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The Peltier Effect and its Use for Measuring Relative Activity of Soil Water

Hans C. Korven

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THE PELTIER EFFECT AND ITS USE FOR MEASURING
RELATIVE ACTIVITY OF SOIL WATER

by

Hans C. Korven

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

MASTER OF SCIENCE

in

Irrigation Science

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1958
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Hans Korven
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INTRODUCTION AND REVIEW OF LITERATURE

Soil moisture measurement embraces two basic concepts, namely, water content and relative activity. The measurement of moisture content, either on a weight or volume basis, yields the amount or quantity of water in the soil. The measurement of relative activity or the energy required to remove unit of water is related to the availability of the soil moisture to the plant. The measurement of soil bulk density, irrigation efficiency, and the amount of water to apply in an irrigation are a few examples that require the use of the moisture content concept. Whereas the first concept determines the amount of water to apply; the second concept, since it is related to the tenacity with which water is held in the soil or the availability of soil water to the plant, determines the correct time to irrigate. Other examples of phenomena that relate closely to the relative activity concept are found in the study of seepage loss from canals and in the design of drainage systems to lower the water table (water movement).

The two concepts are distinctly different, and as will be shown later a method which measures one accurately may have appreciable error if used to measure the other. It is difficult, however, to maintain a clear distinction between them because, for example, the irrigation of a field includes both concepts. In addition, when a method is introduced that is faster and simpler than previous methods there is a natural tendency to explore all possibilities of adapting it to the concept it was not designed for. The following discussion of methods...
for measuring soil moisture has, therefore, been divided into the two concepts.

The moisture content concept

The moisture content measurement is the older and more common concept of the two and can be symbolized by the equally old and well-established gravimetric method. The auger and oven method, however, is slow, laborious, and does not lend itself to the measurement of soil moisture in situ. The search for a quicker, simpler, and more adequate method began before the turn of the century when Whitney et al. (42) attempted to determine the quantity of water in the soil by measuring the electrical resistance between 2 electrodes inserted in the soil. A recent development, the neutron method (Belcher et al., 5, and Holmes, 17) has overcome the most serious disadvantages of the gravimetric method and according to Stewart and Taylor (33) can be made to measure the moisture in a field with equal accuracy since more observations are possible within the same time interval.

The relative activity concept

The relative activity of water in soils includes three components: capillary, adsorptive, and osmotic potentials. Relative activity is the same as the vapor pressure ratio. In addition, relative activity times 100 is equal to relative humidity. These terms will, therefore, be used interchangeably.

The development of a method for measuring relative activity has received the attention of soil scientists for the past 50 years. As a result, several methods have been developed, but at the present time there is no completely satisfactory method. The main difficulty has been to develop a method which will measure all three components. The second difficulty is one of measuring the whole range.
Davidson and Schofield (11) present a review of methods for measuring the relative activity of soil water by the vapor pressure method using porous absorbers. The list includes Xanthium seeds, tapered tubes of porous porcelain (soil points), lead pencils, filter papers, and Portland stones. These absorbers have enjoyed only limited success because they must be calibrated and it has proved difficult to obtain a calibrated absorber that remains constant.

The common methods for determining relative activity of soil water measure only the capillary and adsorptive components commonly known as soil moisture suction. The tensiometer (Richards, 21, 22), pressure membrane (Richards and Fireman, 24), and centrifuge (Russell and Richards, 26) measure soil moisture suction directly. However, of these methods only the tensiometer can be used in the field. Porous electrical resistance units commonly known as blocks (Bouyoucos and Mick, 8, Colman and Hendrix, 9, and Bouyoucos, 7) also measure soil moisture suction but not directly. Blocks measure the resistance between the electrodes which is a function of the quantity of water in the block. The quantity of water in the block, however, is a function of the adsorptive and capillary potentials of the soil water. It is necessary, therefore, to calibrate the blocks to read suction. In addition, the salt content of the soil interferes with the block readings more seriously than is the case with the other methods. Blocks, nevertheless, have proved valuable because they can be used in the

1. Probably tension is more common. Suction, however, will be used as suggested at the Western Soil Science Society of America meeting held in Palo Alto, California, on August 27, 1957. It was generally agreed that the adoption of suction in place of tension would overcome the disadvantage of tension implying that the soil water is under a tensile stress. In addition, suction generally describes the phenomenon and is well understood by workers in other fields as well.
field and they measure the whole moisture range whereas the tensiometers are limited to suctions of between 0 and 0.85 atmospheres.²

In addition, the blocks do not require the degree of service demanded by the tensiometers. A common procedure (Taylor, 35) in field irrigation research is to use both the tensiometers and blocks because the former is superior in the wet range whereas the blocks are better in the dry range.

Methods based on the dielectric constant and thermal conductivity of water have also been studied. Selected references on the method based on the dielectric constant are Fletcher (15), Anderson (3), and recently de Plater (12). The heat conductivity method introduced by Shaw and Baver (28) (29) has recently received the attention of Bloodworth and Page (6). These methods do not seem to be too promising. Thorne and Russell (40) conclude "In general, the determination of soil moisture by dielectric means appears to have many inherent difficulties." Edlefsen and Smith (14) explain that the polarization phenomenon of water confounds the capacitance method because it changes the dielectric constant of water which is assumed to be 80. For this reason the capacitance method depends upon both the moisture content and relative activity concepts at the same time. This means the measurements are of doubtful value. The thermal conductivity method also, according to Taylor (36) appears to depend upon both characteristics.

² At the same meeting referred to in 1 the suggestion of L. A. Richards to substitute bar for atmosphere was also discussed. The main advantage of adopting bar is that it is a unit of the metric system, being $10^6$ dynes per cm². It was generally agreed, however, that atmosphere should not be discontinued because the term is generally understood and used, particularly in other fields. For this reason and also because the pressures on the membrane and plate were calculated on an atmosphere basis this term will be used in this thesis.
The freezing point depression and vapor pressure methods measure the total relative activity. These methods, however, have not been used extensively because of inherent weaknesses and their limitation as laboratory procedures.

Davidson and Schofield (11) cite several disadvantages of the freezing point depression method, but the main problem is that freezing the soil dries it. An accurate determination, therefore, demands a calculation of the amount of ice formed. Furthermore, since the potential decreases with increase in temperature (Stewart, 32) the potential determined at the freezing point has to be corrected to the soil temperature.

The vapor pressure method received a great deal of attention in the first 35 years of the Twentieth Century with the most active interest occurring in the 1920's. The dessicator method introduced by Patten and Gallagher (19) in 1908 followed by the dynamic method by Thomas (38) (39) and the airstream or saturation method by Puri et al. (20), Edlefsen (13), and Alexander and Haring (2) were all based on the same general principle. The soil was subjected to a vapor pressure ratio of a known value. At equilibrium the moisture content of the soil was determined and related to relative activity. This relationship is not a single-valued function which results in hysteresis. In other words, the soil does not at all times contain the same moisture at a given suction, the amount varying according to whether the soil is drying or wetting. Schofield (27) states:

There is no doubt, however, that over the central portion of the moisture range (that of most importance in the field) the suction this soil can exert in taking up moisture is only onequarter that required to withdraw water from it at the same moisture content.
This same hysteresis effect causes difficulty when, for instance, block readings are calibrated to read soil moisture content. Croney et al. (10), Aitcheson et al. (1), and Taylor (36) strongly recommend using the soil suction-block resistance relationship rather than the moisture content-block resistance relationship because the former is constant for all soils.

In addition to the problem of hysteresis these methods are slow and insensitive in the range between permanent wilting percentage and saturation. Robins (25) concluded that 75 to 95 days were required to reach equilibrium.

Of the various methods used by the early workers for measuring the vapor pressure ratio, the incidental method discussed by Edlefsen (13) is interesting. This method was similar in principle to the more recent hygrometer and thermocouple techniques. Edlefsen measured the vapor pressure ratio by reading the resistance between 2 electrodes embedded in glass wool which was sealed in the chamber. The resistance varied with the amount of water condensed on the glass wool which was directly related to the vapor pressure ratio. The resistance readings were checked against the mercury manometer and checked quite well except in the range between permanent wilting percentage and field capacity.

Steiger (31) developed an electric hygrometer using lithium chloride and polyvinyl alcohol. The resistance was measured on an a-c Wheatstone bridge and the element showed improved sensitivity in the range of 80 to 100 per cent relative humidity. Steiger pointed out that a very important use of devices to measure high relative humidity was in the measurement of "free energy" of soil moisture.
He concluded, however, that the present hygrometer was not sufficiently sensitive for this purpose. He speculated that using a lower concentration of lithium chloride or possibly using other salts would achieve the desired results.

Richards has been investigating the possibilities of using a small thermocouple to measure relative activity of soil water. The junction wires are "Chromel P and Constantan 1.3 x 10^{-3} inches in diameter with 60 microvolts per degree Centigrade thermo electric power."

The operating principle of this technique is to measure the difference in temperature between the wet and dry junction which is directly related to relative activity. One junction is wetted by dipping it in water. When the thermocouple is placed over the relative activity to be measured the water from the wet junction evaporates until the dew point temperature of the atmosphere is reached. The difference in temperature between the dew point (wet junction) and the actual temperature (dry junction) produces an e. m. f. which is measured on a sensitive galvanometer.

Richards reports the following progress:

Using wet and dry thermojunctions we have succeeded very satisfactorily in measuring the aqueous vapor pressure of osmotic solutions contained in filter paper but for reasons about which we can now only speculate the soil measurement is much more difficult.

PURPOSE OF STUDY

The purpose of this study is to adapt to soils a technique described by Spanner (30) for measuring the "suction pressure" of plant materials. Recently it has come to the attention of the writer that a similar study is being investigated in England. A short note in the 1955 Annual Report of the Rothamsted Experimental Station states the technique is being "exploited" and that "Encouraging progress has been made."

This technique differs from that used by Richards in two respects. The junction wires of the thermocouple described in this study are bismuth and an alloy of 95 per cent bismuth and 5 per cent tin giving a thermo-electric power of 126 microvolts per degree Centigrade whereas Richards is using chromel P and constantan giving 63 microvolts per degree. The wet junction, instead of being dipped in water as Richards did, is cooled below the dew point by the Peltier effect which is described as follows by Spanner (30, p. 146):

When two metals are placed in contact they assume, in general, a difference of electrical potential, the so-called Peltier coefficient. Peltier discovered in 1834 that on passing a current across such a junction there is a liberation or absorption of heat at the point of union--the temperature rising or falling according as the current flowed down or up the potential gradient.

If \( P \) is the Peltier coefficient (in volts) and \( I \) the current (in amperes), the rate of liberation or absorption of energy at the junction is \( PI \) watts. When the current flows there are naturally two factors to consider: firstly, the irreversible heating of the conductors by the ordinary Joule effect (this being proportional to the square of the current), and secondly, the reversible heating or cooling by the Peltier effect (proportional, as mentioned above, to the first power).
From this it follows that the degree of cooling which can be obtained by using the Peltier effect is limited—it will increase with the current only up to the point at which the Joule heating begins to predominate.

Suppose now that the junction of a fine thermocouple is placed in an atmosphere of very humid air, and a current passed in the sense required to cool it. Then, if the degree of cooling is sufficient to bring the junction below the dew-point, moisture will condense on it and the thermocouple will become potentially a delicate 'wet-bulb' thermometer. The dew will re-evaporate on breaking the circuit and a minute e. m. f. will be generated more or less proportional to the 'wet-bulb' depression associated with the atmosphere surrounding the junction. If a sensitive galvanometer be connected to the thermocouple, it would seem possible to calibrate this apparatus by enclosing the junction in a chamber containing solutions of known osmotic strengths, and once calibrated, it could be used for measuring the suction potential of living tissues.

Spanner obtained a relationship between relative activity and maximum galvanometer deflection; the galvanometer deflection increased as the relative activity decreased.

This study was selected for several reasons.

1. A satisfactory method for measuring the relative activity of soil water has not been developed.

2. This technique showed considerable promise because
   a. It measures the osmotic potential as well as the adsorptive and capillary potentials. In other words, it measures the total relative activity.
   b. It measures the dew point temperature depression at any given temperature which is a single-valued function of vapor pressure.
   c. It is faster than methods presently available. Spanner obtained equilibrium conditions within 15 minutes.
d. It is sensitive. Spanner showed remarkable sensitivity in the range from 0.98 to 1.00 relative activity.

3. Two methods are available for measuring soil moisture content (the other concept); the gravimetric and neutron methods.
THE THERMOCOUPLE

Description

The thermocouple assembly and enlarged view of the junction are shown in Figure 1. The assembly is designed to fit into a 29 x 200 mm. test tube because the constant temperature bath which was available for use was fitted with this size test tube. The lead wires are sealed in a disc of one-quarter inch lucite which fits inside the test tube. The stem is a plastic tube one-quarter inch in diameter which is fastened to the disc by polystyrene cement. The lead wires are painted different colors for identification and threaded through the tube. Two rubber stoppers are threaded on the stem. The stopper near the disc serves to seal the thermocouple in a small volume and the other stopper, which fits into the top of the test tube, serves as a support and second seal.

The enlarged view of the base shows the junction in more detail. The lead wires are 30-gauge enamelled copper. The portion of the lead wires to which the junction wires are attached is about 3 mm. long and the 2 wires are about 2 mm. apart and parallel. The junction wires are of dissimilar metals. One wire is bismuth 0.001 inches in diameter (25 microns) while the other is an alloy of 95 per cent bismuth and 5 per cent tin 0.0014 inches in diameter (35 microns). These wires were purchased from Baker and Co., Inc., 113 Astor Street, Newark 5, New Jersey.

The above size and type of wires were selected because Spanner (30) obtained best results with this combination. The following quotation from Spanner (30, p. 156) describes the basis for selection.
Figure 1. Sketch of thermocouple assembly and enlarged view of junction.
In designing the thermocouple assembly several points had to be kept in mind. With regard to the thermocouple itself it was obviously desirable to make it as small as convenient, since not only does any air movement then have much less effect on the 'wet-bulb' reading (R. W. Powell, 1936), but speed of response is increased and the disturbing effect of the junction on the surrounding moist atmosphere is reduced. Again, the wires should be short and connected to relatively massive copper leads, since this not only increases the available degree of cooling of the free junction (by conducting away the heat which inevitably accompanies it elsewhere in the circuit—see Appendix 1), but it also reduces the electrical resistance and so the waste heat liberated on the passage of the current. Further, it virtually limits change of temperature to the free junction. The most satisfactory materials for the wires appeared to be bismuth and an alloy of bismuth with 5 per cent tin. This combination has a high thermo-electric power; the wires can easily be drawn out fine by the Taylor process (see Strong, 1938); they can be readily soldered with Wood's metal or welded by a condenser discharge, and they are stable in moist air.

The "high thermo-electric power" referred to by Spanner is 126 microvolts per degree Centigrade as compared to 63 for a junction made of chromel P and constantan as listed by Baker and Co. (4). The latter combination is being presently investigated by Richards.

According to Spanner the maximum cooling with a thermocouple consisting of bismuth and an alloy of 95 per cent bismuth and 5 per cent tin is 4.9° C. at an optimum current of 1.5 ma.

The thermocouples constructed had total resistances (including 2-foot leads) which varied from 2 to 5 ohms. The usual resistance, however, was between 4 and 5 ohms. The results, which will be discussed later, were obtained with thermocouples of 4.0 and 4.3 ohms resistance. These resistances are lower than the 6 to 7 ohms resistance cited by Spanner. Using the figures 2150 ohms per mil per foot for 95 per cent bismuth and 5 per cent tin and 700 ohms per mil per

4. Richards, L. A. Personal communication.
foot for the bismuth from Baker and Co. (4), the resistance for a
junction using 3 mm. lengths of wire should be about 3 ohms. It
appears, therefore, that the thermocouples were as well or better
constructed than those constructed by Spanner.

The enlarged view in Figure 1 shows that the base holds 2
junctions. In the early stages a pair of junctions were made each
time but actually only 1 junction was used at a time. It was planned
to connect the 2 junctions in series as suggested by Spanner but it
was not possible to construct 2 junctions with sufficiently similar
characteristics to combine them. In several instances only 1 junction
of the 2 functioned. In the latter stages the supply of wire dwindled
to the point where only 1 junction was made at a time in order to
preserve the supply.

Construction tools

The handling and soldering of such fine wires requires a special
technique. It is realized that a description, regardless how detailed,
cannot take the place of repeated practice. Nevertheless, a detailed
description is given in the hope that it may prove helpful. The general
principle of construction is given by Strong (34, pp. 313-315) and a
study of this procedure is strongly recommended because the following
discussion is simply an adjunct to it.

The tools used in constructing the thermocouple are shown in
Figure 2. The tinned darning needle in a suitable handle and the
heated looped wire are used together and forms the soldering iron.
In one phase of the construction the heated wire is used alone as a
soldering iron. The looped wire is 20-gauge (0.32 inches) nichrome wire
with a resistance of 0.61 ohms per foot, the 2 ends of which are silver
Figure 2. Construction tools
soldered to individual lengths of any suitable large diameter wire (9-gauge). These wires are separated by a piece of wood and then taped. This forms a suitable handle which is not hot to the touch.
The large wires are then soldered to a lamp cord which is plugged into a variac connected to a 120-volt line. By means of the variac the heat of the looped wire is regulated. The second needle (a sewing needle) is not heated and is used to manipulate the wires and solder.
In a special instance this needle is used to apply the flux which is a saturated solution of zinc chloride and distilled water. The soldering needle, when cold, is also used for manipulating the solder and wires because it is quite often more convenient to use it than picking up the other. A pointed wooden match or toothpick worked better than the needle for applying the flux to the copper wires. In the case of the needle the flux formed into a drop about one-eighth inch from its end leaving the point dry. This characteristic, however, proves beneficial when applying flux to the junction of the 2 small wires. Wood's metal is used for soldering the joints because it melts at a lower temperature than common solder. In order to get pieces of solder small enough to be in keeping with the size of wires it is necessary to form the supply into very thin layers. This is accomplished by holding a stick of Wood's metal 2 or 3 feet above a smooth flat surface and heating it so the drop splatters when it hits. Small pieces about one-half mm. square are then cut with the razor blade. Most of the work is done under a 10-power magnifying glass. The plastic squeeze bottle is used to wash the excess flux from the thermocouple when it is completed.

Construction technique

Holes in the lucite base are made with the heated needle which
is not withdrawn until it has cooled. After the wires have been threaded through they are sealed in place by heating the lucite.

The copper wires are then bared and tinned in a manner similar to the usual tinning procedure. The difference in technique is simply one of size. The piece of solder is placed on the wire and the tinning done with the point of the heated needle.

Making the thermocouple requires above all a steady hand. A technique which helps to steady the point of the needle is to insert the needle in the wire loop so both hands are used. It is, of course, very helpful to work in a comfortable position with both forearms well supported on a large surface. An office desk is ideal.

After the copper wires have been tinned they are again fluxed in readiness for the junction wires. A length of the fine wire, about 3 mm. proved a good working length, is cut from the supply by touching it with the heated needle. Since the cut length usually adheres to the needle it is transferred directly to the copper wire. Unfortunately, however, the wire sometimes drops off and it is usually difficult to get it to re-adhere. It is helpful in such cases to moisten the needle ever so slightly. There is a very fine point here of having the needle moist enough to pick up the wire and still dry enough to let go when the wire is located. In this connection an excess of flux on the base will cause the same difficulty. A wet wire either clings to the needle or the copper wire with the end result that it is usually necessary to start over again with a dry wire. When the wire is located a piece of solder is laid on the junction of the two. In this phase of the soldering the solder is melted by heating the copper wire rather than touching the solder directly. Even though this technique seemed the
only satisfactory one it presented a certain difficulty. Sometimes
the wire, which has been so carefully placed, moves and the solder
curls away. Usually, however, the wire is slightly attached so more
flux can be applied. Another piece of solder is then placed on the
area vacated by the solder and heat applied at the other end of the
copper wire. This sometimes rectifies the situation. A point of
cautions is to avoid using too hot a needle particularly when soldering
the smaller wire. The most satisfactory arrangement is to heat the
looped wire to a faint red glow and make contact with the needle about
one-half inch from its point.

The technique used for soldering the 2 wires together to form
the free junction is described by Strong (14, p. 314). Only two
additional hints are required. The most satisfactory way of applying
the flux is to use the cold needle. The flux forms into a drop about
one-eighth of an inch from its point and the flux can be applied without
disturbing the wires by touching the junction with the drop. The
heated wire loop is again adjusted to a faint red glow and held about
one-eighth of an inch from the joint. It is very difficult to tell
when a joint has been attained (only rarely was the jerk described by
Strong noticed) so a satisfactory junction was determined by connecting
a voltmeter across the thermocouple.

On completion of the thermocouple it is essential to remove all
the excess flux. Zinc chloride is soluble in water but simply soaking
the thermocouple in distilled water did not remove the flux. The most
satisfactory arrangement seemed to be to use a spray of distilled water
from the plastic squeeze bottle. As will be shown during the dis-
cussion of results, however, this technique was not always satisfactory.
The time required to make a thermocouple varies with experience and luck. The shortest time for making 1 junction (soldering the 2 small wires to the copper lead wires and joining their free ends) was about 1 hour.
APPARATUS

A general view of the apparatus is shown in Figure 3. The main components of the equipment are the controlled temperature bath, the temperature control circuit, and the measuring circuit.

**Controlled temperature bath**

A bath designed for freezing point determinations was available and used with no change in design. This bath is very similar to the bath described in detail by Richards and Campbell (23). The only major difference is in the stirrer. In the bath used the stirrer is driven from below rather than from above as described by Richards and Campbell. The refrigerator unit runs continuously while the heater is turned off and on. The rates of heating and cooling can be adjusted to obtain the desired degree of balance. The heating rate is adjusted by regulating the setting on the variac while the cooling rate is adjusted by regulating the expansion valve.

**Bath temperature control circuit**

**Description.** The circuit for controlling the temperature of the bath is shown in Figure 4. The basic components are as follows:

A Western Electric Type 14B thermistor

A Leeds & Northrup Type P mirror galvanometer with characteristics as follows:

Sensitivity = 0.008 microamperes per mm.

Period = 8.2 seconds

Critical damping resistance = 10,000 ohms

Coil resistance = 125 ohms
Figure 3. General view of the apparatus
Figure 4. Bath temperature control circuit
A photoelectric cell

An American Instrument Company electronic power relay consisting of a thyratron tube, power transformer, and power relay

A Leeds & Northrup 4-decade enclosed switch Wheatstone bridge.

The circuit can be grouped into two parts which are connected by a beam of light. One part of the circuit consists of the thermistor, galvanometer, and a 2-volt d-c power source connected to the Wheatstone bridge. The other part of the circuit consists of the photoelectric cell, electronic power relay, and bath heater. The beam of light from the 5-volt lamp is focused on the mirror of the galvanometer and the reflected light connects the 2 circuits when it shines on the photoelectric cell located 1 meter away.

Operation. The thermistor, immersed directly in the bath fluid (kerosene), serves as the temperature detecting element. The thermistor resistance, which changes with a change in temperature, causes the galvanometer mirror to deflect. The beam of light, reflected from the mirror, shines on the photoelectric cell. This opens the circuit and shuts off the heater. Since the refrigerator unit runs continuously, the reflected light moves away from the photoelectric cell which again closes the circuit. This reverses the direction of travel of the light so it again strikes the cell and re-opens the circuit. This cycle is repeated and the distance the light travels depends on the adjustment of the heating and cooling rates.

Performance. The temperature control circuit worked very well, particularly after transferring from the laboratory to the constant temperature room adjusted to ± .5° C. The transfer of location aided in two ways. First, it eliminated the necessity of readjusting the cooling and heating rates as the temperature in the laboratory changed.
Second, the constant intensity of illumination in the room (artificial lighting only) provided a constant intensity of light on the photoelectric cell. This meant that the photoelectric cell triggered the relay at the same point in the travel of the reflected light. An example of the sensitivity of the photoelectric cell was when the temperature of the bath increased about 0.005° C. when 1 bulb out of the 4 in the room burned out.

While it is important to maintain a constant external light it is equally important to maintain a constant intensity of the reflected beam. In the early stages difficulty was experienced in this regard because the intensity of light required to trigger the cell was so high that it was necessary to increase the voltage to the maximum and sometimes above the bulb rating. This undesirable situation was rectified by placing a 1.2-volt d-c source in series with the cell and relay which decreased the intensity of light required.

Another difficulty experienced in the early stages was the change in resistance of the thermistor with time at a constant temperature. This drift in resistance over a period of 1 month is shown in Table 1 while Figure 5 shows the calibration curve.

The temperature-thermistor resistance relationship shown in Table 1 and Figure 5 was obtained by checking the change in thermistor resistance with temperature against a Beckmann Differential thermometer graduated in 0.01° C. with a range of 5° C. The 0° C. point was obtained in a stirred mixture of distilled water and distilled water ice cubes contained in a Dewar flask. The mercury level in the thermometer was regulated until the reading was near the lower limit of its range. The thermometer was then transferred to the controlled
Figure 5. Calibration curve for Western Electric Type 14B thermistor used in bath.
temperature bath and when the 0°C. reading was obtained the thermistor resistance was recorded. Temperature-thermistor resistance points were taken at approximately 1.5°C. intervals. The mercury level in the Beckmann thermometer, therefore, had to be changed about every third reading. This change was made while holding the temperature of the bath constant. This procedure was quite satisfactory; on return to the zero point the thermometer reading in the ice bath was only 0.02°C. high.

In addition to this general drift there was a period of fluctuation before the thermistor settled down. During this unsettled period the resistance fluctuated between 2321 and 2332 ohms. The thermistor held steady for the duration of the study, a period of about 2 months.

Table 1. Thermistor 14B resistances over a temperature range of 0°C. to 25°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thermistor resistance (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>July 6</td>
</tr>
<tr>
<td>0.0*</td>
<td>6835</td>
</tr>
<tr>
<td>1.2</td>
<td>6468</td>
</tr>
<tr>
<td>2.8</td>
<td>6017</td>
</tr>
<tr>
<td>4.9</td>
<td>5465</td>
</tr>
<tr>
<td>6.9</td>
<td>4998</td>
</tr>
<tr>
<td>8.9</td>
<td>4572</td>
</tr>
<tr>
<td>10.8</td>
<td>4210</td>
</tr>
<tr>
<td>12.3</td>
<td>3944</td>
</tr>
<tr>
<td>13.7</td>
<td>3712</td>
</tr>
<tr>
<td>15.4</td>
<td>3453</td>
</tr>
<tr>
<td>17.0</td>
<td>3226</td>
</tr>
<tr>
<td>18.2</td>
<td>3068</td>
</tr>
<tr>
<td>19.6</td>
<td>2895</td>
</tr>
<tr>
<td>21.3</td>
<td>2697</td>
</tr>
<tr>
<td>22.5</td>
<td>2567</td>
</tr>
<tr>
<td>23.7</td>
<td>2445</td>
</tr>
<tr>
<td>25.0</td>
<td>2321</td>
</tr>
</tbody>
</table>

*0°C. point - distilled water and distilled water ice cubes.

The variation in bath temperature when located in the constant temperature room together with stabilized thermistor and more constant intensity of light beam was approximately 0.003°C. This variation was
observed by reading the Beckmann Differential Thermometer graduated in 0.01° C. with a 10-power magnifying glass. The variation was also checked by measuring the distance travelled by the light reflected from the galvanometer. For a change in temperature of 0.1° C., the light travelled 18 cm. When the bath was in operation the travel distance varied from 0.5 to 0.75 cm, which is a temperature variation in the range of 0.002° C. to 0.004° C.

The temperature variation of the atmosphere in the test tube was not measured but would in all probability be less. In the final analysis, however, the action of the galvanometer connected to the thermocouple indicated a sufficiently fine degree of control. No noticeable motion on the galvanometer was detected as the heating element turned on and off. Incidentally, there were no fluctuations when in the laboratory either. However, it was more difficult to keep the bath operating for the reasons discussed above. In other words, having the bath in a constant temperature room may not be a necessity.

**Measuring circuit**

**Description.** The circuit for measuring the relative activity is shown in Figure 6. This is a simple circuit consisting of a regulated power source, reversing switch, galvanometer, and thermocouple assembly which was immersed in the bath.

The only part of this circuit requiring description is the galvanometer since the thermocouple has been described previously. The galvanometer in this circuit is a Leeds & Northrup with enclosed lamp and scale. The characteristics are as follows:

- **Sensitivity** - 0.5 microvolts per mm.
- **Period** - 3.2 seconds
Figure 6. Measuring circuit
Critical damping resistance - 65 ohms

Coil resistance - 16 ohms

The characteristics of this galvanometer are similar to the one used by Spanner. The main difference is in the sensitivity; the one used in this study being one-fifth as sensitive as the one used by Spanner. However, in this case, where the resistance of the thermocouple is small, the most critical characteristic is the coil resistance. For example, a galvanometer with increased sensitivity but with a coil resistance of 466 ohms did not reach maximum deflection as quickly as the one finally selected. The scale on the galvanometer used was only 5 cm. long which was considered too short a range in which to detect 7 or 8 points. The lid was, therefore, removed and a longer scale attached. With the longer scale it was possible to operate the galvanometer with no shunt across it for the second thermocouple, which is desirable because its action is then faster.

This circuit is also in two parts. One part consists of the thermocouple assembly, variable resistance, milliammeter, and a 1.2-volt d-c line source. The other part consists of the thermocouple and the galvanometer. The reversing switch connects and disconnects the thermocouple from the 2 circuits.

Operation. The thermocouple is first connected to the power source and a predetermined current passed through the galvanometer for a specified time in such a direction as to cool the junction. At the end of the time this circuit is broken and the thermocouple immediately connected to the galvanometer by means of the reversing switch. The resulting maximum galvanometer deflection is recorded and in the early stages of the study the return swing of the galvanometer was also recorded.
PROCEDURE

**General performance of the thermocouple**

1. The thermocouple, as shown in Figure 1, was sealed in the test tube above either a sulphuric acid solution or a soil sample. The procedure finally adopted for inserting and sealing the thermocouple in the test tube was as follows:

   a. A small slit was cut in the periphery of the stopper to allow air to escape as the thermocouple was inserted.

   b. The stopper was greased with vacuum grease and in addition a layer of grease was placed in a band around the inside of the test tube about one-half inch above the surface of the solution or soil sample. This prevented the slit from plugging with grease before the thermocouple reached its final position. When the junction was about one-quarter inch above the surface the thermocouple was rotated which plugged the slit and sealed it in place. The upper stopper was then sealed in place.

2. The procedure for determining whether the Peltier cooling effect was being obtained was to pass current through the thermocouple first in one direction and then the other. The resulting galvanometer reaction was recorded by noting the position of the swing at 5-second intervals until it returned to zero.

3. A preliminary test was then conducted to determine whether the maximum galvanometer deflection varied with change in relative activity. This was determined by placing the thermocouple over 0.01 and 1.0 molal solutions of sulphuric acid and passing the same current through it in both instances.
4. The optimum magnitude and duration of current to pass through the thermocouple was then studied by passing a series of combinations through it and observing the galvanometer reaction over its complete swing. Since Spanner used 2 ma. for 10 seconds this combination was tested first.

**Calibration of the thermocouple**

The thermocouple was calibrated over a series of solutions of sulphuric acid. All readings recorded were at a bath temperature of 25°C. The actual temperature of the bath was checked with a mercury thermometer graduated in 0.1°C, which had been calibrated to 0.01°C by the National Bureau of Standards. The calibrated thermometer was borrowed from Dr. N. Bauer of the Chemistry Department.

The selection of molalities was determined by relative activities given in Table 2; the desired values being taken from a larger table in Kortüm and Bockris (18, p. 671).

<table>
<thead>
<tr>
<th>H₂SO₄ m</th>
<th>a₀ω at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.99951</td>
</tr>
<tr>
<td>0.02</td>
<td>0.99912</td>
</tr>
<tr>
<td>0.05</td>
<td>0.99801</td>
</tr>
<tr>
<td>0.1</td>
<td>0.99628</td>
</tr>
<tr>
<td>0.2</td>
<td>0.99278</td>
</tr>
<tr>
<td>0.3</td>
<td>0.98921</td>
</tr>
<tr>
<td>0.4</td>
<td>0.98565</td>
</tr>
</tbody>
</table>

Solutions of the above molalities were prepared with the actual molality being determined by titrating against sodium carbonate. The titrations were conducted in triplicate and the results are recorded in Table 3.
Table 3. $\text{H}_2\text{SO}_4$ solution molalities with relative activities

<table>
<thead>
<tr>
<th>$\text{H}_2\text{SO}_4$ molality</th>
<th>$a_\omega$ at 25° C.*</th>
<th>$a_\omega$ at 25° C. corrected**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.9995</td>
<td>0.9994</td>
</tr>
<tr>
<td>0.016</td>
<td>0.9942</td>
<td>0.9941</td>
</tr>
<tr>
<td>0.050</td>
<td>0.9980</td>
<td>0.9979</td>
</tr>
<tr>
<td>0.094</td>
<td>0.9965</td>
<td>0.9964</td>
</tr>
<tr>
<td>0.179</td>
<td>0.9935</td>
<td>0.9934</td>
</tr>
<tr>
<td>0.277</td>
<td>0.9901</td>
<td>0.9900</td>
</tr>
<tr>
<td>0.369</td>
<td>0.9867</td>
<td>0.9866</td>
</tr>
</tbody>
</table>

* $a_\omega$ were picked off a curve obtained by plotting values in Table 1.
** $a_\omega$ corrected to atmospheric pressure at Logan, Utah.

The correction for reduction in atmospheric pressure at Logan, Utah, from that at sea level was calculated according to the formula

$$\Delta P = -2.3026 \frac{RT}{V} \log \frac{P}{P_0}$$

where $\Delta P$ is the change in atmospheric pressure expressed in atmospheres (760-640 = 120 cm. Hg or 0.15789 atm.)

2.3026 converts natural log to common log

$R$ is the universal gas constant = 82.057 cm$^3$ atm. per °C. per mole.

$T$ is the absolute temperature = 298.15° K at 25° C.

$V$ is the partial molar volume at 25° C. - or

$$18.016 = 18.069 \text{ cm}^3 \text{ per mole} \cdot 0.99704$$

$$- \log \frac{P}{P_0} = \frac{0.15789 \times 18.069}{82.057 \times 298.15 \times 2.3026} = \frac{0.000050643}{P_0}$$

$$\log \frac{P}{P_0} = 0.99995$$

$$P' = 0.99988$$

Readings over soil samples

The procedure for obtaining readings over soil samples was similar to the procedure used for calibrating the thermocouple.
A series of soil water relative activities was established by the pressure plate and pressure membrane methods (41). Benjamin silty clay loam was used. The soil was placed in the apparatus in a layer about one-eighth inch thick. When the soil reached equilibrium, 4 small samples were removed from the layer at random, placed in the test tube and the thermocouple sealed in place. Four random samples were also removed and placed in a soil can for immediate water content determination. The water content of the sample in the test tube was also determined after thermocouple readings had been obtained. This procedure was followed in order to check whether the sample had lost any water in the time interval required to get the reading.

The relative activities corresponding to the various pressures were calculated according to the formula on page 32 and are shown in Table 4.

Table 4. Relative activities of soil water as determined by the pressure membrane and pressure plate

<table>
<thead>
<tr>
<th>P (atm)</th>
<th>( a_w ) corrected*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>0.9997</td>
</tr>
<tr>
<td>1.25</td>
<td>0.9990</td>
</tr>
<tr>
<td>2.50</td>
<td>0.9981</td>
</tr>
<tr>
<td>5.0</td>
<td>0.9983</td>
</tr>
<tr>
<td>10.0</td>
<td>0.9925</td>
</tr>
<tr>
<td>15.0</td>
<td>0.9889</td>
</tr>
</tbody>
</table>

* \( a_w \) corrected to atmospheric pressure at Logan, Utah.

The relative activity of soil water as determined by the pressure membrane may not be a precise measurement of the true relative activity. Relative activity is defined by Guggenheim (16, p. 227) as the ratio of the absolute activity \( \lambda_i \) of \( i \) in a liquid mixture and its absolute activity \( \lambda^0_i \) in the pure liquid at the same temperature and pressure.

\[
\text{Or } a_i = \frac{\lambda_i}{\lambda^0_i}
\]
Using the notation of Taylor (37) for the case of water in the soil
the relationship becomes

\[ a_\omega^0 = \frac{\lambda_\omega (P^a W^a)_{\omega}}{\lambda_\omega^{0}} \]

where \( a_\omega^0 \) is the relative activity of the soil water with
respect to the standard which is defined as the relative
activity of pure free water at 1 atm. pressure and 25°C.

\( \lambda_\omega (P^a W^a)_{\omega} \) is the absolute activity of the soil water,
\( \lambda_\omega^{0} \) is the absolute activity of the water in standard state.

Absolute activity is defined by Guggenheim (16, p. 111) by the
following relationship:

\[ \lambda = \frac{u}{RT} \]

or rewritten

\[ u = RT \ln \lambda \]

where \( u \) is the molar chemical potential

\( R \) is the universal gas constant per mole

\( T \) is the absolute temperature

\( \lambda \) is the absolute activity

Relative activity of the soil water, as determined by the pressure
membrane, is related to the absolute activity of the water in the
exudate rather than to pure free water or

\[ a_\omega = \frac{\lambda_\omega (P^a W^a)}{\lambda_\omega (P_\beta W_\beta)} \]

where \( a_\omega \) is the relative activity of the soil water as determined
by the pressure membrane

\( \lambda_\omega (P^a W^a) \) is the absolute activity of the soil water
\( \lambda_\omega (P_\beta W_\beta) \) is the absolute activity of the water in the
exudate or the reference.
Since the absolute activity in the exudate will be equal to or less than the absolute activity of the water in the standard state, the relative activity of the soil water as determined by the pressure membrane will be equal to or greater than the relative activity based on the standard.

It is predicted, therefore, that the thermocouple readings over soil samples, if plotted according to the relative activities determined by the pressure membrane, will fall on or below the calibration curve.
RESULTS AND DISCUSSION

General performance of the thermocouple

The Peltier cooling effect was easily and quickly determined as shown by the typical heating and cooling curves shown in Figure 7. When the junction is heated the galvanometer returns to zero or near zero quickly. When the junction is cooled, however, the galvanometer takes considerably longer to return to zero. The tendency for the galvanometer to hang near the maximum deflection is evidence that dew has condensed on the junction because the presence of water fixes the temperature difference between the wet and dry junctions.

The preliminary test with the thermocouple over 0.01 and 1.0 molal solutions of sulphuric acid produced a difference in the maximum galvanometer deflection. Furthermore, since the deflection increased as the relative activity decreased, which agreed with the results shown by Spanner, it was concluded that the thermocouple as constructed was functioning.

The combination of 2 ma. of current flowing for 10 seconds, as used by Spanner, did not prove satisfactory. This amount of current did not provide the characteristic hanging near the maximum when the thermocouple was placed over solutions of low relative activity. The galvanometer behaved almost as if the thermocouple had been heated, returning to zero very quickly. Spanner points out that the maximum deflection is not a reliable indication of the "relative humidity" of the atmosphere if the dew has evaporated before the galvanometer reaches its maximum swing. The amount of water condensed is increased
Figure 7. Heating and cooling curves—
thermocouple over 0.1 molal
sulphuric acid solution

5 ma. 10 sec.
25° C.
as the magnitude and/or the duration of the current is increased. The effect of increasing the magnitude of the current on the maximum deflection is shown by the bar graphs in Figure 8. Figure 8 shows the rise and fall of the maximum deflection as the current is increased. The maximum cooling effect, indicated by the largest maximum deflection, was obtained with a current of 6 ma. The cooling effect, however, is depressed more by currents higher than 6 ma. than by currents lower than 6 ma.

Figure 9 shows that as the duration of the current is increased the time for the galvanometer to return to zero is increased.

The final selection of magnitude and duration of current is rather arbitrary. For the most reliable results the current should be sufficiently large to insure the formation of adequate dew as mentioned previously. For maximum life of the thermocouple, however, it is desirable to use as small a current as possible. For rapidity of reading it is also desirable to condense as little water as possible. After repeated trials a magnitude of 5 ma. for a duration of 10 seconds was selected. This combination caused the galvanometer to hang near the maximum at the lowest relative activity of interest and enabled readings to be taken at relatively short intervals of time. The typical galvanometer reaction over the complete series of solutions is shown in Figure 10. Figure 10 shows the decrease in maximum galvanometer deflection and the increase in time required to return to zero as the relative activity is increased.

A total of 15 thermocouples was made. Of this number only 6 functioned and of the 6 only 2 lasted long enough to get sufficient data for discussion purposes. The thermocouples are susceptible to breakage from jars or direct contact. Barring jars and contacts,
Figure 8. Effect of varying magnitude of current on maximum galvanometer deflection
Figure 9. Effect of varying duration of current on cooling curves.
Time from breaking circuit min.

Figure 10. Cooling curves—thermocouple over sulphuric acid solutions
However, the thermocouples are capable of providing a large number of readings. For instance, the second thermocouple has provided about 350 readings and was still functioning at the end of the study.

In the early stages of the study 1 thermocouple was treated by dipping it in liquid beeswax to determine whether such a treatment would improve its general performance. This thermocouple, however, did not function after treatment. Another thermocouple was given the same treatment but in this instance the wax was too hot and destroyed the junction wires. Since at that time the supply of wires was dwindling the thermocouple was used without treatment.

**Calibration of the thermocouple**

Figure 11 shows the calibration readings for the first thermocouple. The lines on which the readings are plotted are located according to the relative activity of the solution determined by titrating. The line, however, is labelled with the approximate molalities to facilitate the discussion. The date of the reading has been included to indicate lapse of time between any 2 readings or over a series of readings.

A calibration curve is not drawn for the first thermocouple because the maximum galvanometer deflection gradually decreased with time. It was speculated at this time that the reason for this gradual lowering might be because equilibrium conditions had not been attained. The readings in this case were taken as soon as the galvanometer reached zero or very near zero. The time between readings, therefore, varied depending on the relative activity of the solution. When over the 0.4 molal solution the readings were taken at 3-minute intervals while when over 0.01 molal solution the time interval between readings was about
Figure II. Calibration readings — first thermocouple over sulphuric acid solutions [molality indicated]
20 minutes. Final readings were accepted when 2 consecutive readings were the same.

The reading procedure was, therefore, changed when studying the second thermocouple. Readings were taken at 1-hour intervals and the first 3 readings over solutions extended over the complete series—2 readings at each end and 1 at the midpoint of the series. Figure 12 shows the effect of time from placing the thermocouple over the solution on the maximum galvanometer deflection. The lower curve indicates that in all probability equilibrium conditions have been reached. Unfortunately, however, the upper curve shows the more common situation. The readings do not remain constant for a period of an hour or two but the curve has definitely levelled out. It was felt, therefore, that the final readings by this procedure represented equilibrium or very near equilibrium conditions.

Figure 13 shows a straight line relationship between relative activity and maximum galvanometer deflection for the second thermocouple. Two curves are shown—the upper curve when there was no shunt and the lower curve when there was a 9-ohm shunt across the galvanometer. The reason for the two curves was a natural development. In order to keep the galvanometer deflection on scale with the first thermocouple it was necessary to use a 9-ohm shunt. The shunt was left across the galvanometer when readings were taken of the second thermocouple. The maximum deflections were sufficiently small, however, to allow the removal of the shunt. The two conditions were maintained to determine if there was any difference. A comparison of the 2 curves shows that with this thermocouple the desirable arrangement is to operate with no shunt because the upper curve (no shunt) is steeper
Figure 12. Galvanometer deflections with time from placing thermocouple in bath

- 5 ma. 10 sec.
- 25 °C.
- 0.3 m solution
- 0.33 atm. soil sample
Figure 13. Calibration curves — second thermocouple over sulphuric acid solutions
than the lower one. The first thermocouple, however, produced better results with a 9-ohm shunt than did the second with no shunt.

**Thermocouple readings over solutions and soil samples**

Figure 14 shows the 9-ohm shunt calibration curve for the second thermocouple plus additional readings over solutions and a series of readings over soil samples. The results for the no shunt readings were similar.

Table 5 shows per cent soil moisture content on a dry weight basis (Pw) before and after a series of thermocouple readings.

Table 5. Pw's before and after thermocouple readings over the soil samples

| Pw % Before thermocouple readings | Pw % After thermocouple readings | Error *%
|-----------------------------------|---------------------------------|---------
| 0.33                             | 22.8                            | 21.8    | +4.3   |
| 2.50                             | 17.0                            | 17.8    | -4.7   |
| 5.0                              | 14.2                            | 15.0    | -5.6   |
| 15.0                             | 10.8                            | 10.4    | +3.7   |

* Error based on Pw before thermocouple readings.

The results show an appreciable difference in Pw before and after thermocouple readings but the error is not always in the same direction. It is assumed, therefore, that the moisture content did not change appreciably while readings were taken. The majority of the error is probably in the figure for "Pw after the thermocouple readings" because of the vacuum grease in the test tube. This grease had to be weighed with the weight of wet and dry soil samples but had to be removed before weighing the test tube. The weight of water, therefore, was correct but the dry soil weight included the weight of grease.

Figure 14 shows a similar lowering of the readings with time over solutions and soil samples as experienced with the first thermocouple.
Figure 14. Reading over solutions and soil samples — second thermocouple and 9-ohm shunt.
second thermocouple (Figure 14) shows this lowering of readings with time very clearly. In the case of the readings over soil samples the first reading was taken before the readings over solutions which established the calibration curve. This reading falls on the curve. Three days later the second reading was taken and it falls slightly below the curve. Readings over soil were taken over the next 6 days and with the passing of time the readings gradually become lower. An exception to this trend is the second or lower reading over the 2.5 atm. soil sample. In this instance, however, the thermocouple when inspected was very wet. It was, therefore, dried by leaving it in the room atmosphere over night before taking the reading over the 0.33 atm. soil sample. Another instance when the thermocouple became very wet was after it had been over the 1.25 atm. soil sample. The last soil reading over the 15 atm. sample was taken 2 days later and falls below the curve but the magnitude of the depression is less than for the soil samples of higher relative activity.

A similar but more striking lessening of the lowering trend is illustrated by a series of readings over the 0.4 molal solution. The reading which falls above the curve was taken after the thermocouple had remained in room atmosphere for 6 days. To check this apparent drying out effect 2 more readings were taken over the same solution. The thermocouple was left sealed over the humid atmosphere for another 36 hours and a reading taken which is again below the line. The thermocouple was then exposed again to the room atmosphere for 5 days and a reading taken which is again above the curve.

The second thermocouple had more of a tendency to become wet than the first one. This was disturbing but nevertheless the same trend of lowering readings was shown by the first thermocouple and it appeared
dry on inspection after removing it from the test tube. However, in an attempt to eliminate this difficulty the base of the thermocouple and as much of the lead wires as possible without breaking the junction wires were coated with polystyrene cement diluted in alcohol. This seemed to help but did not overcome the problem.

Readings after treating the thermocouple

Shortly before the completion of the study the supply of junction wires was replenished. With an ample supply of wires available it was feasible to apply some treatments in an attempt to overcome the problem of lowering readings with time. Two treatments were applied and readings were taken over the 0.4 and 0.01 molal solutions.

The first treatment consisted of spraying the second thermocouple with a clear plastic spray paint labelled "Spraint Ignition Sealer." Before applying the treatment a second junction was soldered to the spare pair of lead wires. This provided an opportunity to check the plastic treatment on a new and an old junction.

The second treatment consisted of dipping a new thermocouple in "Beckman Desicote" which is an "...organo-silicon compound which removes the slightest trace of water from silicate surfaces, leaving a water-repellent coating of molecular thickness."

It was originally planned to treat a thermocouple by dipping it in a solution of ceresin wax (5 per cent) and alcohol (95 per cent). It was not possible, however, to conduct this test because the wax did not arrive in time. The "Desicote" treatment was substituted because it looked promising.

5. Minit Spray Corp., 945 West George Street, Chicago 14, Illinois.
Table 6 shows the reproducibility of readings obtained for the second thermocouple after treating it with the plastic spray.

Table 6. Equilibrium readings, after treating the second thermocouple with the plastic spray, over 0.4 and 0.01 molal solutions for 3 separate series of readings

<table>
<thead>
<tr>
<th>H₂SO₄ solution molality</th>
<th>Max. galvanometer deflection cm.</th>
<th>9-ohm shunt*</th>
<th>no shunt*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st run</td>
<td>2nd run</td>
<td>3rd run</td>
</tr>
<tr>
<td>0.4</td>
<td>12.4-12.5</td>
<td>12.7-12.8</td>
<td>12.6-12.7</td>
</tr>
<tr>
<td>0.01</td>
<td>2.5</td>
<td>2.4-2.5</td>
<td></td>
</tr>
</tbody>
</table>

* across galvanometer.

The results in Table 6 show that treating the thermocouple has overcome the lowering of readings shown in Figure 14. The difference over the 3 runs for the 9-ohm shunt was 0.4 cm, and for no shunt across the galvanometer 0.5 cm. An additional indication that the plastic spray has made the thermocouple more stable was that the readings stayed constant for a longer period than shown in Figure 12. Before treatment it was only rarely that a constant reading was obtained for a period of more than 2 hours after equilibrium had been reached. After treatment, however, it was not uncommon to record the same reading for a period of 5 or 6 hours. In the case of the 0.01 molal solution the same reading was recorded over a period of 9 hours after equilibrium had been reached.

Table 6 provides a limited amount of information for evaluating the thermocouple technique. The readings for the "9-ohm shunt across the galvanometer" will be used as the basis since more readings were recorded.

The precision of the technique is about 1 per cent based on the readings over the 0.4 molal solution which showed the most variation.
It is suggested that this figure is conservative because it was not uncommon throughout the study for duplicate readings, taken within a matter of minutes, to be identical.

The technique measures to within an accuracy of about 4 per cent (3.2 per cent in the dry range and 4.2 per cent in the wet range) the relative activity determined over titrated solutions.

No readings were recorded for the new thermocouple, because it did not function properly. This thermocouple junction was very erratic, particularly in the beginning. The readings on the first run started low and increased but were always lower than those for the second thermocouple. On the second run this was reversed, the new junction read higher than the second one and then lower so that at equilibrium the readings were below those of the second thermocouple. The readings for the new thermocouple could not be recorded because this junction after each series had collected so much water that in one case the free end of the junction was even covered.

The exact reason for some thermocouple junctions collecting water was finally established when it was possible to observe a satisfactory and unsatisfactory thermocouple on the same base. On inspecting the base after drying the thermocouple on completion of the first run over 0.01 molal solution it was evident that the excess flux (zinc chloride) had not been completely removed from the new junction. This junction was washed with the spray of distilled water, being careful not to contaminate the old junction. This did not improve the new junction. The thermocouple was then soaked in water and detergent. No readings are recorded for the third run because the old thermocouple showed signs of collecting water for the first time and the readings were lower and
did not remain as constant as previously. It is assumed that in attempting to remove the excess flux from the new junction some flux was washed on to the old one.

The results of Table 6, however, indicate that the plastic treatment has provided a stable thermocouple. This treatment has, however, increased the time required to attain equilibrium. Before treatment the readings levelled off in about 12 hours whereas after treatment the time required was about 24 hours.

It was not possible to arrive at a definite conclusion in connection with the "Desicote" treatment because the life of this thermocouple was very short. In addition, there may have been a slight trace of flux present because the lead wires were wet on inspection after a series of readings. The "Desicote" treatment may, therefore, be successful if applied to a clean thermocouple.

Throughout the study duplicate readings if taken within a matter of minutes were reliable. This characteristic was so dependable that in the latter stages of the study duplicate readings were discontinued. The only exception was when the junction became wet. This steadiness together with the reproducibility obtained after treatment with plastic should produce a thermocouple that possesses a high order of stability.
SUGGESTED FURTHER DEVELOPMENT

The thermocouple assembly requires improvement in two areas before the technique will be completely satisfactory as a laboratory procedure.

1. A long time is required to reach equilibrium (12-24 hours as compared to 15 minutes as shown by Spanner). The first suggestion for improving this situation is to treat the thermocouple with ceresin wax. It is further suggested that the "Desicote" treatment be tested more completely. If treating the thermocouple does not produce the desired results it is suggested that the sample container designed and used by Spanner be explored. This consisted of a separate small glass cup that was attached to the thermocouple assembly by a ground joint which insured an airtight seal. It is also suggested that an improved design for placing and holding the thermocouple assembly in the bath be explored. As presently designed the openings for the test tubes in the lid of the bath are a close fit which makes it difficult to place the thermocouple without causing the solution to splash up on the junction. In addition, the movement of the test tube caused by the bath stirrer limits the nearness with which the junction can be placed to the surface of the solution.

2. The susceptibility of the thermocouple to breakage from jars and knocks is considered a weakness. It may be possible to make a sturdier thermocouple by fastening the lead wires at some point further up the stem. This should prevent the shock of a jerk on the lead wires travelling directly to the junction.
POSSIBILITIES OF THE THERMOCOUPLE TECHNIQUE AS A FIELD METHOD

It is suggested that the thermocouple technique could be developed into a field method. There are several points which would have to be considered:

1. As presently constructed the time required to reach equilibrium is much too long. Before it can be considered as a field method this time will have to be decreased to a matter of a few minutes.

2. The thermocouple at present is too fragile to be used as a field instrument. One suggestion has been given for making it sturdier.

3. If the time required to reach equilibrium can be shortened to a matter of minutes it should not be necessary to control the temperature. Instead it is suggested that the temperature of the atmosphere could be recorded possibly by thermistor at the time the reading is taken on the thermocouple.

4. The galvanometer is not a suitable field instrument. It is suggested, however, that the e. m. f. produced could possibly be amplified and read electronically.
CONCLUSIONS

A small thermocouple cooled by the Peltier effect shows promise for measuring the relative activity of soil water in the range between permanent wilting percentage and field capacity.

The most important single factor in constructing a successful thermocouple is to remove all trace of excess flux (zinc chloride).

Treating the thermocouple with plastic spray eliminates drift and makes the instrument more stable, but time required to reach equilibrium is increased.

The thermocouple appears to read relative activity of soil water and of sulphuric acid solutions with the same accuracy. Limited results indicate that a thermocouple treated with plastic spray measures to within an accuracy of about 4 per cent the relative activity determined over titrated solutions with a precision of about 1 per cent.

The prediction that the readings over soil samples would fall on or below the calibration curve could not be checked because at that stage in the study the thermocouple was not stable.

For optimum control of bath temperature with a minimum of trouble when using a light reflected on a photoelectric cell it is important to control two factors. The first is to provide a constant external or room light and second to maintain as constant a room temperature as possible. With the bath in a constant temperature room with artificial lighting only, the bath temperature was controlled to within 0.003° C.
It may not be necessary to house the bath in a constant temperature room to obtain satisfactory results. When housed in a room with variable lighting and temperature the bath will, however, require more observation and adjustment.

Further improvements in design are required before the thermocouple will be a completely satisfactory laboratory procedure. For example, until the time needed to reach equilibrium is shortened the technique will be limited in its use because of the precise temperature control required.
LITERATURE CITED


41. United States Salinity Laboratory Staff. Diagnosis and improvement of saline and alkali soils. U. S. D. A. Handbook 60. 1954.