E. C. Campbell (5). After exposing a psychrometer to a saline environment for 72 hours, a plateau was hardly distinguishable, even with a recorder. The contaminating salts changed the vapor pressure relationships of the water on the wire,

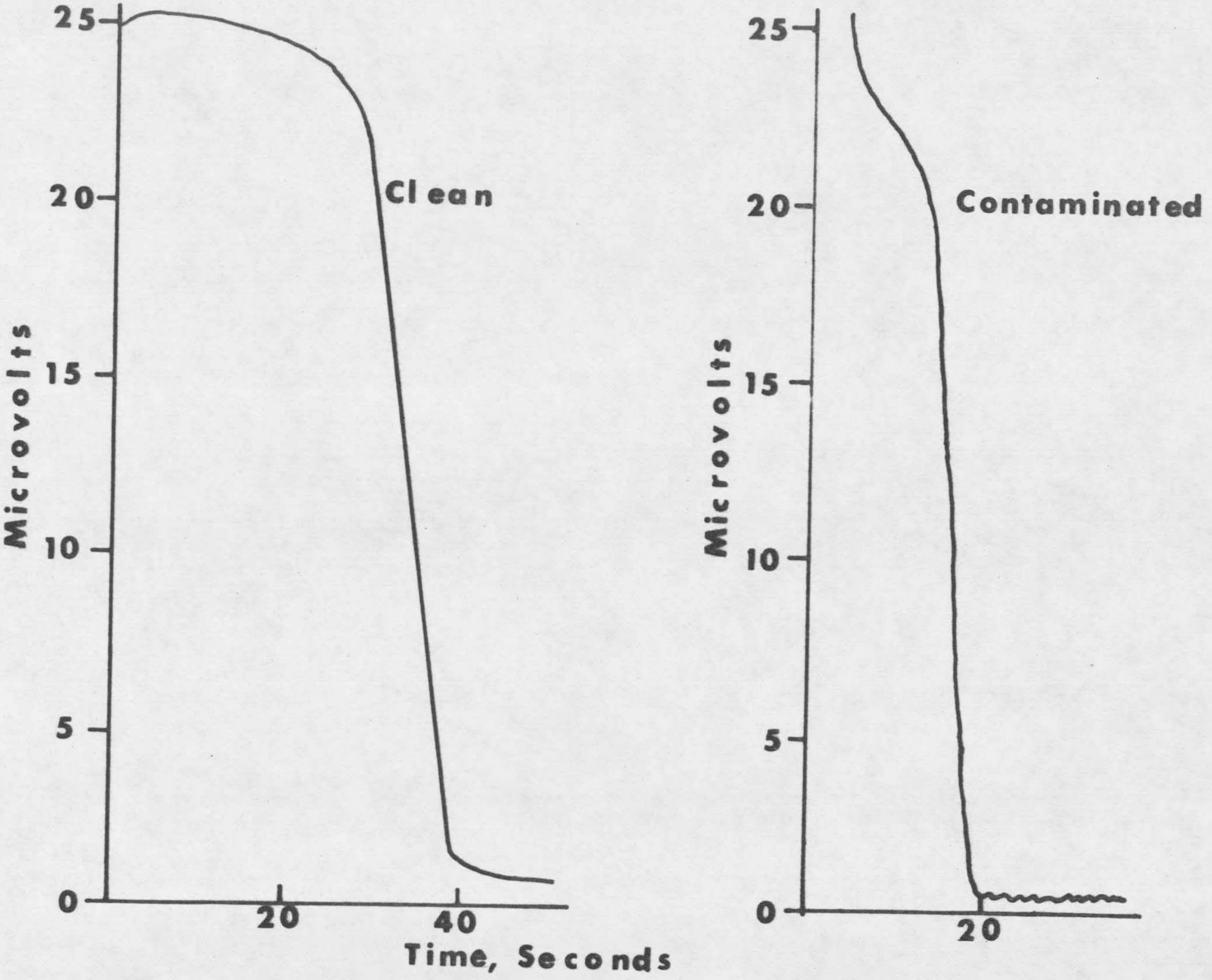


Fig. 4 Effect of Salt Contamination

just as salts changed the water vapor-pressure relationships in the system. As the water evaporated, the vapor pressure changed with the concentration of salts in the water on the wire, thereby changing the evaporation rate with time, and hence, the shape of the curve. However, tangents drawn to the flattest portion of the plateau intersect the zero time line at very nearly the same EMF as the tangent to the normal curve.

A typical curve produced at -2 bars water potential and -3° C is shown in Figure 5. The recorder was absolutely necessary under these conditions, as was the timing device for the cooling cycle, along with the adjustable cooling current and the milliammeter to monitor the current. Cooling rates and times affected the amplitude and shape of the EMF curves. A maximum rise with a flat plateau was sought. For the readings illustrated in Figure 5, the 25-second cooling period produced the desired curve. The 22.5-second curve was typical of undercooled psychrometers, and the 30-second curve was typical of overcooled psychrometers; thus, the shape of the curve was used as a guide to determine the correct cooling time for each psychrometer. The best cooling current for most psychrometers at freezing temperatures was between 8 and 10 milliamperes, with cooling times varying from 15 to 60 seconds, depending upon the characteristics of the individual psychrometer. Psychrometers with coated wires generally required longer cooling times than those with bare wires.

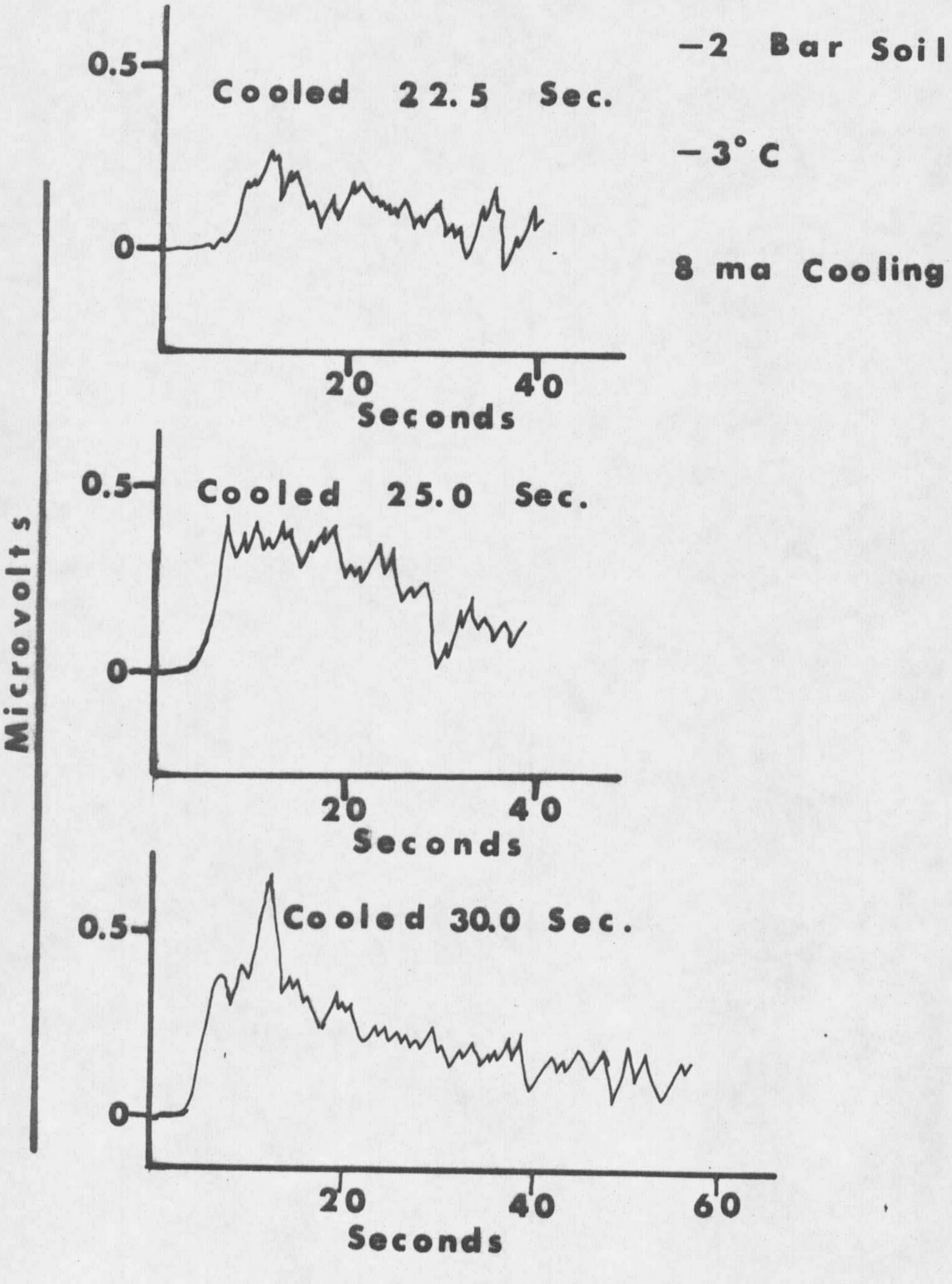


Fig. 5 Typical Psychrometer Curves

Interpretation: Rawlins and Dalton (24) successfully accounted for thermal effects on a thermocouple psychrometer and its associated circuitry, and eliminated these effects by bucking out the steady state-dry bulb EMF and reading ΔT as a thermocouple output. Therefore, only the temperature effects on relative humidity and ΔT remained to be accounted for. Because the psychrometer responds to vapor-pressure changes simply as ΔT changes, ΔT relationships must describe the parameters measured by the psychrometer. Correction factors for temperatures above freezing (+4° to +30° C) have been published for converting thermocouple psychrometer readings to the standard 25° C (20, 22, 34). However, in order to measure soil water potential near and below freezing, temperature correction factors from -20° to +40° C would be needed. We used a technique similar to the one used by Low et al. (18) to develop the needed factors:

A family of equations was derived from data from standard psychrometric reduction tables (15, 33) which described ΔT at several relative humidities above 90%. When these equations were multiplied by simple factors, specific for each relative humidity, they reduced to one equation. Therefore, one equation, which predicts ΔT at 92% relative humidity, was chosen because ΔT data were readily available for the entire temperature range of -20 to +40° C. This equation, which is the one used to develop temperature correction factors for thermocouple psychrometers, follows:

$$\Delta T = y = 0.444136 + 2.20561\ T \times 10^{-2} + 2.3695\ T^2 \times 10^{-4} - 8.74384\ T^3 \times 10^{-6} + 7.37825\ T^4 \times 10^{-8} \qquad [5]$$

where T = dry bulb temperature in °C,

$y = \Delta T = T_{dry} - T_{wet}$ = wet bulb-temperature depression in °C.

The temperature correction factors to convert wet bulb psychrometer readings to 25° C were then derived:

$$CF = y_{25}/y_t = 1.036/y_t \qquad [6]$$

where CF = the correction factor,

y_{25} = 1.036° C at 92% relative humidity, and

y_t = y at each dry bulb temperature of interest.

In addition, when ice bulb conditions are known to exist, ice bulb correction factors available from standard tables (15) must be used to correct the thermocouple psychrometer output to the standard 25° C reading. This correction accounts for the difference in latent heat of supercooled water and ice.

Temperature correction factors from −20° to +40° C are given in Table 1. Wet bulb correction factors are given along with ice bulb correction factors and correction factors derived from the formula given by Wiebe et al. (34):

$$CF = \frac{1}{0.027\ T + 0.325} \qquad [7]$$

for T = +4° to +30° C. No greater accuracy is claimed for the correction factors derived from equation [5] than for those published (20, 22, 34). The correction factors derived over the wider temperature range of −20°

Table 1. Factors to correct psychrometer readings to the standard 25° C.

Temp, °C	Correction Factors		Temp, °C	Correction Factors		Temp, °C	Correction Factors	
	Wet Bulb	Ice Bulb		Wet Bulb			Wet Bulb	
	(a)			(a)	(b)		(a)	(b)
-20	5.772	7.012	1	2.218	-----	26	0.979	0.974
-19	5.749	6.922	2	2.110	-----	27	0.959	0.949
-18	5.674	6.763	3	2.019	-----	28	0.944	0.925
-17	5.540	6.543	4	1.933	2.309	29	0.923	0.903
-16	5.368	6.270	5	1.853	2.174	30	0.906	0.881
-15	5.180	5.993	6	1.774	2.053	31	0.891	-----
-14	4.957	5.681	7	1.704	1.946	32	0.876	-----
-13	4.731	5.369	8	1.639	1.848	33	0.861	-----
-12	4.485	5.041	9	1.579	1.761	34	0.847	-----
-11	4.263	4.745	10	1.524	1.681	35	0.834	-----
-10	4.031	4.442	11	1.472	1.608	36	0.822	-----
- 9	3.823	4.174	12	1.421	1.541	37	0.809	-----
- 8	3.597	3.889	13	1.374	1.479	38	0.798	-----
- 7	3.397	3.638	14	1.330	1.422	39	0.787	-----
- 6	3.217	3.410	15	1.290	1.370	40	0.776	-----
- 5	3.038	3.190	16	1.253	1.321	41	0.766	-----
- 4	2.878	2.993	17	1.219	1.276			
- 3	2.726	2.808	18	1.185	1.233			
- 2	2.584	2.635	19	1.154	1.193			
- 1	2.443	2.467	20	1.124	1.156			
0	2.333	-----	21	1.097	1.121			
			22	1.071	1.088			
			23	1.046	1.057			
			24	1.023	1.028			
			25	1.000	1.000			

(a) Correction factors derived from equation [6].

(b) Correction factors derived from the formula published by Wiebe et al. (34), equation [7].

to + 40° C describe psychrometer behavior as a single, well-behaved function, with no discontinuities. A formula agreeing with equation [7] was derived from a portion of the data used to develop equation [5].

Table 2 illustrates the use of correction factors to determine temperature-corrected ψ values. For example, using the appropriate factors from Table 1, we converted negative water potential readings, collected from a randomly selected psychrometer, to the standard 25° C values shown in Table 2. None of the calculated values in Table 2 exactly equaled the -2.58 bar readings at 25° C or the -2 bar extraction value, but considering the standard deviations, they appear to belong to the same data group, with the possible exception of the -1° C and -3° C readings. Each temperature group reported in Table 2 represents at least 5 separate readings. Two -1° C groups are reported because they were taken at different times. The somewhat higher readings (lower water potential) were typical of readings taken in the -1° C to -3° C range as shown also in Figures 6 and 7. Thermocouple psychrometers generally did not sense water potential developed by freezing (ψ_i). In order to respond to the potential described in equation [4], the thermocouple junction had to be covered with a supercooled water film. Supercooling occasionally occurred, especially in the temperature range of 0° to -3° C, resulting in high transient readings that were very difficult to interpret. The temperature at which supercooling phenomena--wild readings--were first observed was thought to represent the temperature

Table 2. Temperature-corrected readings from a psychrometer in a soil sample extracted to -2 bars water potential. (microvolts) /.48 (correction factor) = $-\psi$

Temperature °C	Reading		Correction Factor	Water Potential	
	μv	± σ		Ψ	± σ
25	1.240	0.398	1.0000	-2.58	0.83
7.1	0.654	0.121	1.7039	-3.25	0.76
- 1	0.632	0.148	2.4670	-3.25	0.76
- 1	0.632	0.148	2.4433	-3.22	0.75
- 3	0.422	0.133	2.8080	-2.47	0.78
- 5	0.311	0.078	3.1900	-2.07	0.52
-10	0.224	0.056	4.4422	-2.07	0.52

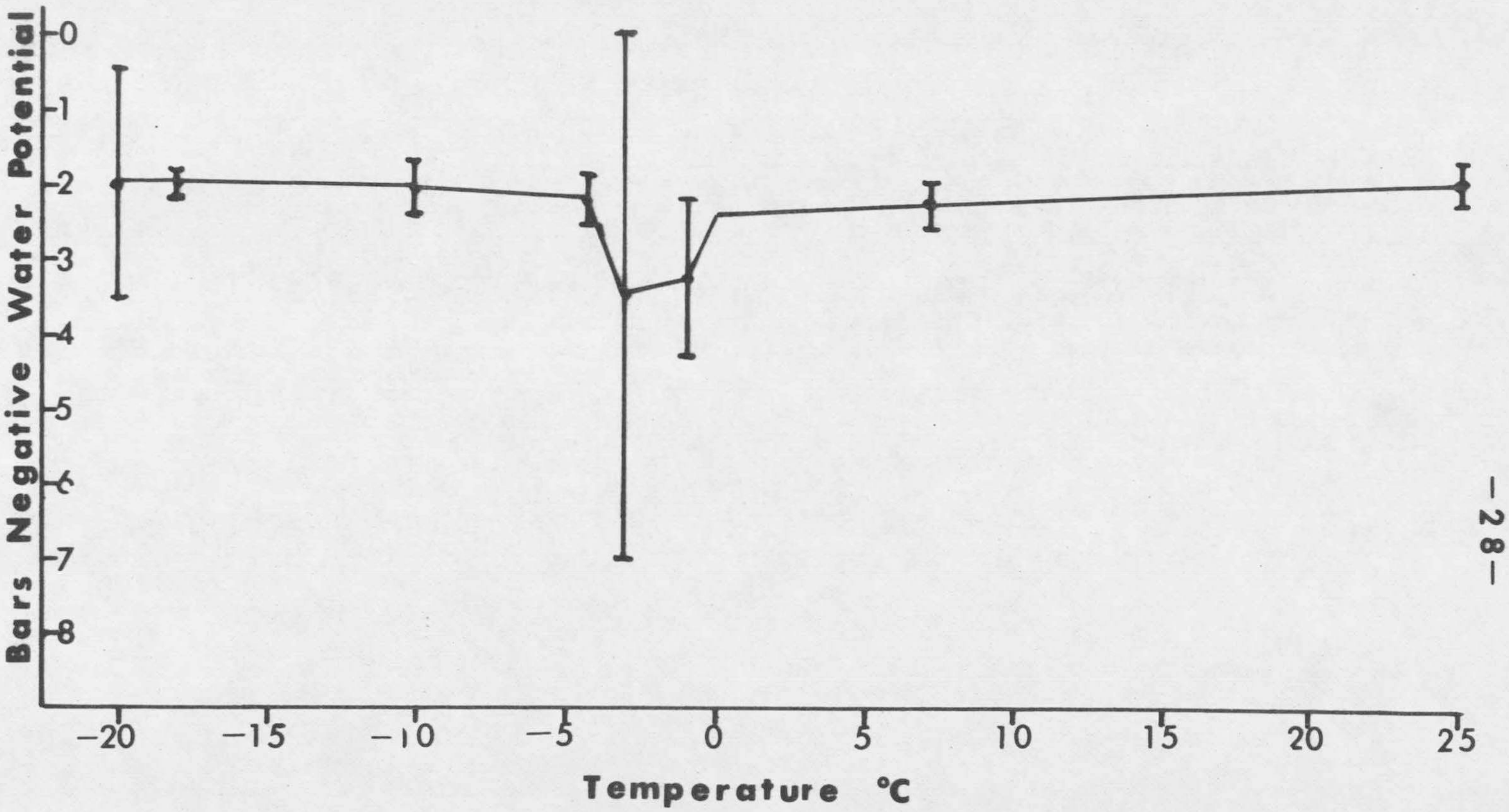


Fig. 6 Response of a Vaseline Coated Thermocouple

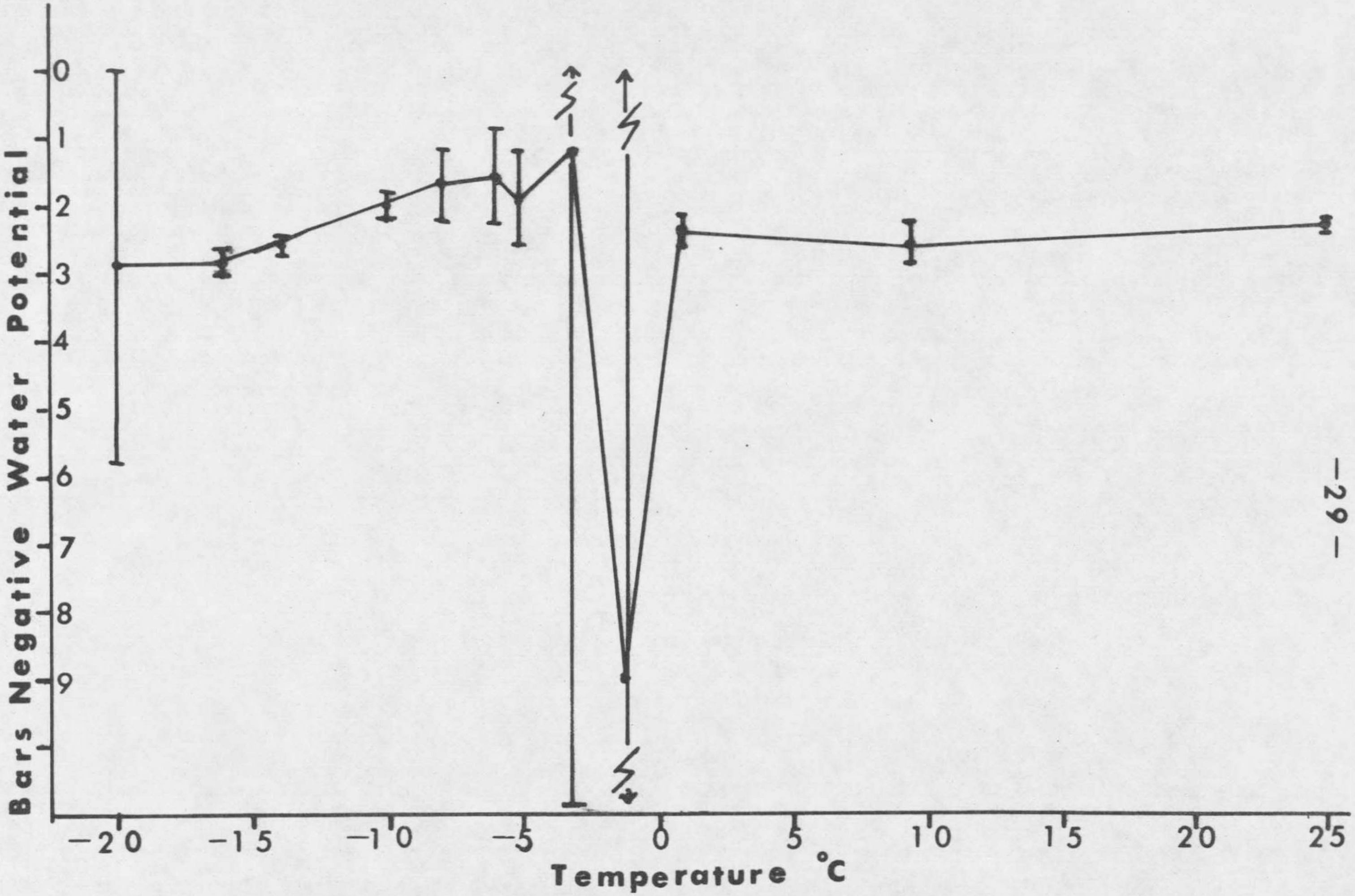


Fig. 7 Summary of All Psychrometer Data From -2 Bar Samples

at which soil water starts to freeze. Readings below -3° C rapidly became more repeatable. One of the psychrometers with Vaseline-coated thermocouple wires seemed to respond as a wet bulb psychrometer at temperatures from 0° to -3° C more often than other psychrometers. The readings from this psychrometer are summarized in Figure 6. The standard deviations of data from this psychrometer were less than those indicated in Figure 7 for all psychrometers. The erratic readings at the interval of -1° to -3° C are also illustrated in Figure 7, which is a summary of all usable data collected from all psychrometers in soil samples extracted to -2 bars water potential. This figure also includes the data from the psychrometer presented in Table 2 and the psychrometer data presented in Figure 6.

The apparent shift in water potential in the -5° to -10° C temperature range shown in Figure 7 is thought to be a result of water migration, because some preliminary data showed a changed potential in this range, such as that shown in Figure 7. At -10 bars water potential, a few scattered psychrometer readings, taken after the freezer thermoregulator setting had been changed but before thermal equilibrium had been established, indicated that some water migration took place within the small soil sample used. When the thermoregulator was set to a lower temperature, psychrometer readings taken before thermal equilibrium were higher (lower water potential) than readings recorded after equilibrium was reached. Conversely when the thermoregulator setting was raised, psychrometer readings taken before thermal equilibrium were lower (higher water potential) than those readings recorded after equilibrium was reached. These data were noted but not recorded because their significance was not realized at the time data was being collected. This water flux was limited and apparently reversed as thermal equilibrium was approached. If we could be certain that no water movement took place, we could develop temperature correction curves from these data. By repeating the experiment using a smaller soil sample and leaving more time for thermal and water equilibrium to take place for each temperature, data for developing emperical temperature correction factors could probably be developed.

Although we collected data from samples extracted to both -2 and -10 bars water potential, we only included data from samples extracted to -2 bars in Figure 7, because no new behavior patterns were exhibited at the -10 bar potential. In other words, the data shown in Figure 7 represents data collected at both potentials.

Thermocouple psychrometers generally appear to behave as ice bulb psychrometers at temperatures below -3° C, according to the following relationship:

$$\psi = RT/\overline{V}_i \ln (p_i/p_i^\circ) \qquad [8]$$

where p_i = the vapor pressure of ice in equilibrium with the soil system, $\overline{V}_i$ = partial molal volume of ice, and the other symbols are used as they have been defined before. Equation [4] predicts that the thermocouple psychrometer wet bulb must be covered with supercooled water in order to sense ψ_i, as this rarely happens, except in the 0° to -3° C range, thermocouple psychrometers behave as ice bulb psychrometers and do not respond to ψ_i.

Readings below -3° C, when multiplied by the appropriate correction factor from Table 1, were similar to the readings obtained at +25° C. Apparently the psychrometers responded only to potentials in the soil other than freezing potential.

Soil ice acts as an infinite water sink as long as heat flux is great enough to maintain a constant freezing temperature.

Soil heat flux is rarely fast enough to remove the latent heat released from freezing water as fast as water movement carries this heat. When such conditions exist, steady state temperature cannot be reached, and breaks in ice lenses occur, resulting in ice layers rather than solid ice (Jumikis 13).

Soil water tables can act as infinite water sources. In 1964, Willis et al. (36) studied water flow in terms of water table change and soil water loss, and described large thermally driven water fluxes.

We can think of the various soil water potentials as vector forces, because they have both magnitude and direction; therefore, we can arrive at some conclusions about the net potentials in freezing soils, and propose some reasons for the observed psychrometer behavior.

First of all, in the case of a closed soil column or a natural soil profile with no accessible free water source, and assuming a constant temperature freezing front, ψ_i develops as the soil freezes, and both liquid and vapor move from the higher to the lower potential levels; that is, toward the freezing front, until $\psi_i = \psi_t$ (2, 10, 13, 36). Flow then stops (considering only the soil column), and there is no net potential, because we have equal potentials in opposite directions and, by vector addition, zero potential. If we lower the temperature of the freezing front, water will again move to the freezing front in response to the lower water potential, until the opposing forces are again equal (natural frozen soil systems seldom, if ever, arrive at equilibrium).

If we then add an infinite water source, and suppose that the ice is free from space limitations so that it can act as an infinite sink (frozen soil will heave, if necessary), water will flow through the soil to the ice front. Supposedly, water flow will arrive at a steady state, driven by the potentials described by vector addition. ψ_m will then define the water film thickness.

These two simplified, but extreme, cases describe the role of the potentials in freezing soil systems. ψ_i is the potential developed by virtue of the presence of ice at temperature T. This potential is a function of T alone, because ice lenses in soil are pure, normal ice, and are essentially free from external pressures. ψ_t tends to restrain water from moving to the ice. Water flux will stop when, by vector addition, ψ_t plus ψ_i equal zero. Thermocouple psychrometers, as used in this experiment, responded only to ψ_t of the unfrozen soil sample, because water migration was nil under the experimental conditions.

SUMMARY

It was possible to read commercial thermocouple psychrometers at -2 and -10 bars water potential and at temperatures as low as -20° C. Within the temperature range of 0° to -3° C, erratic behavior made reading very difficult. Psychrometers with fine-mesh stainless steel covers were easier to clean and required less equilibration time than psychrometers with ceramic covers. Ceramic covers intensified cleaning problems and caused substantial timelag in reaching the equilibrium necessary for psychrometer response. At times, applying a very thin coat of Vaseline on the thermocouple junction appeared to make supercooling possible. However, in the absence of supercooling, the thermocouple psychrometers appeared to behave as ice bulb psychrometers at temperatures below -3° C, and measured only potentials not due to freezing. Coating thermocouple wires with Teflon improved the stability of the psychrometers, but coating the wires with either Teflon or Vaseline increased the required cooling rate and time.

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