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TEMPERATURE DEPENDENCE OF SOIL-MOISTURE POTENTIAL

by

Jacob Willem Kijne

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

of

DOCTOR OF PHILOSOPHY

in

Soil Physics

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Logan, Utah

1964

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Jacob Willem Kijne

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## LIST OF SYMBOLS

<p>A surface area of adsorbent</p> <p>F free energy</p> <p>H enthalpy</p> <p>M molecular weight</p> <p>N number of molecules</p> <p>R gas constant</p> <p>S entropy</p> <p>T absolute temperature</p> <p>V volume</p> <p>P pressure</p> <p>a relative activity</p> <p>h heat</p> <p>m mass</p> <p>n number of moles</p> <p>p vapor pressure of water</p> <p><math>p_0</math> saturated vapor pressure of water</p> <p>r curvature</p> <p>v molar (specific) volume</p> <p>y composition variable</p> <p><math>\psi</math> total soil moisture potential</p> <p><math>\gamma</math> surface tension</p> <p><math>\mu</math> chemical potential</p> <p><math>\theta</math> moisture content</p> <p><math>\Gamma_k</math> mass of component k per unit</p> <p><math>\varrho</math> mass of dry solid</p> <p><math>\phi</math> surface potential, which is difference in chemical potential of adsorbent in dry and moist condition</p>	<p>Superscript * denotes adsorption thermodynamical quantities</p> <p>Bar <sup>-</sup> designates partial specific (molar) quantities</p> <p>Subscripts:</p> <p>A adsorbent</p> <p>ao adsorbent in dry state</p> <p>aw adsorbed water</p> <p>I wetting</p> <p>j, k, m components of soil moisture</p> <p>w soil water</p> <p>wG water vapor</p> <p>ws soil water</p> <p>wf water in liquid state</p> <p>pw free liquid water</p>
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## INTRODUCTION

Teachers have noticed that children draw only those objects which they know by name. Doubtless the adult has a similar tendency, exemplified by the researcher, to limit his observations or to relate them to that which can be expressed in the terminology of an existing or newly developed theory. In this thesis the data obtained from studies of the temperature and pressure dependence of the relative vapor pressure over moist soil samples are analyzed by a thermodynamic approach. Not all of the results can be explained completely by means of this tool. Natural systems, such as a moist soil, are probably too complex for any single theory; but since the language of thermodynamics provides the best known means of conveying the results to others, it is felt that this language should be used throughout the thesis.

The way in which the state of soil water, as expressed by the chemical potential, is influenced under natural conditions is very complex. Four intensive properties (temperature, pressure, soil-moisture content, and the concentration of solutes) and sometimes a fifth (soil-bulk density) are generally considered when the chemical potential of soil water is expressed. Under certain conditions the chemical potential is a function of the relative activity of soil water only. Assuming water vapor to be an ideal gas, the chemical potential becomes a function of relative vapor pressure over moist soil samples. For this reason, several

techniques have been developed to accurately measure the relative humidity over soil samples.

It is well known that temperature changes influence the activity of soil water, as recorded by a tensiometer. The soil water movement due to temperature gradients has been studied quite extensively, most recently by using the approach of thermodynamics of irreversible processes. The soil moisture potential is also influenced by changes in the total pressure on the soil system.

The chemical potential of water in the soil, in a system where several dissolved species may also be adsorbed on the surface of the solids, is of primary interest in describing the state of soil water. Other thermodynamic properties of soil water, which can be evaluated from those changes in the chemical potential resulting from changes in temperature and pressure, are also of interest.

The objective of this study is to evaluate the physical state and several thermodynamic properties of soil water by means of measurements of the relative vapor pressure over moist-soil samples.

## REVIEW OF LITERATURE

Thermodynamic properties of soil water have been evaluated in the past by four general techniques, each of which differs from the others. One technique is based on the differential thermal analysis of solid components of the soil (Barshad, 1952). Another is based on the water retention curves or adsorption isotherms (Martin, 1960). A third is based on heats of wetting (Chessick and Zettlemoyer, 1959). A fourth is based on direct measurements of the partial (molar or specific) Gibbs-free energy of water in the system (Taylor, 1958; Taylor and Stewart, 1960; Low and Anderson, 1958; Box, 1961). The first three methods have been discussed recently in more detail by Kohl (1962) and by others, who have used adsorption and calorimetric methods to evaluate thermodynamic properties of adsorbate-adsorbent systems.

The relation between aqueous vapor pressure over soil systems and their moisture content has intrigued soil physicists for a long time. In 1921, Thomas published an extensive report containing many vapor pressure data obtained from moist soil at a single constant temperature. The soil samples were brought to moisture equilibrium over solutions of different relative humidities contained in desiccators, after which the moisture content was determined gravimetrically. A similar study was done by Alexander and Haring (1936) with certain soil colloids; however, no data were reported for the same colloids under varying temperature and pressure conditions.

An experiment designed to measure the attraction forces between water and porous media was reported by Wilsdon et al. (1935). The materials studied were clays, thoroughly washed to remove all soluble salts and colloidal materials, and sand. The relation between (vapor) pressure and moisture content was studied, using four different methods: (1) direct application of hydrostatic tension to the moist porous system; (2) balancing the tension within the system against a solution of known osmotic pressure--the porous system being separated from the solution by a semi-permeable membrane; (3) balancing the tension against the known or calculated tension of a solution, equilibrium being reached through the vapor phase; (4) determining the freezing point of water within the porous system. Their results show that the pressure (expressed in atm.) in the osmotic and vapor-pressure methods is several times greater than the pressure in the hydrostatic method for the same water content of the porous material. Wilsdon et al. based their explanation of the discrepancy on the concept of molecular orientation in thin liquid films adsorbed on solid surfaces. The vapor pressure at the free surface would correspond to that of a solid, while the two-dimensional pressure along the surface would determine the work done in removing water from the film by a hydrostatic tension. The hydrostatic method, on the one hand, and the osmotic and vapor pressure methods, on the other, only measure the same condition of water when the molecules of water lie beyond the range of the orienting surface forces; i. e., when they exist in the same state as they do under a free-water surface.

The effect of temperature upon the relation between relative humidity and

soil-moisture content was studied by Puri et al. (1925). They concluded that the relative vapor pressure of soils increases considerably with increasing temperature in the range of low humidities but is practically independent of temperature in atmospheres of high humidity. These conclusions were verified by Wadsworth (1939). Robins(1952) studied the same temperature dependence in terms of specific free energy, using the relation

$$\Delta F = \frac{RT}{M} \ln \frac{p}{p_0}$$

where  $\Delta F$  is the specific free energy of soil water;  $M$ , the molecular weight of water; and  $p$  and  $p_0$ , the vapor pressure of soil water and the vapor pressure of pure water at the same temperature, respectively. The Yolo loam soil used in the reported experiment in three different textures was brought to water vapor equilibrium over 14 different sulphuric acid solutions. Robins concluded that the change in specific free energy with temperature was not conclusive, but it appears that the specific free energy increases numerically (i.e., the moisture potential decreases because free-energy values are negative) with increasing temperature. The change was, to a first approximation, proportional to the ratio of the absolute temperatures. This is in agreement with the observation by Puri et al. (1925) that the relative vapor pressure becomes independent of temperature in the high-humidity range. The approximation that the free-energy decrease is proportional to the absolute temperature held better for the wetted samples (adsorption curve) than for the dried (desorption curve). Robin's work demonstrated how difficult it is, with this vapor equilibrium technique, to get



conclusive data on the temperature dependence in the higher range of relative humidities corresponding to the range of soil-moisture contents that plants utilize.

The thermoelectric method of measuring vapor pressure seems to have the necessary sensitivity, however. This method was discussed in detail by Roepke (1942) in commenting on Baldes and Johnson's method. The difference in temperature is measured by means of a thermocouple and a sensitive galvanometer between a drop of an unknown solution and a drop of a reference solution of known molarity. Both drops are suspended in horizontal loops which form the thermocouple in a humidified chamber. The couples are calibrated with drops of two different reference solutions. Roepke (1942) states that it is not necessary that the drops be of exactly the same size for comparison of solutions differing less than 0.02 M NaCl. The rate of evaporation of water from, or condensation on, a drop of solution placed on a thermocouple junction varies in direct proportion to its radius. An increase in size of the drop, however, does not result in a significant, direct effect on its temperature, since the rate at which heat is transferred to the drop is similarly dependent on its size.

Monteith and Owen (1958) and Korven and Taylor (1959) have reported on thermocouple methods to measure water-vapor pressure in equilibrium with soil water; i. e., relative humidities in the range of 95 to 100 percent. Their methods of measurement were based on the Peltier effect. Earlier, Spanner (1951) had indicated the possible use of the Peltier effect in the measurement of soil-moisture potentials.

The Peltier effect is based on the fact that an electric current flowing across a junction of two dissimilar metals causes absorption or liberation of heat, depending on the direction of the current. The difference in temperature between the thermal junction and the reference junction after a cooling current has been sent through the junction for a certain length of time causes a current to flow in the other direction. This difference in temperature, and consequently in the magnitude of the resulting current, is dependent on the relative humidity around the thermal junction of the couple. Probably due to the fact that this method to measure vapor pressure at high humidities is complicated and exacting, none of these papers give data on the temperature dependence of the soil-moisture potential.

Richards and Ogata (1958) have developed a couple, using the same principle as Baldes and Johnson's couple, described by Roepke (1942); i. e., the cooling of the thermal junction is caused by evaporation from a drop of water placed in a loop at the junction. Richards and Ogata (1961) reported that it is possible, under favorable conditions, to measure the relative vapor pressure of soil moisture in wet soils with an accuracy of one or two parts per one hundred thousand. Ehlig (1962) measured the energy status of water in plants with thermocouples of this design; Klute and Richards (1962) used them to evaluate the effect of temperature on relative vapor pressure of soil moisture. Their data are erratic, but in the case of sodium-saturated montmorillonite the total soil-moisture potential seems to be less at 40 C than at 25 or 5 C, which is in agreement with Robins' (1952) conclusion referred to before. Klute and Richards (1962) commented that no

definite conclusions could be drawn concerning the effect of temperature on relative vapor pressure of soil water in Chino clay loam. The results obtained with the vapor pressure technique using montmorillonite are inconsistent with other data, reported also by Klute, obtained by the use of tensiometers and montmorillonite (Wilkinson and Klute, 1962). Klute and his co-workers give no explanation for the discrepancy in data obtained by the two methods.

Earlier, the influence of temperature on soil-moisture suction had been studied by Taylor and Stewart (1960) with the use of tensiometers. An increase in potential with increasing temperature was observed, with which the data of Wilkinson and Klute (1962) are in agreement. Taylor and Stewart (1960) expressed the results also in terms of partial thermodynamic quantities.

An interesting aspect of liquid-vapor system in porous material has been pointed out by Shereshefsky and his associates. Shereshefsky and Carter (1950) observed a lowering of the vapor pressure of water in uniform capillaries, exceeding the value predicted by Kelvin's equation:

$$\ln \frac{p}{p_0} = - \frac{2\gamma V}{RT r}$$

where  $V$  is the molar volume;  $\gamma$ , the surface tension;  $r$ , the curvature; and  $p$ , the vapor pressure over the curved surface. Folman and Shereshefsky (1955) found similar discrepancies between observed and calculated vapor-pressure lowerings for non-aqueous systems, such that a solubility effect cannot reasonably be involved (Shereshefsky, 1928). For aqueous systems, the ratio of actual radius over the value for the radius calculated from Kelvin's equation lies between 7 and

80; the latter value is reached in a capillary with a calculated radius of 0.04 microns. It is interesting to speculate whether or not Kelvin's equation holds for soil systems.

### Structure of water

A separate section of this review should be devoted to the structure of water as it exists in porous media. Martin (1960) concludes from adsorption-isotherm studies on kaolinite that the integral entropy of the sorbed phase approximates, at very low values of the relative vapor pressure, the entropy of a two-dimensional gas, which decays very rapidly at first and then slowly approaches the entropy of normal liquid water at  $p_0$  and  $T$ . In other words, the water molecules in the adsorbed phase on kaolinite have more randomness than water molecules in liquid water.

Martin gives an explanation for these results in terms of sorption sites on the inert sorbent. The first small increment of sorbate water has a large number of possible sorption sites; so that it is quite reasonable that the entropy should approximate that of a two-dimensional gas. For further addition of water, fewer and fewer sorption sites are available. Multilayer formation occurs only when it makes energetically no difference whether water adsorbs on the bare surface or starts a second layer. Consequently, the molecule has then again a greater number of possible sites for sorption than the previous one, which results in an increase in the integral entropy of the adsorbed water. Martin proposes a water structure concept by building inward from the liquid water

to the solid surface, which is an adaptation to the clay-water system of theories on water structure in electrolyte solutions (Frank and Wen 1957). He proposes that water builds tetrahedrons with five molecules per tetrahedron, such that two corners of the tetrahedron are positive and two negative. Non-polar foreign objects introduced into the water tie the water molecules together in a quasi-solid structure (sometimes called iceberg structure).

As expected, the entropy of water in such a system is less than the entropy of free water. Small ions permit iceberg formation in much the same manner as the iceberg forms around a non-polar molecule. Ions larger than K do not permit any iceberg formation. Therefore, their net effect upon the water structure is one of structure breaking. Martin considers kaolinite clay particles as very large "molecules" containing localized positive and negative sites. The clay surface prevents a water structure from forming about any particular charged site on the clay surface.

This same idea has been expressed by Williamson (1948). He distinguishes between water directly adsorbed on the clay mineral surface, which would have a low density, and water "compressed around cations" (which must be the small cations, according to Martin) with a density greater than that of liquid water. The entropy of the water can be negative only if the exchangeable cation hydration (iceberg formation) is sufficient to overcome the structure-breaking effect of the clay particle. This is unlikely, in view of the fact that there is no hydration of the Li-ion below  $p/p_0 = 0.7$ . Therefore, it can be expected that the entropy of the adsorbed water will be larger; i. e., more randomness, than liquid water.

This concept has been confirmed by data reported by Zettlemoyer et al. (1953), Goates and Bennett (1957), Barshad (1960), Jurinak and Volman (1961a, b), and Kohl (1962), among others.

Several equations have been developed to describe the adsorption of water in the multilayer region. Non-swelling materials as kaolinite gave good results with the BET equation (Marshall, 1958) and, recently, with the Frenkel-Halsey-Hill equation (Jurinak, 1963). The FHH equation is based on the assumption that, as the adsorption film thickens at the higher relative pressure, any individuality of the surface vanishes; and the adsorbate finds itself in an environment closely approaching that of the bulk liquid.

The determining factor in multilayer adsorption is the difference in potential energy of the field emanating from the surface as compared with the field in the bulk liquid. Jurinak (1963) found that this isotherm equation described the water adsorption over a wide range of relative pressures in kaolinite systems. The BET equation does not work for swelling materials such as montmorillonite (Marshall, 1958). Norrish (1954) pointed out that in the swelling of montmorillonite the free energy of water forming an additional hydration shell around an interlayer cation must be greater than the work done in increasing the interlayer spacing to accommodate the shell.

Van Olphen (1962), in reinterpreting Norrish's results, proposed a cross-linking of stacks of parallel layers by a relatively small number of non-parallel plates. The cross-linking force was estimated to be high enough to counteract the Gouy double-layer repulsive forces, which could not be done by van der Waal's

attractive forces alone. Van Olphen and Deeds (1962) encountered stepwise hydration of Na Wyoming bentonite-  $\alpha$ -picoline water systems. The authors pointed out, however, that the concept of stepwise hydration is still somewhat speculative.

Ross and Olivier (1961) entertain a model of a mobile adsorbed film, assuming the adsorbed film to be a two-dimensional gas on a heterogeneous substrate. A number of different adsorbents are shown to be described by a Gaussian distribution of adsorption energies. However, one of the basic assumptions employed in this model, i. e.—the molecules are negligibly polarized by the electric field of the surface—does not hold for water vapor adsorption.

An important part of the adsorption of vapors by porous bodies at high relative pressures is supposed to be by the mechanism of capillary condensation (Wadsworth, 1944). It has been proposed that capillary condensation occurs spontaneously after completion of the monolayer and also, to the contrary, that capillary condensation is preceded by multilayer formation. Therefore, adsorption effects must be taken into account in the application of the capillary theory to ideal porous systems.

According to Jurinak et al. (1962), polymolecular adsorption accounts for all adsorption of water on glass spheres up to relative pressures of 0.98 with no indication of condensation. Li-kaolinite shows no evidence of ion hydration or capillary condensation up to a relative pressure of 0.972, and Na kaolinite shows multilayer adsorption up to  $p/p_0 = 0.9$ , where ion hydration is initiated (Jurinak, 1963; Johansen and Dunning, 1959).

Hysteresis in the adsorption-desorption isotherm is characteristic of capillary condensation. It is frequently considered that the lower limit of the hysteresis loop is also the lower limit of capillary condensation, but Carman (1953) shows that capillary condensation extends below this point. According to Carman, hysteresis arises from the delay in permeation of a meniscus and occurs in the adsorption condensation portion of the hysteresis loop. Other mechanisms involved in hysteresis have been proposed and are reviewed by Adamson (1960), page 522-26.

Capillary condensation alone cannot account for the hysteresis in water vapor sorption on kaolinite, as observed by Martin (1959). Variations in the hydration of the exchangeable ions associated with the clays play a role also. The extent of surface hydration—i. e., surface coverage by hydroxyl groups—has a pronounced influence on subsequent reversible adsorption of water vapor. Makrides and Hackerman (1959) have observed that the extent of adsorption of water vapor diminishes with increasing dehydration of the surface. The decrease is approximately equal to the loss of hydroxyl groups, suggesting a 1:1 correspondence between adsorbed water molecules and surface hydroxyl groups.

From thermodynamics it is known that the pressure dependence of soil-moisture potential gives a method to evaluate the density, or specific volume, of adsorbed water (see chapter on Theory). Peck (1960) concludes from theoretical considerations that the moisture content tension curves are different when determined by suction or by pressure methods. He considers the moisture potential to be dependent on three variables only: temperature and pressure-induced changes in air volume, water volume, and surface tension of water, which does



not include double layer and adsorption forces. This makes his theory questionable. That the moisture content - potential curves are different when determined with suction or pressure methods had been pointed out before by Taylor (1958).

It could be expected that the density of adsorbed water is less than that of free water, in agreement with the entropy data and interpretation offered by Martin (1960). This is actually reported by Anderson and Low (1958) from simultaneous measurements of the change in volume of the paste and of the expressed water when a clay-water paste was compressed. At distances of 10 A, the density of water in Li, Na, and K bentonites were 0.975, 0.972, and 0.981, respectively. The same authors (Low and Anderson, 1958) concluded from pycnometer measurements, by which method they could not measure closer than 84 A, that the partial specific volume of water in Li, Na, and K bentonite suspensions was the same as that of free water. Viscosity data, reported by Low (1960), again supported a less dense structure of adsorbed water. Deeds and van Olphen (1961), using pycnometer techniques, concluded that the density of the first two monolayers of water which are adsorbed between the unit layers is slightly below normal in most expanding clays, but that the density of water adsorbed beyond the first two monolayers of water is normal within the experimental error.

The difference in values obtained by Anderson and Low (1958), on the one hand, and those by Deeds and van Olphen, on the other, is such that Graham (1962) expresses strong doubts whether variation of water density has been demonstrated at all for water at distances greater than a few molecular layers from the clay surface. He questions in particular the method employed by Anderson and Low

(1958). Mackenzie (1958) criticizes the approach by Anderson and Low, also, and cites values of the specific volume of bound water of less than unity; i. e., a more dense structure.

A more dense water structure is also reported by de Wit and Arens (1952). They give a value as low as 0.71 for the specific volume of water for a moisture content in montmorillonite of 11.6 percent. Orchiston (1953) supports the concept of a more dense water structure from adsorption data interpreted with the BET equation. A change in slope of  $\log p/p_0$  against  $1/x^2$ , where  $x$  is the mass of adsorbate (a procedure proposed by Harkins and Jura, 1944), shows two linear regions, indicating a phase change in the condensed film from a water structure with a density greater than that of liquid water to a water structure with a density less than that of liquid water. Bahrani (1963) interprets his study of the pressure dependence of soil-water matric potential, using pressure-plate apparatus to measure this potential, as indicating a more dense structure of soil water. However, this interpretation is from differential quantities, which, according to Hill (1950), is not a valid procedure. Whether soil water is less or more dense than free water is still an open question that needs to be investigated.

## THEORY

Hill (1950) has given two equivalent ways of analyzing the thermodynamic properties of an adsorbate (water) on a solid adsorbent (soil solid). One is analogous to "solution thermodynamics," and the other is called "adsorption thermodynamics." His approach has been applied to soil water by Taylor and Kijne (1963) for measurements on tensiometers, pressure membrane, and psychrometric systems. Here, only the development for the vapor-pressure measurements will be presented and somewhat extended.

For the chemical potential of soil water, using solution thermodynamics we have

$$d\mu_{wS} = -\bar{S}_w dT + \bar{v}_w dP + \left(\frac{\partial \mu_w}{\partial \theta}\right)_{T,P,\Gamma_k} d\theta + \sum_{k=1}^{m-1} \left(\frac{\partial \mu_w}{\partial \Gamma_k}\right)_{P,T,\theta,\Gamma_j} d\Gamma_k \quad [1]$$

where  $\bar{S}_w = \left(\frac{\partial S}{\partial n_w}\right)_{P,\theta,\Gamma_k}$  is the partial molar entropy of adsorbed water,

$\bar{v}_w = \left(\frac{\partial V}{\partial n_w}\right)_{\theta,T,\Gamma_k}$  the partial molar volume of adsorbed water;  $\theta = \frac{n_w M_w}{m_a}$

the mass of water held by a unit mass of dry solid;  $n_w$ , the number of moles of water;  $M_w$ , the molecular weight of water;  $m_a$ , the mass of the adsorbent (solid);  $T$ , Kelvin temperature; and  $\Gamma_k = \frac{n_k M_k}{m_a}$  the mass of component  $k$  per unit mass of dry solid. The term  $\Gamma_j$  indicates all but one of the  $\Gamma_k$  components, and  $P$  is the "hydrostatic pressure" exerted by a hypothetical

inert piston or (in part) by a hypothetical inert additional gas. If a curved interface is involved, there may be ambiguity in  $P$  when thus defined (Bolt and Frissel, 1960). Hill (1950), however, stresses that for thermodynamic reasons the pressure  $P$  exerted on an adsorbent-adsorbate has precisely the same meaning as the pressure  $P$  exerted on a solution. The effect of a curved interface is, therefore, contained in either the water content ( $\theta$ ) or in the surface-potential ( $\phi$ ) term.

From adsorption thermodynamics, the equation (equivalent to [1]) for the chemical potential of soil water in the same system is

$$d\mu_{ws} = -\bar{S}_w^* dT + \bar{v}_w^* dP + \bar{N}_{aw}^* d\phi + \sum_{k=1}^{m-1} \left( \frac{\partial \mu_w}{\partial y_k} \right)_{P, T, \phi, y_j} dy_k \quad [2]$$

where  $y_k$  is the composition variable for solute  $k$ ;  $\phi = \mu_{a0} - \mu_a$  the difference in chemical potential of the adsorbent in its dry (vapor pressure  $p = 0$ ) and moist ( $p > 0$ ) conditions, where  $\bar{S}_w^* = \left( \frac{\partial S}{\partial n_w} \right)_{P, \phi, y_k}$ ;  $\bar{v}_w^* = \left( \frac{\partial V}{\partial n_w} \right)_{T, \phi, y_k}$  and  $\bar{N}_{aw}^* = \left( \frac{\partial \mu_w}{\partial \phi} \right)_{P, T, y_k}$ . It has been argued that the concept of surface potential is not valid in localized adsorption; however, we have lost only the physical meaning. The function defined by the equation is not influenced by localization or non-localization of the film (Whalen, 1961). At equilibrium, the chemical potential of water in the adsorbed state, in the liquid state, and in the gaseous state are all equal. We may thus use either the liquid or the gaseous state as a standard to which we refer the properties of the adsorbed state. For the gaseous state we have

$$d\mu_{vG} = -S_{vG} dT + \bar{v}_{vG} dp \quad [3]$$

where  $S_{WG}$  is the entropy of water vapor and  $\bar{v}_{WG}$  the partial specific volume of water vapor. None of the  $k$  components exist in the gaseous state, and we have assumed that the components of air (except water vapor) are inert.

By equating [1] and [3] for equilibrium between the adsorbed and gaseous phases, we get

$$\bar{v}_{wG} dp = (S_{wG} - \bar{S}_w) dT + \bar{v}_w dp + \left( \frac{\partial \mu_w}{\partial \theta} \right)_{T, P, \Gamma_k} d\theta + \sum_{k=1}^{m-1} \left( \frac{\partial \mu_w}{\partial y_k} \right)_{T, P, \Gamma_j, \theta} dy_k \quad [4]$$

When [2] and [3] are combined, we have

$$\bar{v}_{wG} dp = (S_{wG} - \bar{S}_w) dT + \bar{v}_w dp + \bar{N}_{aw}^k d\theta + \sum_{k=1}^{m-1} \left( \frac{\partial \mu_w}{\partial y_k} \right)_{P, T, \theta, y_j} dy_k \quad [5]$$

The value of  $\phi$  can be determined from experimental data by the equation

$$\phi = RT \int_{\phi}^{\theta} \frac{\theta}{P} d\theta \quad [6]$$

This equation is not exclusively a surface equation, and  $\phi$  has the dimensions of a potential (joules/mole). Further,  $\phi$  should not be confused with the difference in surface tension of the clean surface and the surface tension of the surface with adsorbate ( $\Delta\gamma$ ); these two terms are related, however, since  $\phi N_A = (\Delta\gamma)A$  where  $A$  is the surface area of the adsorbent and  $N_A$  is the number of moles of the adsorbent. It is, therefore, not necessary to know the absolute value of  $\Delta\gamma$  a two-dimensional spreading pressure, or of  $A$  in order to use equation [5] (Hill, 1949).

In equations [4], [5], and [6] the assumptions involved are that the adsorbent (soil) is inert and that the ideal gas law is valid for the water vapor. In addition, it is assumed that [6] can be evaluated down to zero. It is well

known that the adsorbent involved (Millville silt loam soil, the clay fraction mostly consisting of montmorillonite) is not entirely inert. Nevertheless, the thermodynamic functions remain well-defined quantities; but it is not proper to assign all of the variations to the water molecules.

The differential values of entropy and enthalpy can be calculated from the temperature dependence of vapor pressure in [4]. Rearranging [4] gives for constant T and P

$$(dp)_{T,P} = \frac{1}{V_{wG}} \left( \frac{\partial u_w}{\partial \theta} \right)_{T,P,\Gamma_k} d\theta + \frac{1}{V_{wG}} \sum_{k=1}^{m-1} \left( \frac{\partial u_w}{\partial \Gamma_k} \right)_{P,T,\theta,\Gamma_j} d\Gamma_k \quad [7]$$

The last term on the right of [7] has been called the osmotic effect or the osmotic-potential contribution. The temperature dependence of the vapor pressure at constant P and  $\theta$  can be found from [4] to be

$$\left( \frac{dp}{dT} \right)_{P,\theta} = \frac{S_{wG} - \bar{S}_w}{V_{wG}} + \frac{1}{V_{wG}} \sum_{k=1}^{m-1} \left( \frac{\partial u_w}{\partial \Gamma_k} \right)_{P,T,\theta,\Gamma_j} \frac{d\Gamma_k}{dT} \quad [8]$$

Similarly, [5] gives for the calculation of the corresponding integral values

$$(dp)_{T,P} = \frac{1}{V_{wG}} \bar{H}_{wG}^* d\phi + \frac{1}{V_{wG}} \sum_{k=1}^{m-1} \left( \frac{\partial u_w}{\partial y_k} \right)_{P,T,\phi,y_j} dy_k \quad [9]$$

and

$$\left( \frac{dp}{dT} \right)_{P,\phi} = \frac{S_{wG} - \bar{S}_w}{V_{wG}} + \frac{1}{V_{wG}} \sum_{k=1}^{m-1} \left( \frac{\partial u_w}{\partial y_k} \right)_{P,T,\phi,y_j} \frac{dy_k}{dT} \quad [10]$$

The equation for the potential of water in a solution containing  $X_k$  moles per liter of component k is given by

$$du_{wf} = -\bar{S}_{wf} dT + \bar{V}_{wf} dP_f + \sum_{k=1}^{m-1} \left( \frac{\partial u_{wf}}{\partial X_k} \right)_{P,T,X_j} dX_k \quad [11]$$

where the subscript *f* denotes the liquid state. When [11] is combined with [1] and [2], equations corresponding to [7] to [10], for tensiometer and pressure-plate or membrane methods, can be derived (Taylor and Kijne, 1963). Comparing those with equations [7] to [10], we see that vapor-pressure measurements include the influence of solutes on the system, which influence is not measured by the tensiometer and pressure-plate or membrane methods. This may contribute to the discrepancy in values obtained by using the different methods as found by Wilsdon *et al.* (1935).

The pressure dependence of the vapor pressure at constant *T* and  $\theta$  can be found from [4] to be

$$\left(\frac{dp}{dP}\right)_{T,\theta} = \frac{\bar{v}_w}{\bar{v}_w G} + \frac{1}{\bar{v}_w G} \sum_{k=1}^{m-1} \left(\frac{\partial \bar{v}_w}{\partial \Gamma_k}\right)_{T,P,\theta,\Gamma_j} \frac{d\Gamma_k}{dP} \quad [12]$$

It seems valid to assume that the mass of component *k* per unit mass of dry solid ( $\Gamma_k$ ) is independent of a change in pressure; hence, the last term on the right of [12] becomes trivial. If we treat the vapor as a perfect gas, then  $\bar{v}_w G = RT/p$ , and we obtain

$$RT \left(\frac{d \ln p}{d P}\right)_{T,\theta} = \bar{v}_w \quad [13]$$

which is the partial specific (molar) volume of water in the system. The corresponding equations for the integral quantity are derived from [5] to be

$$\left(\frac{dp}{dP}\right)_{T,\phi} = \frac{\bar{v}_w^2}{\bar{v}_w G} + \frac{1}{\bar{v}_w G} \sum_{k=1}^{m-1} \left(\frac{\partial \bar{v}_w}{\partial y_k}\right)_{P,T,\phi,y_j} \frac{dy_k}{dP} \quad [14]$$

and

$$RT \left(\frac{d \ln p}{d P}\right)_{T,\phi} = \frac{\bar{v}_w^2}{\bar{v}_w} \quad [15]$$

where  $\bar{v}_w^*$  is the integral volume of one mole of water adsorbed on a unit amount of dry soil at a particular temperature and surface potential.



## EXPERIMENTAL PROCEDURE

The relative vapor pressure of soil water is measured with thermocouples made according to the design of Richards and Ogata (1958). The thermal junction of the thermocouple consists of a silver loop with a radius of 2 mm and is attached to constantan and chromel-P wires, all of which are suspended over the soil sample. The wires from which the couple is made are 0.001" in diameter. Evaporation from a spherical drop of water suspended inside the silver loop causes the cooling of the couple. The amount of cooling, which is an indication of the water activity in the chamber, is measured by the emf output of the thermocouple. The emf output is measured on a Leeds and Northrup K 3 potentiometer. A diagram of this arrangement is given in Figure 1.

All junctions were thermally controlled and shielded to avoid interference so that the emf could be measured to 0.01  $\mu$ V precision. The thermocouple psychrometers were calibrated at different temperatures or different pressures by measuring their emf output over KCl solutions of known water activity. A sample calibration curve is shown in Figure 2. The small temperature corrections for the relation between water activity and molality of KCl solutions were obtained from data given by Hornibrook *et al.* (1942) and Robinson and Stokes (1955). The pertinent values are given in Table 1. The dependence of vapor pressure of KCl solutions on total pressure is negligible for the pressure range involved (Guggenheim, 1959, p. 230).

The emf output of the thermocouples was measured 1 1/2, 4, and 6 hours

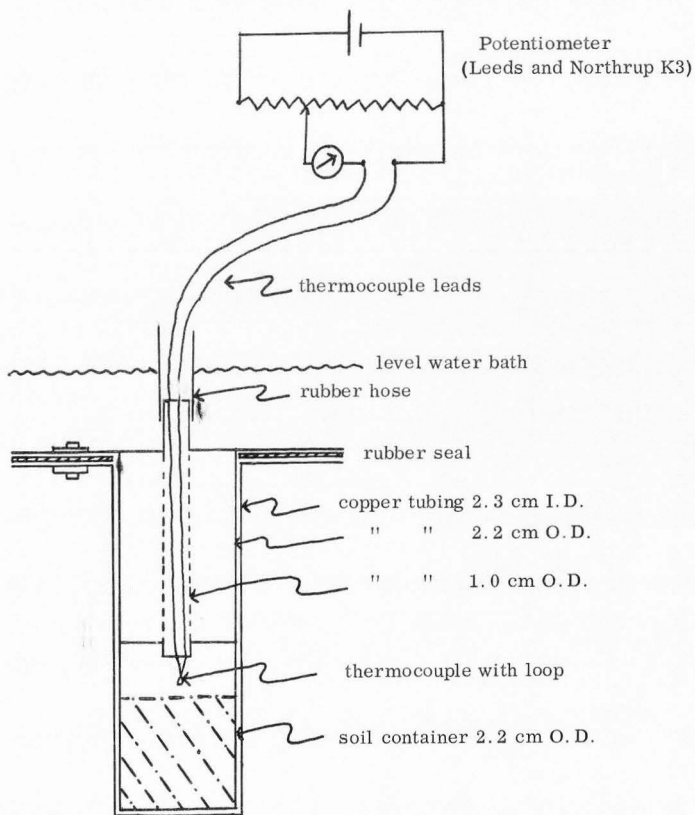


Figure 1. Schematic diagram of psychrometer

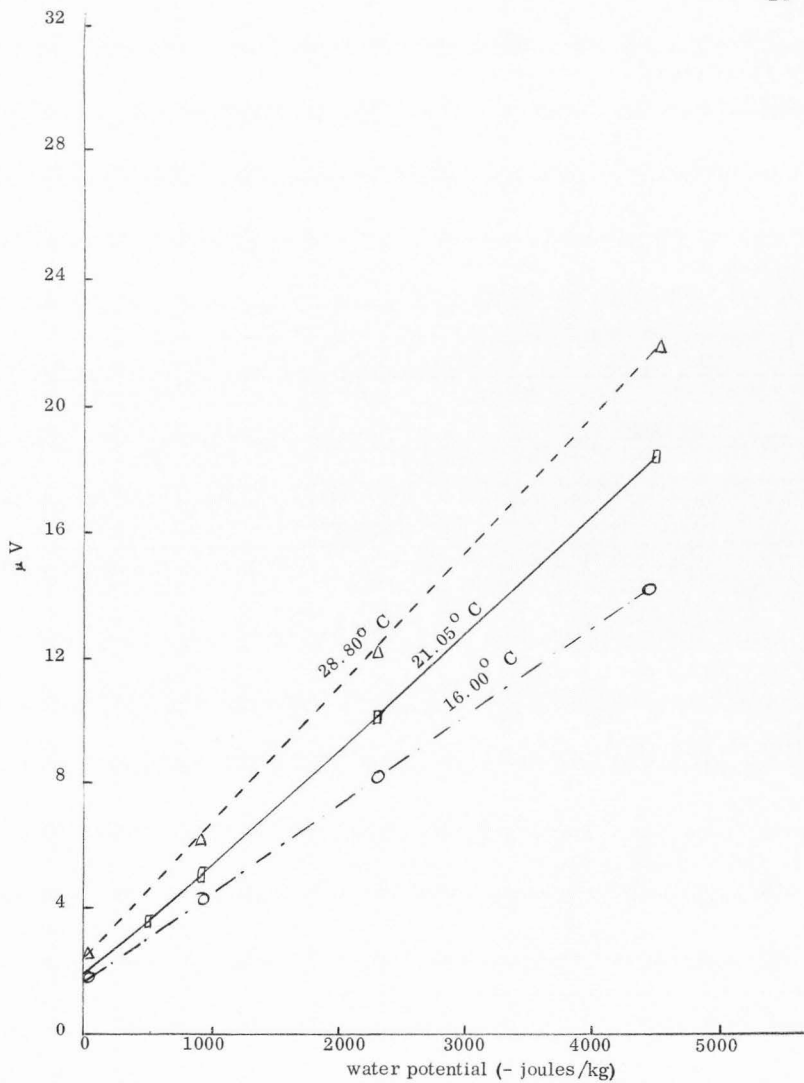


Figure 2. Calibration curve for psychrometer, relating potentiometer reading in  $\mu V$  with water potential in joules/kg.

Table 1. Values of the free energy of KCl calibration solutions for four different temperatures

Molarity KCl solution	$\Delta F$ in -joules/kg				
	$a_w$ at 25 <sup>0</sup> C	12.00 <sup>0</sup> C	16.00 <sup>0</sup> C	21.05 <sup>0</sup> C	28.80 <sup>0</sup> C
0.1 M	.99667	439.854	446.024	453.814	465.768
0.2 M	.99343	868.484	880.667	887.597	919.650
0.3 M	.99025	1291.048	1309.158	1332.022	1367.108
0.5 M	.98389	2138.905	2168.909	2206.787	2264.915
1.0 M	.96814	4265.372	4325.206	4400.741	4516.660

after the sample tubes had been placed in the bath. The output after 1 1/2 hours was higher, up to 10 percent, than at 6 hours, both over the calibration solutions and the soil samples. After 6 hours, the output stayed constant for a period of at least 1 hour, after which it dropped gradually. Constant monitoring of the temperature inside the innerbath indicated that the time at which the emf became constant coincided with the time at which the temperature became stable in the innerbath. The time during which the emf output of the thermocouple remained constant after temperature equilibrium was obtained was dependent on the relative humidity around the couple. It was observed that a marked decrease in emf had occurred by the time that the drop on the couple had become a flat water film inside the silver loop.

A maximum drift of about 3 percent in the emf output was noticed when the thermocouples were recalibrated over the same solutions after two or three months. It is, therefore, necessary to recalibrate the thermocouples at regular intervals.

The method of Richards and Ogata (1958) was modified to permit complete immersion of the sample tubes, as was similarly reported by Klute and Richards (1962). The tubes were immersed in a constant-temperature bath controlled to a precision greater than  $\pm 0.001$  C (Kijne and Taylor, 1963). A single sample of Millville silt loam at a given predetermined water content was sealed in the measuring chamber so that only heat could be exchanged with the surroundings. The temperature of the bath and, in a second series of experiments, the pressure of the air over the sample, could be varied as desired. Measurements were made over the same sample at four different temperatures from 12.0 to 28.8°C. The measurements were limited to the relative vapor pressure range from 0.9600 to 1.0000.

Bulk soil samples were prepared in a pressure-membrane apparatus. The soil had previously been screened and wetted in a standardized manner and was then brought to equilibrium at the desired air pressure. After the soil had been removed from the pressure cell, it was sieved through a No. 20 sieve (0.84 mm sieve opening), and the moisture content was determined by drying to constant weight at 105°C. The soil was stored in dark, sealed containers in a constant temperature room, controlled to 0.5°C. From these bulk samples, subsamples were taken and placed in the soil sample tubes in the psychrometers.

The necessary supplemental data in the relative vapor-pressure range from 0.000 to 0.939 were obtained from heat of wetting measurements. There exists an extensive literature on microcalorimetry in general (Sturtevant, 1945;

Swietoslawsky, 1946; Berghausen, 1954; Kraus, 1954; Pierce et al., 1958) and on calorimeters used for heat-of-wetting measurements in particular (Zettlemoyer, et al. 1953; Slabaugh, 1955; Makrides and Hackerman, 1959). Zettlemoyer et al. were probably the first to describe the use of thermistor type calorimeters for heat-of-wetting measurements.

The calorimeters which were used in this study were modifications of those described by Pierce et al. (1958), as shown in Figure 3. The heat output was measured with a 100.000  $\Omega$  thermistor in a Wheatstone bridge circuit and recorded on a Bristol recorder. The calorimeter was calibrated before each measurement by putting a known amount of current through the heater for a period of 1 minute and observing the deflection on the recorder. The schematic diagram of the heating arrangement is given in Figure 4.

Both the resistance of the calibration heater and the current chosen were such that the amount of heat liberated in 1 minute produced about 4/5 of a full-scale deflection on the recorder. A similar deflection was produced in about the same time by the wetting of the driest samples. The two calorimeters used were connected in turn with the same calibration and temperature-recording unit in order to make readings. Heats of wetting were measured with a precision of 0.01 calorie per gram of soil.

Samples were prepared in sealed bulbs that are broken beneath the water surface so as to introduce the dry soil there. The bulbs, blown from pyrex tubing 0.277" in diameter, had about a 3 cc volume. They were weighed empty and again after they were filled with powdered oven-dry Millville silt-loam soil. They were

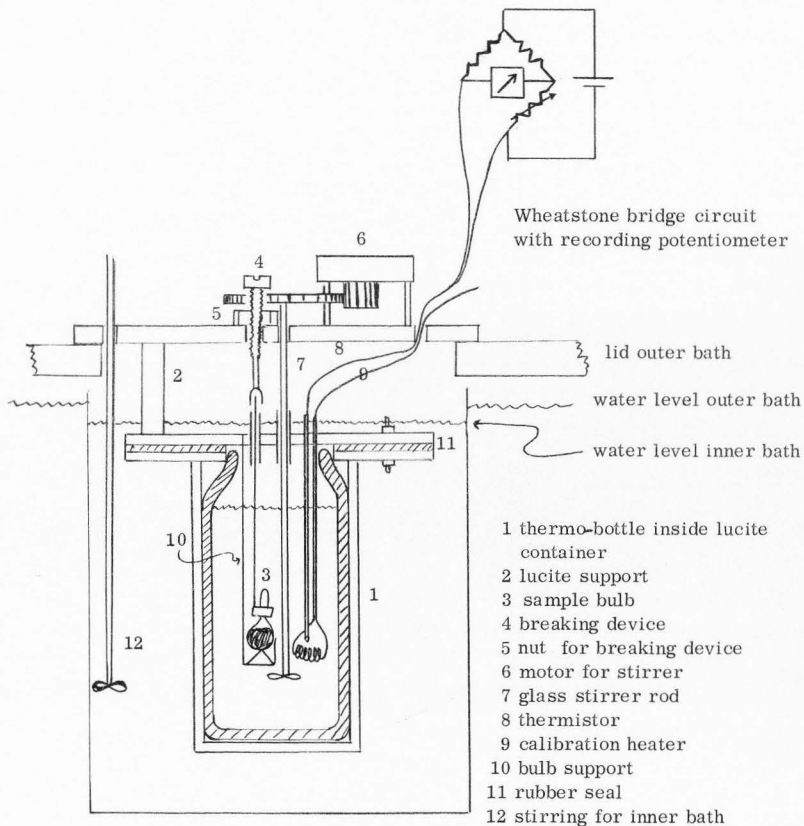


Figure 3. Diagram of calorimeter for heat of wetting measurements

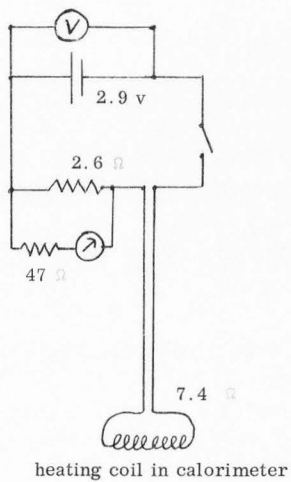


Figure 4. Diagram of calibration circuit for calorimeter



then allowed to reach water-vapor equilibrium in atmospheres of different relative humidities in evacuated desiccators, after which they were again weighed and sealed. These weights, accurate to 0.01 gram, were thus determined for the samples when dry and after they had attained their moisture-content equilibrium. The relative humidities in the desiccators were controlled with  $P_2O_5$  to give zero vapor pressure, and with four different sulfuric acid solutions to give 93.9, 58.3, 18.8, and 3.2 percent relative humidity. Evacuation of the desiccators greatly reduces the time required to reach equilibrium. The desiccators were first evacuated for 12 hours and then placed in a dark air bath controlled to  $0.1^\circ C$ .

The temperature of the air bath could be varied as desired. After removing the bulbs from the desiccators and sealing them, they were placed in one of the two calorimeters. Each calorimeter was placed in a separate water bath contained within a larger water bath which was controlled to  $0.1^\circ C$ . Temperature equilibrium inside the calorimeter was reached in about 10 hours, at which time the temperature of the liquid in the calorimeter changed less than  $0.001^\circ C$  in 15 minutes, which was about the time it took for one calibration and measurement.

The heat-of-breaking of the thin-walled sample bulbs was negligibly small. In most heat-of-wetting studies, this heat-of-breaking is ignored when the adsorbate is water. Gunderjahn *et al.* (1958) concluded that the main source of heat-of-breaking is due to the turbulent flow with which the liquid moves into the broken bulb. The bulbs used in this study were smaller than most sample bulbs in use; consequently, this heat source was reduced.

In this calorimeter study, only the total immediate heat-of-wetting was observed. A slow evolution of heat, as noticed by Gunderjahn et al. (1959) for a period of several hours, could not be detected.

## EXPERIMENTAL DATA AND ANALYSIS

The psychrometric method was used to determine the relative humidity over samples of Millville silt loam at soil-moisture contents varying between 3.85 and 16.12 percent water. The soil water potential may be expressed in terms of free energy (-joules/kg), using the relation

$$\Delta\mu = \frac{RT}{M} \ln a_w \quad [16]$$

where  $a_w$  is the relative activity of soil water, which is taken as  $p/p_0$ , or the ratio of the water vapor pressure of the sample divided by the saturated vapor pressure at the same temperature. Over a period of time many data were obtained in this way. A substantial part of these data are presented in Table 2. The relative humidity was measured on the same sample at three or four temperatures. Part of the data were obtained while improvements were still being made on the equipment, which explains that in certain cases only the data from two temperatures are given.

One of the disadvantages of this particular psychrometric method is the introduction of a drop of water on the thermocouple inside a small container in which the relative humidity is to be measured. This drop evaporates and is condensed on the soil, thus changing the potential of the soil water. The drop of water is completely evaporated over relative dry samples within 24 hours. This limits to two or three days the duration that one sample can be used. Returning

Table 2. Soil water potential of Millville silt loam at different moisture contents

Moisture content (% dry weight)	Temperature (degrees C)			
	12.00	16.00	21.05	28.80
	-joules/kg	-joules/kg	-joules/kg	-joules/kg
3.85	5111	6312		6765
4.32	2476	2698	3194	3612
4.36		5436		6862
4.36		2925	3846	
4.36		1060	2017	3668
4.36	1008	1008	2378	4812
6.69	2068	2458		2831
6.69		2297	2487	
7.29	1488	1696	1726	2204
7.31	1936	2244	2202	
7.31	1067	1322	1318	
7.72	1778	2044		
7.73	1594	1763	1875	
7.94			1060	1646
8.10	1264	1389	1617	1743
8.14	2661	2738	2500	
8.54	1383	1322	1672	1702
8.55	1449	1670	1889	
8.7	1020		1515	1725 <sup>a</sup>
8.7	1110		1170	1290 <sup>a</sup>
9.06	198	881	1291	809
9.59	543	681	1658	
9.8	1700		2100	2040 <sup>a</sup>
9.8	1590		1300	1670 <sup>a</sup>
9.8	1080		1200	1360 <sup>b</sup>
9.8	990		1040	1110 <sup>b</sup>
10.11	1120		1175	1795 <sup>b</sup>
10.11	960		1150	2060 <sup>b</sup>
10.26		1416	1971	
10.26		1223	1345	1548
10.26		868	1169	
10.26		788	1074	1493
10.26		735		1018

<sup>a</sup>Measurements taken with increasing temperature.

<sup>b</sup>Measurements taken with decreasing temperature.

Table 2. (cont'd.)

Moisture content (% dry weight)	Temperature (degrees C)			
	12.00	16.00	21.05	28.80
11.28	-joules/kg 118	-joules/kg 240	-joules/kg 489	-joules/kg 739
11.8		629	883	1479
11.8	184	307	598	655
12.1	329	708	1100	1255
12.2			149	153
12.3		1255	1318	
12.4	896	1095	747	1367
12.8		1202	1211	
13.1			652	1172
13.1			109	209
13.19	1778	1549	1780	1827
13.90	342	494		
13.90			299	321
13.90	342	574	924	1241
14.90		187	326	
14.92		134	639	
15.65	263			377
15.73		134	258	600
15.75			299	390
16.12	394	508		
16.12			313	363

to the same temperature after such a period, a higher value of the water potential was sometimes obtained. In those cases, only data of two subsequent days were used. Series were sometimes run from high temperature to low temperature and vice versa, and sometimes in an arbitrary sequence, as is indicated in Table 2. This was done in order to eliminate the influence of time on the potential. The temperature dependence dominated over the time dependence, as can be seen from these data.

The measurements show consistent temperature-induced changes for the individual samples. However, there is quite a variation in the potential of samples with the same or nearly the same moisture content. This may be, in part, a result of differences in packing. Small real changes in moisture content cause large differences in potential. In the beginning, only the water content of the bulk samples, from which the sub-samples were taken, was determined; and it was assumed, perhaps incorrectly at times, that the water content of these bulk samples was uniform and remained unchanged for two or three weeks.

It can be seen from the data in Table 2 and also from Figure 5 that the soil-water potential decreases with increasing temperature, which is contrary to the results obtained with tensiometers. In Figure 5, the smoothed relation between water potential and soil-water content from Table 2 has been plotted for four temperatures without showing actual data points. Some data of the water potential in moist glass beads (average diameter  $29 \mu$ ) and in washed sand, presented in Table 3, also show a decrease in potential with increasing temperature.

For the whole range of vapor pressures, vapor pressure is plotted in

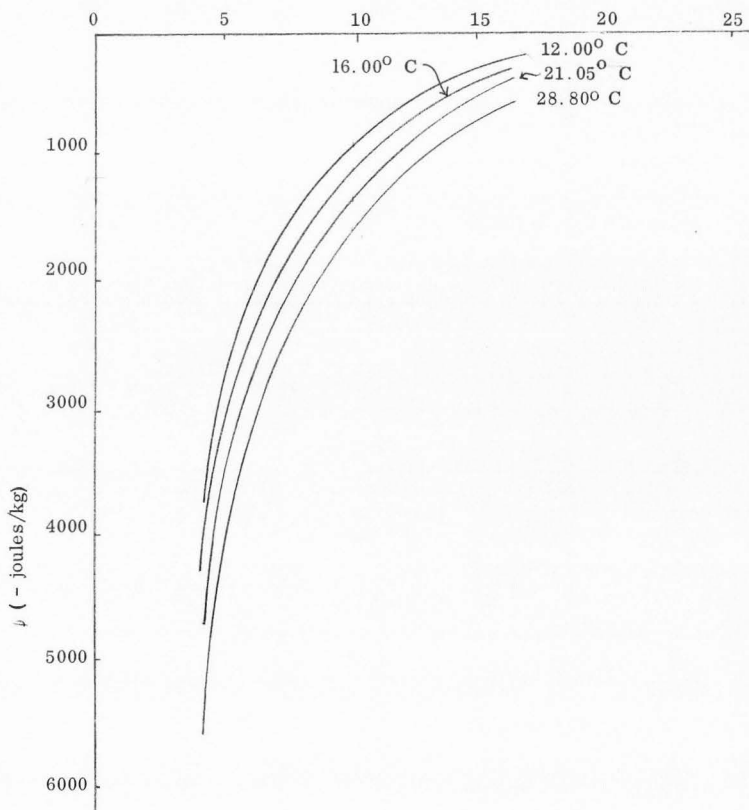


Figure 5. Soil water potential (-joules/kg) as a function of water content at different temperatures for Millville silt loam.

Table 3. Total water potential in -joules/kg at different temperatures for glass beads and sand at different moisture contents

Moisture content (% dry weight)	Temperature (degrees C)			
	12.00	16.00	21.05	28.80
<u>Glass beads</u>				
7.4	805		1020	1325
	395		1020	1340
<u>Sand</u>				
0.34	420	680	885	
0.22	1385	1485	1795	
	1580	1925	2200	
0.16	3215	3420	3640	



Figure 6 as a function of soil-water content for Millville silt loam. The values for the dry range, below a moisture content of 3 percent, were obtained gravimetrically from the samples that had been brought to equilibrium at different vapor pressures. The resulting sigmoidal curves are in good agreement with those for the drier range obtained by Thomas (1921), determined by a similar method, and by Kohl (1962), determined with an adsorption-balance method, both using the same Millville silt loam obtained from the Utah State Greenville Experimental Farm, as was used in this study.

According to [8], differential values of  $(S_{WG} - \bar{S}_W)$  and  $(H_{WG} - \bar{H}_W)$  are obtained directly, from a plot of vapor pressure as a function of temperature. This plot is given in Figure 7, which was derived from Figure 6. The change in the composition of the solution phase as a result of temperature changes is assumed to be negligible. The differential values calculated from Figure 7 are given in Table 4. Due to uncertainties inherent in plotting and determining slopes from these plots, the accuracy is  $\pm 2.5$  joules/mole-degree for the entropy values and  $\pm 0.8$  kilo joules/mole for the enthalpy values.

Values of the surface potential  $\phi$  were determined in accordance with [6], by graphically integrating, by means of a planimeter, the curve relating the ratio of moisture content over vapor pressure versus vapor pressure for the different temperatures. These curves, reduced in size, are presented in Figure 8.

According to [10], integral values of  $(S_{WG} - \bar{S}_W^*)$  and  $(H_{WG} - \bar{H}_W^*)$  can be obtained directly from a plot of vapor pressure as a function of temperature at

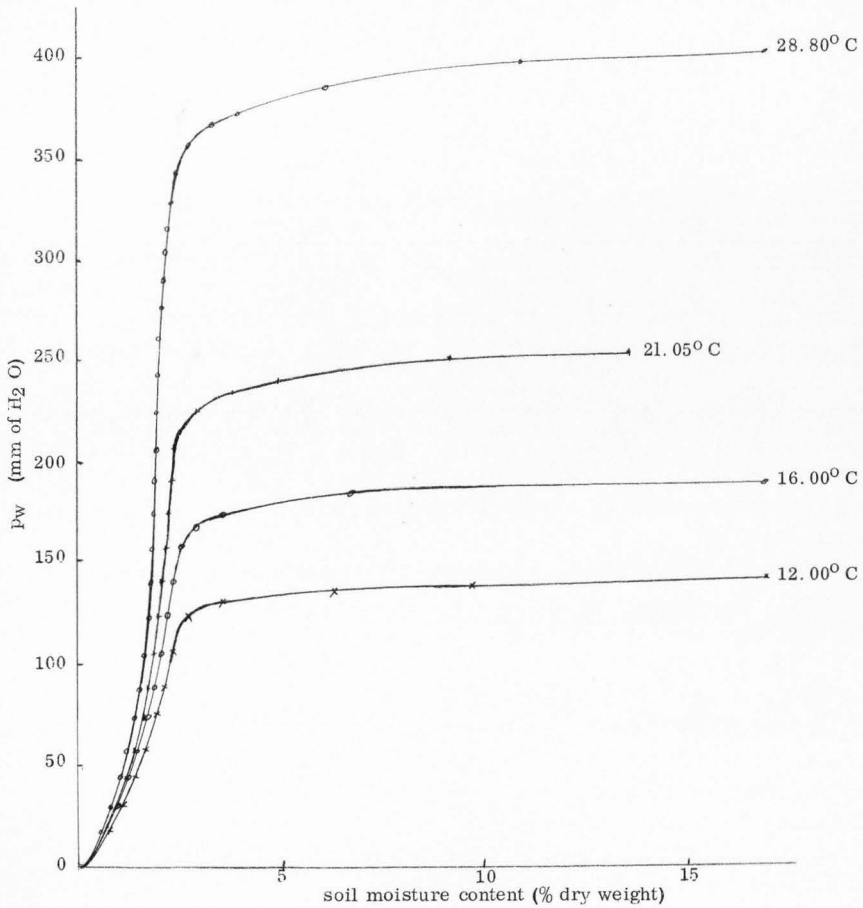


Figure 6. Variation of vapor pressure with soil moisture content for Millville silt loam at four different temperatures.

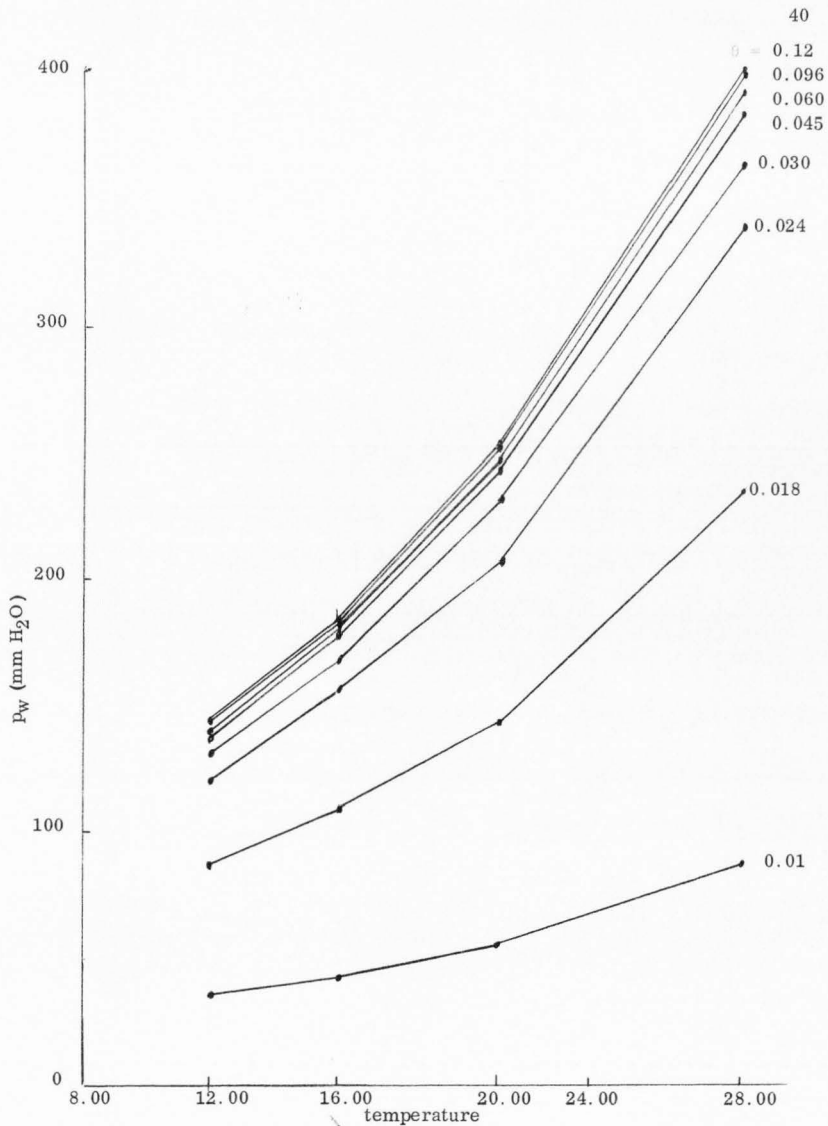


Figure 7. Variation of vapor pressure with temperature for Millville silt loam at different soil-moisture contents

Table 4. Differential values of  $(S_{WG} - \bar{S}_W)$  and  $(H_{WG} - \bar{H}_W)$  at different temperatures and soil-moisture contents

$\theta$	12.00 <sup>o</sup> C		16.00 <sup>o</sup> C		21.05 <sup>o</sup> C		28.80 <sup>o</sup> C	
	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$
0.010	93	29	141	44	181	57	229	73
0.018	127	36	146	43	175	53	213	66
0.024	165	46	145	42	144	43	289	88
0.030	166	45	157	46	151	45	166	50
0.045	177	48	159	46	166	49	146	44
0.060	152	42	164	47	164	48	146	44
0.096	150	41	162	47	174	51	146	44
0.120	150	41	161	47	173	51	146	44
0.150	150	41	161	47	173	51	146	44

Units of  $\theta$  are gram H<sub>2</sub>O/gram soil dry weight.

Units of  $(S_{WG} - \bar{S}_W)$  joules/mole-degree.

Units of  $(H_{WG} - \bar{H}_W)$  kilo joules/mole

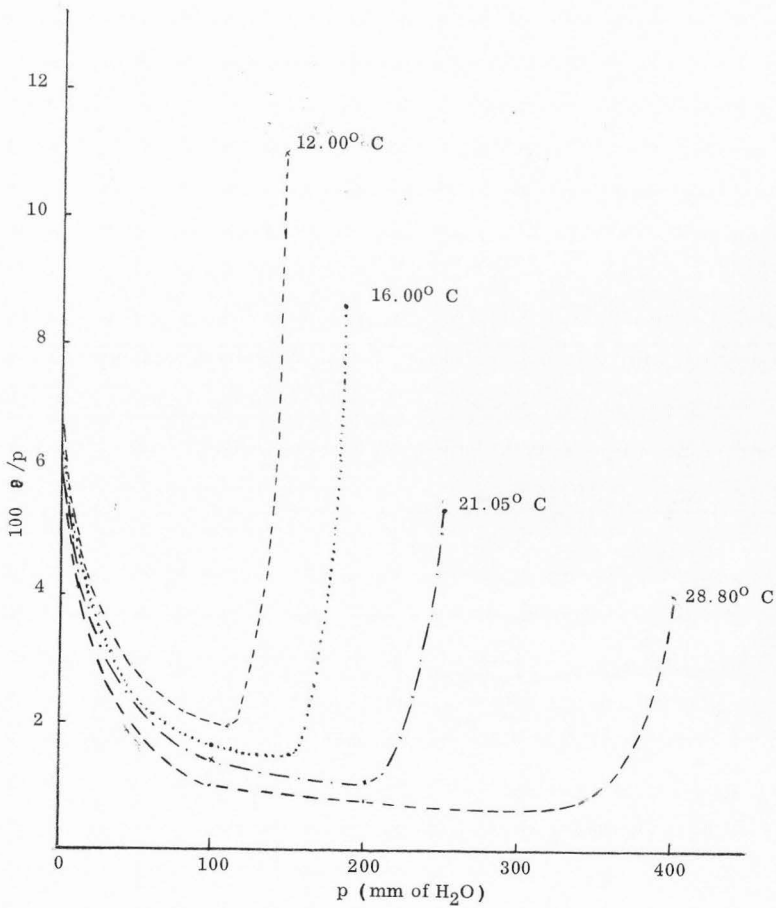


Figure 8. Variation of the ratio of moisture content over vapor pressure with vapor pressure for Millville silt loam

constant surface potential. In order to get this curve, it is first necessary to obtain from the experimental data a curve for vapor pressure as a function of surface potential. This is shown in Figure 9, where the vapor pressure is plotted as a function of  $\phi$  for the four temperatures. At selected values of  $\phi$ , vapor pressure is read from the curve of 9 at several temperatures; and thus Figure 10 was constructed. The integral values of  $(S_{WG} - \bar{S}_W^*)$  and  $(H_{WG} - \bar{H}_W^*)$  for four temperatures, obtained from Figure 10, are presented in Table 5.

#### Heat of wetting measurements

An indication of the relative randomness of soil-water molecules and free-water molecules can be obtained from heat of wetting measurements of moist-soil samples. Heat of wetting data for Millville silt loam, averaged for two or three measurements, are given in Table 6 for three temperatures. These values are between those for bentonite (Zettlemoyer, *et al.*, 1955) and those for Li kaolinite (Kohl, 1962).

The data can be used to determine integral values of  $(\bar{S}_W^* - S_{pw})$  and  $(\bar{H}_W^* - H_{pw})$  from the equations, taken from Jura and Hill (1952) which are in our notation:

$$T(\bar{S}_W^* - S_{pw}) = [h_{aw} - h_{ao}] + \phi - RT \ln p/p_0 \quad [17]$$

and

$$(\bar{H}_W^* - H_{pw}) = [h_{aw} - h_{ao}] + \phi \quad [18]$$

in which  $h_{ao}$  is the heat of wetting of the clean adsorbent;  $h_{aw}$ , the heat of wetting of the adsorbent preadsorbed with  $N_{aw}$  molecules of water; and the

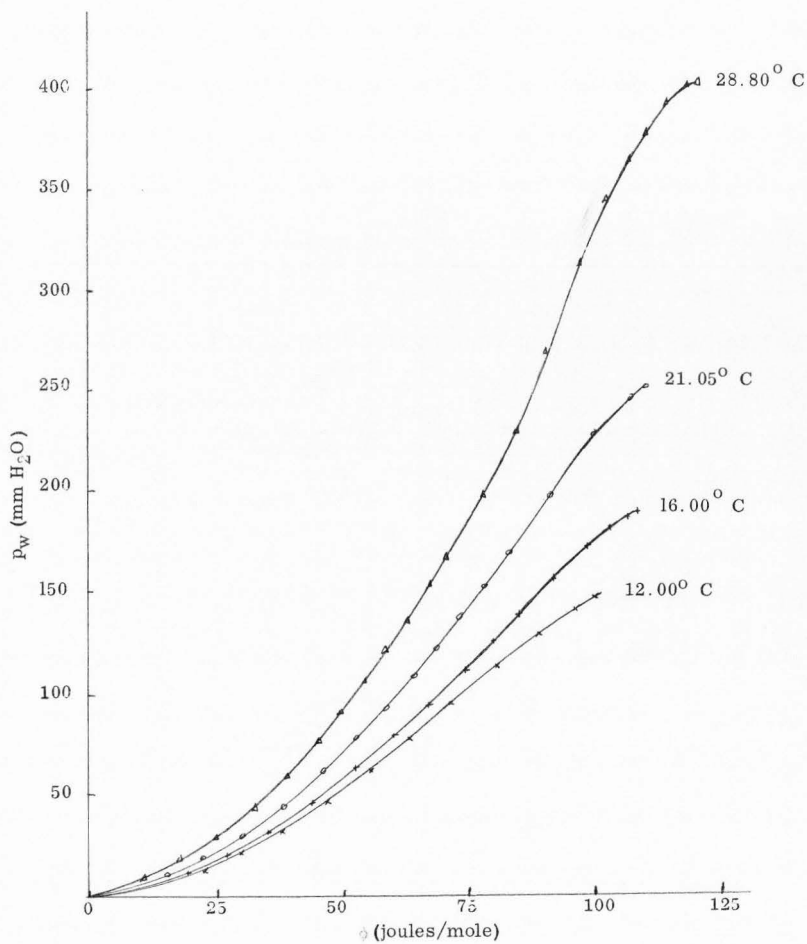


Figure 9. Variation of vapor pressure with surface potential for Millville silt loam at different temperatures.

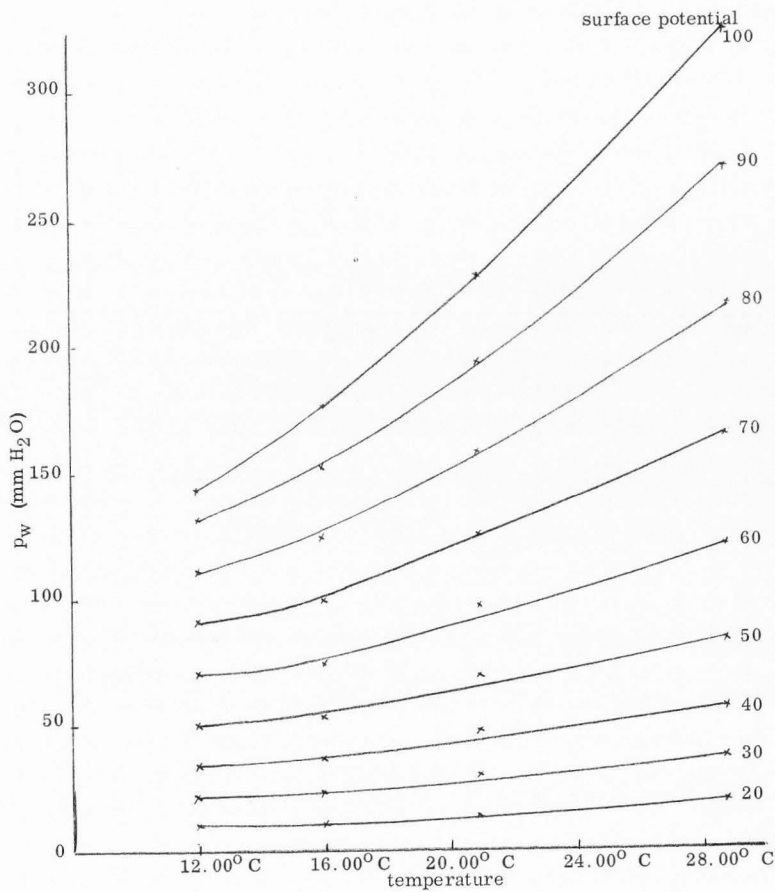


Figure 10. Variation of vapor pressure with temperature for Millville silt loam at different values of surface potential.



Table 5. Integral values of  $(S_{wG} - \bar{S}_w^*)$  and  $(H_{wG} - \bar{H}_w^*)$  for Millville loam at different surface potentials  $\phi$  and four temperatures

$\phi$	12.00°C		16.00°C		21.05°C		28.80°C	
	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$
20	90	20	105	24	120	29	159	40
30	72	16	75	16	78	17	84	19
40	64	15	69	16	75	18	87	21
50	52	12	56	13	61	15	71	17
60	76	20	79	21	83	22	89	24
70	80	22	82	23	85	24	94	26
80	80	22	86	24	93	27	108	31
90	79	22	86	24	94	28	112	33
100	106	30	108	31	110	31	114	34

Units of  $\phi$  are joules/mole;

of  $(S_{wG} - \bar{S}_w^*)$ , joules/mole-degree;

of  $(H_{wG} - \bar{H}_w^*)$ , kilo joules/mole.

Table 6. Heats of wetting of Millville loam samples, with different moisture contents, pre-adsorbed at different temperatures

16.00°C		21.05°C		28.80°C	
Moisture content	Heat	Moisture content	Heat	Moisture content	Heat
%	j/m	%	j/m	%	j/m
2.6	0.0	2.7	0.0	2.5	5.0
2.0	4.5	1.3	6.5	1.1	12.4
0.6	57.2	0.1	78.4	0.2	85.8
0.3	93.8	0.05	93.2	0.1	131.5
0.0	110.3	0.0	126.2	0.0	143.3

subscript pw, pure free water. The  $\phi$  values corresponding with the moisture contents of the samples were obtained from Figures 6 and 9. Using these values of  $\phi$  and the measured heats-of-wetting as given in Table 6, entropy values and enthalpy values were determined from [17] and [18]. These values are presented in Table 7.

#### Psychrometric measurements with varying pressure

Data on the pressure dependence of the total soil-water potential of moist Millville silt loam samples at 21.05 C are given in Table 8. From [13], it is known that the pressure dependence of  $\ln p$  permits calculation of the partial specific volume of water in the system. Similarly, for pure water,

$$RT \left( \frac{d \ln p/p_w}{dp} \right)_T = v_{pw} \quad [19]$$

where  $v_{pw}$  is the specific volume of pure water. When [19] is subtracted from [13], it is seen that the pressure dependence of the soil-water potential gives the difference in specific volume of soil water and pure water:

$$RT \left( \frac{d \ln p/p_w}{dp} \right)_{T,\theta} = \left( \frac{d\psi}{dp} \right)_{T,\theta} = \bar{v}_w - v_{pw} \quad [20]$$

This equation is the same as equation [39] in Bahrani (1963). Values for  $(\bar{v}_w - v_{pw})$  are given in Table 8.

Table 7. Integral values of  $(\bar{S}_W^* - S_{pw})$  and  $(\bar{H}_W^* - H_{pw})$  for Millville silt loam, obtained from heats of wetting

16.00° C			21.05° C			28.80° C		
$\phi$	$\Delta S$	$\Delta H$	$\phi$	$\Delta S$	$\Delta H$	$\phi$	$\Delta S$	$\Delta H$
93	1.1	0	97	1.1	0	104	1.1	0
81	2.3	0	55	9.1	0	99	1.8	0
28	18.4	0	1	45.7	0	6	41.1	0
0	37.5	0	0	53.1	0	7	40.1	0

The units of  $\Delta S$  are joules/mole-degree.

The units of  $\Delta H$  are kilojoules/mole.

Table 8. Total soil-moisture potential and the difference in specific volume of soil water and pure water for Millville silt loam samples at varying moisture contents and for two different values of external pressure and 21.05° C.

Moisture content % dry wt.	Moisture potential at an applied air pressure of		$\bar{v}_W - v_{pw}$ cc/gr
	0 cm Hg	40 cm Hg	
	- joules/kg	-joules/kg	
21.4	200	200	0.0
21.4	210	220	-0.2
17.5	305	310	-0.1
11.9	1400	1400	0.0
9.8	1690	1700	-0.2
8.7	3600	3600	0.0
5.1	6100	6100	0.0

## DISCUSSION

Soil water-potential when measured psychrometrically varies inversely with temperature for Millville silt loam and for two other materials--sand and glass beads--which were tested. This is shown by the data in Tables 2 and 3 and by Figure 5. The inverse relation between potential and temperature confirms the data obtained by Robins (1952) and by Klute and Richards (1962) with sodium saturated montmorillonite.

Kelvin's equation:

$$RT \ln p/p_0 = - \frac{2\gamma V}{r} \quad [21]$$

predicts that the water potential varies directly with temperature. In this equation,  $V$  is molar volume;  $\gamma$ , surface tension;  $r$ , curvature;  $p$ , vapor pressure over the curved surface; and  $p_0$ , the vapor pressure of a flat-water surface at the same temperature as for  $p$ . In general, in applications of Kelvin's equation, it is assumed that the right-hand side of [21] increases (becomes less negative) with increasing temperature. The surface tension of water decreases with an increase in temperature, and molar volume and radius of curvature are assumed to remain constant with a change in temperature. Combination of [16] and [21] results in

$$\Delta u = - \frac{2\gamma V}{r H} \quad [22]$$

It is shown that  $\Delta u$  decreases (becomes more negative) with increasing temperature, contrary to what Kelvin's equation predicts. Shereshefsky and coworkers

(1950) have shown that Kelvin's equation does not predict the right magnitude of the vapor-pressure lowering in some porous materials. Apparently, also, Kelvin's equation does not correctly predict the changes in vapor pressure resulting from temperature changes, because this equation does not take into account the temperature effects on the molar volume of soil water and the apparent radius of curvature of soil water.

It should be pointed out that a decrease in potential with increasing temperature does not contradict the observed experimental result that water moves from hot to cold areas in porous media (Cary, 1961). The flow of other materials, such as solutes, heat, or electricity, may influence the flow of water and cause it to move in a direction opposite to a partial molar free-energy gradient, which possibility was analyzed by Kemper (1961), among others. In those cases, the only criterion for equilibrium is that the entropy of the system is maximal at equilibrium.

The differential entropy values in Table 4 show at all four temperatures an absolute or relative minimum value between a moisture content of 1 and 2.4 percent. A similar minimum in the entropy curves was reported by Martin (1960). These minimum values at low moisture contents may be associated with swelling of the soil. It is, however, impossible to draw any definite conclusions from these differential quantities, due to uncertainties of determination and interpretation (Hill, 1950).

The integral values of  $(S_{WG} - \bar{S}_W^*)$  for Millville loam, given in Table 5 for different temperatures and surface potentials, indicate that the entropy of

water molecules in the adsorbed state is less than the entropy of water in the gaseous state; or, in other words, the water molecules are more orderly in the adsorbed than in the gaseous state. The entropy of vaporization ( $S_{WG} - S_{PW}$ ), where  $S_{PW}$  is the entropy of free liquid water, is about 119 joules/mole-degree at 25° C. The obtained values of ( $S_{WG} - \bar{S}_W^*$ ), given in Table 5, are all, except two, less than 119 joules/mole-degree. This means that ( $S_{WG} - \bar{S}_W^*$ ) is less than ( $S_{WG} - S_{PW}$ ), or the entropy of soil water is more than the entropy of free liquid water (soil-water molecules are, on the average, less orderly than pure free-water molecules). The difference between the entropy of soil water and the entropy of pure water reaches its maximum value for relative dry soil ( $\phi$  values from 30 to 50 joules/mole) and decreases with increasing moisture content (higher  $\phi$  values). This observed difference in entropy values is in agreement with earlier conclusions (Martin, 1960) that sorbed water molecules are arranged less orderly than are free liquid-water molecules.

The two values of ( $S_{WG} - \bar{S}_W^*$ ) in Table 5, which are more than 119 joules/mole-degree, are at the lowest surface potential. This may be associated with swelling of the soil or with hydration of ions, which would make it incorrect to assign the entire entropy change to the soil water.

Some uncertainty exists relative to the calculated values of Table 5. The curves in Figure 8, below a moisture content of 3 percent, are for samples that were prepared by adsorption of water by dry soil exposed to a higher relative humidity; hence, they are adsorption curves. Above a moisture content of 3 percent, the samples were dried from initially wet soil; hence, the curves are

for desorption. The error introduced, due to the hysteresis involved, might have a small but consistent influence on all  $\phi$  values, because they are calculated from Figure 8. The entropy of soil water, however, would still be more than that of free water, even if the  $\phi$  values were as much as 10 percent in error. It is estimated that the  $\phi$  values are more likely about 1 percent larger than they would have been if samples prepared by adsorption of water had been used, also, for the wet range.

The heat-of-wetting values in Table 6 vary inversely with soil-water content. For the samples with zero-moisture content, the heat of wetting was lowest when equilibrium was reached in the desiccator at a lower temperature. The difference in heat of wetting for soil samples with the same moisture content but equilibrated at different temperatures is statistically not significant. The samples with zero-moisture content were obtained in desiccators with  $P_2O_5$ . It has been observed (Puri *et al.*, 1925) that drying of soil samples over such strong desiccants causes a dissolution of calcium salts and organic compounds, exposing a greater adsorbing surface for water. The lower heat of wetting of these samples at the lower temperature might be the result of a temperature effect on the dissolution of the compounds, such that less surface area is available for adsorption of water at the lower temperature.

The entropy data derived from the heats-of-wetting, presented in Table 7, confirm the earlier conclusion that the entropy of soil water is more than the entropy of pure water; hence, the water molecules are less orderly in



soil water than in pure water. The positive difference between the entropy of soil water and pure water seems to reach its maximum value for relative dry soil (low surface potential values) and decreases with increasing moisture content. This was also indicated by the entropy values in Table 5, as was pointed out before. Therefore, with increasing moisture content of the soil, the water molecules become more orderly until they approach in wet soil the orderliness of pure free-water molecules. This is in agreement with the earlier description of the structure of water as it exists in porous media.

Oster and Low (1963), however, concluded from specific conductance studies on montmorillonite that water became less orderly with increasing water contents of the clay, although they did not include any actual entropy values. They attributed the increase in entropy of the system during the hydration process to the water molecules, although it is known that swelling occurs when water is added to montmorillonite. The entropy increase observed by Oster and Low (1963) may be the same as the increase in the difference between the entropy of soil water and pure water upon a change in surface potential from 20 to 50 joules/mole (noticeable in the values of Table 5 and expressed there as a decrease in the difference between the entropy of water in the gaseous state and the entropy of soil water).

The equipment used to determine the pressure dependence of the total moisture potential is not suitable for Millville loam samples drier than about 3.5 percent moisture. For this reason, no values of the surface potential could

be determined to permit calculation of integral values of the partial molar volume of soil water, since, according to [6], this requires  $p = 0$  as the limit of integration. However, the relation between surface potential and vapor pressure is known from the psychrometric measurements for 21.05°C and with no applied air pressure.

It is possible to estimate the values of the surface potential at the applied air pressures of 20 and 40 cm Hg, relative to the value of  $\phi$  at atmospheric pressure. For it is known from Figures 9 and 10 that an increase in moisture potential with decreasing temperature results in a larger  $\phi$  value for the same vapor pressure at the lower temperature. Assuming that a plot of the relation between surface potential and vapor pressure at different applied pressures is similar to the curves in Figure 9, that is, assuming that the curves do not intercept for the different applied pressures, the inverse relation between moisture potential and total pressure (Table 8) should give a larger  $\phi$  value for the same vapor pressure at the lower total pressure. A plot of vapor pressure ( $p$ ) as a function of applied pressure at constant surface potential would then be similar to figure 10 when pressure instead of temperature is plotted on the X-axis.

The dependence of the vapor pressure of pure water ( $p_0$ ) on total pressure can be ignored for the pressure range involved (Guggenheim, 1959, p. 230). Therefore, the direction of the variation of soil water potential ( $RT \ln p/p_0$ ) as a function of applied pressure, under conditions of constant temperature and surface potential,

is known; and an estimated plot of this relation is given in Figure 11. The variation of total soil-water potential with pressure at constant surface potential and temperature permits evaluation of the difference between the integral specific volume of soil water and pure water according to:

$$\left( \frac{d\psi}{dP} \right)_{T, \phi} = \bar{v}_w^s - \bar{v}_w^l \quad [23]$$

which equation is equivalent to [ 20 ] , for conditions of constant surface potential.

The expected increase in potential with an increase in total pressure (Figure 11) suggests that the partial molar volume of soil water is larger than that for pure water. In other words, the density of adsorbed water is less than that of free water, which is in agreement with the entropy data reported in this study and with several density data reported in the literature. Bahrani (1963) concluded that the density of water increased when it is mixed with unsaturated soil. His conclusion is based on the pressure dependence of soil water matric potential, determined with pressure-plate apparatus. This method does not measure the influence of solutes on the system, which Bahrani (1963, p. 57) assumed to be negligible. Another more important consideration, however, is that Bahrani's conclusion is based on interpretation from differential values, which is a questionable procedure (Hill, 1950). The differential values of the partial specific volume of soil water reported by Bahrani (1963) and those reported in Table 8 of this thesis are in good agreement both in magnitude and sign.

One fallacy in the method by which the pressure dependence of the total

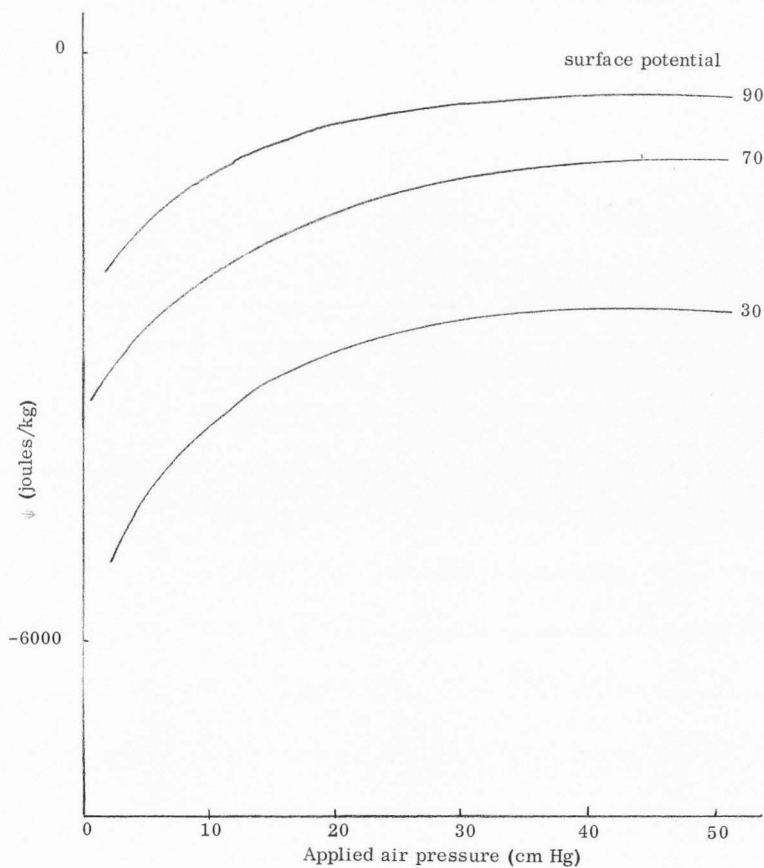


Figure 11. An estimated plot of the relation between soil-water potential and applied air pressure, under conditions of constant temperature and surface potential

soil-water potential was determined in this study should be pointed out. The increase in total pressure was brought about by an increase in air pressure; consequently, the carbon dioxide pressure was increased. Data reported by Reitemeyer and Richards (1944) show that  $\text{CO}_2$  reacts with calcareous constituents of the soil to increase the concentration of Ca and Mg bicarbonate in the liquid expressed from a pressure membrane apparatus with an increase in the applied air pressure. This is confirmed for the Millville silt loam soil by the results of a study by Soane (1958), which showed that the electrical conductivity of the solution expressed from a pressure plate apparatus increased steadily (the salt concentration increased) with applied air pressure and increased temperature. Soane's (1958) data indicate that this effect becomes significant only at applied air pressures of over 2 bars. Nevertheless, the pressure dependence of the total soil-water potential could be due partly to an osmotic effect rather than entirely to interaction between water molecules and adsorbent. The conclusion on the relative values of the partial molar volume of soil water and pure water is based on these pressure-dependence data and is therefore somewhat speculative.

The total soil-water potential of Millville silt loam, as shown by relative vapor-pressure measurements, was seen to decrease with increasing temperature. This could, perhaps, also be interpreted as an osmotic effect due to an increased concentration of solutes in the soil solution. Soane (1958) observed, as was mentioned earlier, that the electrical conductivity of a solution expressed from a pressure membrane apparatus increased with increasing temperature. This

temperature-induced effect increased with applied air pressure and appeared to be very small at atmospheric pressure.

The increase in salt concentration of the soil solution may result from temperature effects on the exchangeable and non-exchangeable ions in the soil. Not much is known about the interaction of water molecules and exchangeable ions and its temperature dependence. There is some evidence that the release of non-exchangeable ions is greatly increased as the temperature increases (Burns and Barber, 1961; Haagsma and Miller, 1963). The concentration of the various ions in the soil solution, however, does not follow the same pattern as the moisture content or the temperature of the soil changes. The total dissolved quantities of some ions increase with the addition of water, while concurrently those of other ions may decrease (Reitemeyer, 1946).

Clay particles which fix cations may have a wide range of bonding energies, because the charge deficiencies on the mineral surface may originate from geometrically and energetically different levels, such as substitution in the tetrahedral or octahedral layer or as broken bonds around the edges. Evidence has been presented that the montmorillonite particles are tied together mostly at their edges in Na systems, whereas in Ca systems the particles are more likely to be bonded surface to surface. Grim (1952) concludes, therefore, that a small amount of replacement of Na by Ca ions, or vice versa, could cause a shift of particle bonds with a consequent great change in physical properties of the system. Variations in bond strength between the particles result in changes in the amount of water that will be adsorbed between the particles.

The temperature-induced changes in the thermodynamic quantities of the soil system which appear to result in an inverse relation between soil-moisture potential and temperature under conditions of constant water content, may, therefore, be attributed to three factors: a) interaction between water molecules and the surface of the adsorbent; b) increase in the release of exchangeable and non-exchangeable ions; c) replacement of specific ions on the soil particles, and a consequent change in the physical properties of the system.

The inverse relation between water potential and temperature was also observed for glass beads and sand (Table 3). These materials do not have exchangeable ions and are supposed to be inert. Jurinak *et al.* (1962) have noticed, however, that an aqueous slurry of the glass beads used also in this study produced a pH of 9.7. Washing with dilute acid temporarily reduced the pH, but after a short time the beads assumed their original alkaline status. From this observation, Jurinak *et al.* concluded that the beads were made of a soluble alkali silicate glass.

Although the sand samples had been washed with distilled water before they were used, there is no assurance that all the materials adsorbed on the silica surface had been removed. Adamson (1960, p. 524) indicates that only repeated adsorption and desorption cycles will remove all adsorbed impurities. Consequently, the possibility cannot be ruled out that temperature-induced osmotic effects resulted in the observed change in thermodynamic quantities of the soil system as well as of the glass beads and the sand samples.

However, several points suggest that the changes in the thermodynamic

quantities are more likely due to an interaction between water molecules and the surface of the adsorbent: first, the close similarity between the observed temperature dependence of the water potential in so diverse materials as Millville silt loam, glass beads and sand samples; second, Soane's (1958) observation that the temperature-induced increase in salt concentration of the soil solution is small at atmospheric pressure; third, Jurinak et al. (1962) showed that poly-molecular adsorption of water takes place on the surface of glass beads, even of Pyrex beads, which they had prepared and which were known to be much less soluble than the commercial beads.

It can be concluded, therefore, that changes in the thermodynamic quantities of the system, which were induced by temperature changes, are primarily due to the interaction between water molecules and the surface of the adsorbents. Osmotic effects may have an additional effect on these quantities, which is of less importance than the interaction effect. Hence, it is justifiable to interpret the observed inverse relation between soil-water potential and temperature in terms of entropy changes of soil water, as has been done in this thesis.



## SUMMARY AND CONCLUSIONS

The temperature and pressure dependence of the total water potential of moist Millville silt loam samples have been studied using a psychrometric vapor-pressure technique, accompanied by a vapor-equilibrium method at low moisture contents. The data, supplemented with heats-of-wetting, are analyzed in such a manner as to arrive at differential and integral entropy and enthalpy values for soil water.

The following conclusions were drawn from these analyses:

1. Total soil-water potential decreases with increasing temperature, for Millville loam and for other materials tested: glass beads and washed sand.
2. Temperature-induced changes in the thermodynamic quantities of a soil system are primarily due to the interaction between water molecules and the surface of the adsorbent.
3. The partial molar volume and the apparent radius of curvature of soil-water are affected by temperature.
4. Differential entropy values show a minimum value between a moisture content of 1 and 2.4 percent, which may be associated with swelling of the soil.
5. Integral entropy values indicate that the soil-water molecules are more orderly in the adsorbed than in the gaseous state, and less orderly, on the average, than in the free-liquid state.

6. Beyond a surface potential of 50 joules/mole, the soil water molecules become more orderly with increasing moisture content and approach the orderliness of free-liquid water molecules.
7. The partial specific volume of adsorbed water is more than that of free liquid water.

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## APPENDIX

## Propositions

## Outline of Defense, Presented February 20, 1963

1. Uptake of potassium by plant roots is an important factor in reducing excess quantities of potassium in the soil.

The occurrence of high potassium contents in soils is rare. Only in a few cases have toxic effects from potassium been reported. There is also evidence that toxicity resulting from high potassium contents may be lessened when offset by high calcium concentrations. In general, high potassium concentrations result in Fe and Mg deficiency.

Excess amounts of K occur frequently, however, in soils which are in equilibrium with sea and brackish water due to long inundations. Examples of such soils are those found in parts of the Netherlands. The ionic composition of sea water that flooded parts of the Netherlands and of brackish water that flooded parts farther inland, is given in Table 9.

Table 9. Ionic composition of sea water and brackish water

	Na	K	Mg	Ca
Sea water	77.2%	1.8%	17.6%	3.4%
Brackish water	76.4%	1.7%	16.5%	5.4%

The exchange complex of two types of soil in equilibrium with these solutions was studied in the laboratory, and the results are quoted in Table 10 (van der Molen, 1957).

Table 10. Exchangeable cations of soils in full equilibrium with solutions

	Percentage of exchangeable cations			
	Na	K	Mg	Ca
Pool soil	41.0%	9.3%	33.7%	16.0%
	34.3%	8.1%	40.4%	17.2%
New land soil	40.8%	11.8%	34.9%	12.5%
	30.3%	10.2%	41.4%	18.1%
	25.1%	8.8%	41.5%	24.6%
Same, original composition	0.2%	5.3%	8.3%	86.2%

K is preferentially adsorbed of the ions present in sea water, as is shown by the percentage of K, which is about six times as high on the exchange complex as it is in sea water. Ca and Mg are also more, and Na is less adsorbed. At increasing dilution of sea water, the percentage of adsorbed bivalent ions increases at the expense of the monovalent ions.

In flooded soils, however, full equilibrium is seldom reached. It is reached only after very prolonged inundations or in cases where flooded soils are falling dry at each low tide and are flooded again at the next high tide. When limited amounts of flood water penetrate, the ionic composition of the penetrating water is considerably altered by ion exchange with the active matter of the soil. The ionic composition of soils inundated for about a year with water of different

salinity (expressed as average Cl content in grams NaCl per liter) is given in Table 11 (van der Molen, 1957).

Table 11. Ionic composition of soils inundated for about 1 year

Salinity of H <sub>2</sub> O	Exchangeable cations			
	Na	K	Mg	Ca
	<i>%</i>	<i>%</i>	<i>%</i>	<i>%</i>
25	27.0	6.4	26.6	40.0
25	20.4	6.3	25.2	48.1
22	20.4	4.6	23.5	51.5
11	9.6	4.0	18.2	68.2
7	8.6	3.2	16.2	72.0
0	1.0	3.5	4.9	90.6

The amounts of exchangeable K are increased by an inundation with salt water from approximately 3.5 percent of the exchange capacity to about 6.5 percent. This means an increase in K in the upper 20 cm of soil of 500 kg/ha for a light soil (exchange capacity of 15 meq/100 gr). This amount would be twice as high for a heavy soil with double the exchange capacity. Van der Molen gives data on controls of gypsum trial fields that can be considered fairly representative for natural regeneration of soil that had been subjected to natural percolation with sea water for about 16 months. These data are plotted as relative amounts in Figure 12 for six years after drainage started. It shows a rapid decrease in soluble salts but slow reduction in K and Mg.

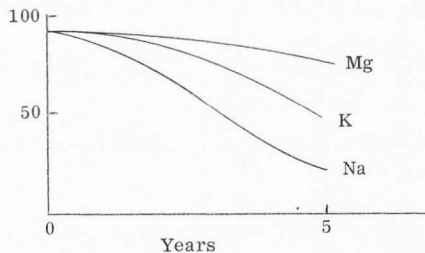


Figure 12. Relative amounts of Mg, K, and Na during regeneration of inundated soils.

Under normal conditions, about 500 kg/ha of K will be consumed during a rotation of three crops of small grains and one crop of sugar beets in about four years. This will be different for flooded soils, but it is reasonable to expect that the excess amounts of K will be exhausted in a few years of cropping. An Na extraction by plants of the same magnitude would diminish the exchangeable Na percentage in the topsoil from 25 to 22 percent only, which is small in comparison with the much larger decrease caused by other processes. It has been shown conclusively that the same general principles are operative in ordinary alkali soils as they are in soils subject to inundation. For that reason, the uptake of K by plant roots can be expected to be important also in reducing excess quantities of K in soils in which there is such an excess due to factors other than inundation.

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2. If we could get information from metabolic processes in the plant cell soon enough, it would give a valuable indication for the proper time of irrigation.

At present we are inclined to focus our attention on the soil in order to determine the proper time for irrigation. When the plant is considered, however, the irrigation schedule is mostly based on the appearance of signs of wilting. Recently, measurements of stomatal aperture by infiltration have proved to be a sensitive indication of the moisture potential.

Two main groups of external factors affect, directly or indirectly, the energy status of the plant moisture: a) the rate of water loss, dependent on atmospheric temperature, wind velocity, light intensity, and relative humidity; b) the rate of water absorption, dependent on soil moisture potential near the roots, the rate of water movement, and the distance over which the water has to move.

At equilibrium, the chemical potential of water inside a plant cell is equal to the chemical potential of the water in the medium around the cell. Again at

equilibrium the latter is determined by the relative humidity of the surrounding air for exposed cells. Higher plants are able to protect themselves from fluctuations in the relative humidity. A potential gradient occurs when there is not enough water in the cell to ensure complete turgidity. The decrease in turgidity is compensated by an increase in the osmotic value of the cell water, i. e., by transformation of starch into sugar.

What physiological processes result in a change in chemical potential? A recent review paper (Kramer, 1963) considers long-range effects. We are concerned, however, mainly with the changes resulting from short periods of drought when we want to use these changes as a basis for irrigation frequency. It has been known for quite some time that before wilting occurs, the amount of monosaccharides and sucrose decreases because of reduced photosynthesis. Gates (1955, 1957) has found that the changes in response to water shortage are initiated relatively early in the drying cycle. He concluded from his studies that the water content is closely related with the active carbon assimilation in leaves, protein synthesis, and active metabolism in the cell. It has been shown that the amount of protein sulphur decreases under conditions of water deficiency. Gates and Bonner (1959) reported an increased rate of destruction of RNA in leaves of moisture-stressed plants, coinciding with decreased accumulation of phosphorus and occurring after one or two days of stress. Similar results were reported by Shah and Loomis (1961).

The structure of protoplasm is considered to be based on intra- and inter-molecular bonds, which join in certain points and are of particular strength.



This structural pattern depends on hydration of the colloid and, hence, on the water relations of plant cells. A remarkable similarity has been noticed between the Watson and Creek model of DNA and the structure of the tetrahedral water lattice (Jacobson, 1953, 1954). A single complex protein molecule can bind to its polar groups (hydroxyl, carboxyl, amino and amine groups) some 20,000 water molecules. Loss of water, consequently, leads to shrinkage of the protoplasm.

Stocker (1960) distinguishes between the shrinkage of the hydrophylic groups of protein molecules during what he calls the reaction phase and the transformations of the protoplasmic structure in the restitution phase. Change in the protoplasmic structure results, in turn, in changes in the enzymatic processes, which affect the metabolic processes, one of which is the breakdown of starch and a concomitant increase in certain sugars. Another observed consequence is a change in relative amounts of proteins and amino acids in favor of the latter.

The works from which the preceding summary was made provide ample proof for the statement that water deficiency has a direct influence on the life processes through a change of the energy status of cell water and an indirect influence through changes in the structure of protoplasm. In order to find in any of these occurring changes a reliable basis for irrigation schedules, it is necessary to be able to distinguish between these phenomena caused by water deficiency and similar changes caused by other factors.

Perhaps it is possible to find, through intensive study, an enzyme whose

activity is uniquely determined by water potential and only to an insignificant degree by other external factors. I do not feel competent to indicate how these perhaps minute changes might be measured. Spectrophotometric measurements appear to be useful for this purpose (Nieman and Poulsen, 1963). Further research in plant physiology seems to contain challenging possibilities in this direction.

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3. The possibility that water movement toward the roots in soils drier than field capacity fills a substantial part of the plants' need for water cannot be ruled out a priori.

There is considerable speculation in the literature about the possibilities for water movement in soils drier than field capacity (one-third bar equivalent suction). Kramer (1962) expresses the point of view probably held by most researchers in this field in saying: "Movement towards roots in soil drier than field capacity is so slow that extension of roots into new soil masses is almost essential for survival." This does not rule out water movement entirely, however.

Absorption of water is initiated and controlled primarily by transpiration. The lag of absorption behind transpiration is determined by the sum of resistance along the path of water movement. The rate of water movement to the root and rate of root growth into moist soils control this lag. The potential drop across the leaf-air boundary is very much greater than the total resistance in the rest

of the plant. The largest fraction of the total resistance in the plant is the resistance across the root surface and in the root itself (Jensen *et al.*, 1961). A solution of the flow equation for movement of water to roots, considering the root as a line source, has been presented by Gardner (1960). He concluded that the conductivity and diffusivity become very small when the suction increases.

In a recent steady state experiment, the suction was measured with tensiometers spaced at depth intervals of 10 cm (Gardner and Ehlig, 1962). Total flux, as determined by rate of supply of water to keep the water-table at -110 cm, is presented in Figure 13. The dotted line denotes the soil flux, as calculated from the hydraulic gradient and the unsaturated conductivity of the soil. The authors point out that the slope of the soil-flux line with respect to depth is a measure of rate of uptake by plant roots. They concluded that, with all species, much water moved upward from the water for 20 to 40 cm before entering the root system, even though roots penetrated to the bottom of the cylinder. Similar results were obtained by non-steady state experiments.

A different growth response of corn seedlings was observed in different mixtures of clay and sandy soil, all having the same soil-moisture (matrix) potential (Peters, 1957). The better growth in finer soils was explained by the higher hydraulic conductivity, but possibly differences in fertility and non-uniform root distribution have influenced the growth rate also.

A plot of transpiration rate versus soil suction for three different soils (Gardner and Ehlig, 1962) supports the hypothesis that water availability is limited by the rate of water transmission through the soil. It is necessary to

know the water-potential gradient near the root. It has been stated that the suction at the root does not exceed soil suction appreciably until the equivalent suction in the soil is above a few bars (Ehlig, 1962, among others). Taylor (1962) estimated that the soil-moisture potential would become uniform in Pachappa soil during the night, if the equivalent suction is less than 1 bar. The estimated lag of the root-water potential behind the soil-water potential is plotted in Figure 14, redrawn from Taylor's paper. This estimation is based on the assumption that transpiration begins immediately at sunrise at the average rate and continues at that rate for 12 hours and then stops abruptly.

The distance water will move to a simulated plant root under certain conditions has been studied by Read (1958). He found that the distance water will move was greater than the limits of his experimental plot (14 cm radius), in the center of which the water was extracted. In Table 12, some of his results are reproduced. The net loss of water per unit volume of soil was nearly uniform at all tensiometer locations.

Suberized roots provide 20 to 30 times as much absorbing surface as unsuberized roots. Therefore, even if  $1/10$  as permeable as unsuberized roots, suberized roots will might be the principal path of entry for water. It should be realized that measurements of the soil matric potential, when measured with tensiometers or resistance blocks, overestimate the actual soil-water potential at the root surface.

I am convinced that psychrometric measurements can give, under controlled conditions, a more accurate value for the soil moisture potential near

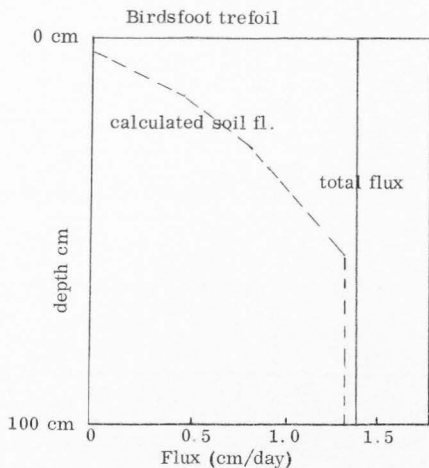


Figure 13. Soil moisture flux as a function of depth  
(Gardner and Ehlig, 1962)

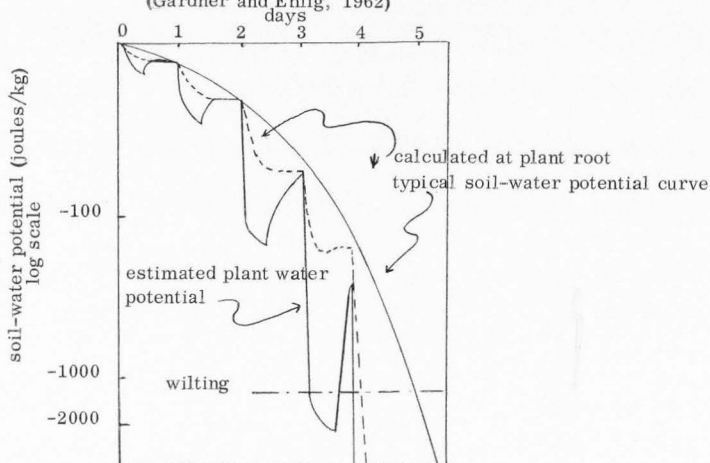


Figure 14. Estimated lag of the root-water potential  
behind the soil-water potential (Taylor,  
1962)

Table 12. Tensiometer readings in cm of water at different distances from suction cup

Time (hours)	Volume (ml)	Distance from suction cups		
		2 cm	8 cm	14 cm
0	0	187	199	200
101	55	348	341	355
155	69.8	427	410	414
239.5	78.4	495	474	480

Volume = volume of water removed from unsaturated loam with extracting tension = 600 cm of water at center cup.

Accuracy = 10 cm of water tension.

the root surface. A careful dissection of the soil near the root surface permits determination of soil moisture potential gradients near the roots at several soil moisture contents and at different evaporating demand of the atmospheric surroundings of the plant. Perhaps other techniques as microwave measurements and gamma ray absorption methods can be adopted for this purpose as well. With such measurements the question of water movement toward roots in soils drier than field capacity can quantitatively be answered.

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4. Seasonal K-values in the Blaney and Criddle formula can be estimated from a curve of the ration of evapotranspiration over evaporation plotted during the season.

Blaney and Criddle's formula provides a method for estimating evapotranspiration of water by irrigated crops. It is an empirical relation:  $U = KF = \sum kf$ , in which U = water used by evapotranspiration.

K = annual crop coefficient

F = consumptive use factor

k = monthly crop coefficient

f = monthly c. u. factor =  $\frac{t p}{100}$

t = mean monthly temperature in °F

p = monthly percent of annual daytime hours dependent on the location

$\sum$ , the summation is made over the months of the growing season

It can be expected that k varies during the season to account for the changes occurring in a maturing crop. Figure 15 gives a plot of the variation of k during the season, calculated from data for 1951-1956 from the Greenville Experimental Farm, Logan, Utah. The seasonal K values and the spread in the maximum monthly k value for six crops are given in Table 13.

Pan evaporation, used also to estimate evapotranspiration, is based on the concept that evaporation from a pan integrates many of the weather factors that influence evapotranspiration. The correlation coefficient between pan

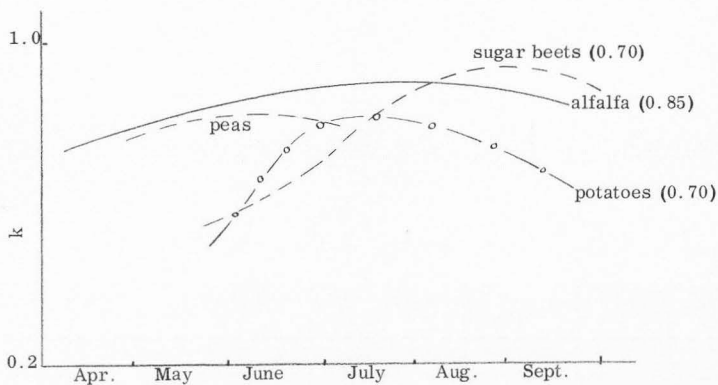


Figure 15. Variation in  $k$  during the season for four crops.

Table 13.  $K$  values and the variation in monthly  $k$  values for six crops

Crop	$K$	Maximum monthly $k$
Alfalfa	0.85	0.95 - 1.25
Corn	0.75	0.80 - 1.20
Cotton	0.70	0.75 - 1.10
Pasture	0.75	0.85 - 1.15
Potatoes	0.70	0.85 - 1.00
Sugar beets	0.70	0.85 - 1.00

evaporation and field evapotranspiration is the slope of the line found by plotting field evapotranspiration versus pan evaporation from controlled experiments. The degree of reliability depends on the number of measurements.

A plot of the dimensionless ratio of evapotranspiration over evaporation during the season is similar in shape to a plot of the seasonal variation of the monthly  $k$  coefficient, since the denominator in both ratios is an index of the potential evaporation. It can be expected, therefore, that crops with a high seasonal  $K$  value are then harvested just after the optimal value of the ratio of evapotranspiration over evaporation has been reached, while crops with a lower  $K$  value are harvested when the ratio has decreased to lower values. This has been found to be true to some extent. Figure 16 shows a plot of the seasonal variation in the ratio of evapotranspiration over evaporation during the growing season.

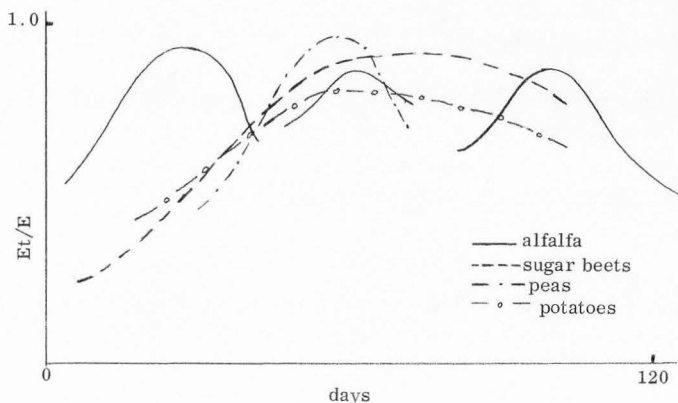


Figure 16. Seasonal variation in the ratio of evapotranspiration over evaporation.

The relation between the area under the curve in Figure 16 and the known K value of alfalfa, sugar beets, and potatoes (Table 14) predicts the following K value: peas 60, sweet corn 60, tomatoes 70 to 75, pasture 80 to 85.

Table 14. Relation between area under ratio-curve and seasonal K-values

Crop	Evapotranspiration days	K-value
Alfalfa	104	0.85
Sugar beets	70	0.70 - 0.80
Potatoes	64	0.70
Peas	33	
Sweet corn	35 <sup>a</sup>	
Tomatoes	72 <sup>a</sup>	
Pasture	99 <sup>b</sup>	

<sup>a</sup>Data from Peck.

<sup>b</sup>Data from Harrold and Dreibelbis.

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5. For a better mutual understanding in the world, it is necessary not to idealize our own situation.

The defense of this proposition consists of a subjective analysis of "our own situation," based on some observations made the last four years in the United States. One observation is basic to my thinking and evaluation of the situation--that is, the dividing of the world into a "black" and a "white" part, a good and a bad. The Salt Lake Tribune on Thanksgiving Day, 1959, carried a cartoon showing Uncle Sam sitting at the table with a turkey on his plate, obviously thanking God for it. The rest of the globe was dark. It is not hard to be thankful with a turkey on your plate, indeed.

Another example is, in my opinion, the frequent use of the words "our great country," most astonishingly used in prayer, where reference is being made to the United States. Identifying the free Western World with a so-called Christian world or considering America a Christian nation are consequences of the attitudes that we are on God's side and that we (the Western World) are a "called" nation.

The same black-white scheme is apparent, also, in our evaluation of heads of states, considering them either demi-gods or devils rather than human beings with human strengths and weaknesses. This view precludes an understanding of Khrushchchev's disappointment after the U<sub>2</sub> incident, when he felt cheated by someone he had trusted after Camp David.

Are we, in our visits abroad, looking for Communists and their conspiracies and focussing on the lack of shoes and on the existence of sheds at the outskirts of foreign cities because we expect to find such conditions there instead of searching for progress being made? The rioting in Japan, prior to the planned visit to Japan by President Eisenhower, was thought to be Communist-inspired; but possibly it was as much a reaction of distrust by the younger generation in Japan against the authority of the prewar, older generation. Were the riots by students in San Francisco some years ago--the so-called Operation Abolition, that is, for the abolishment of the House Committee on Unamerican Activities--Communist inspired? What is Communism? It is, anyway, not the same as Socialism, as many seem to think.

George F. Kennan, in "Russia and the West under Lenin and Stalin," writes: "The first thing to go should be the search for absolutes . . . in world affairs. No other people as a whole is entirely our enemy. No other people at all--not even ourselves--is entirely our friend." Absolutes induce ideologies. We have seen in World War II how ideologies can result in warfare, awakening memories of the great religious wars of past centuries. I do not intend to say that World War II was waged unjustly as a war for justice and freedom against tyranny and

violence. However, this thinking in terms of absolutes fostered a mentality that could support an all-out war where all the means were justified. One example of this was the bombing of some German cities such as Dresden, which appeared later as unnecessary, since such bombings probably did not move German capitulation forward significantly. Perhaps the same could be said of the atom bombing of Hiroshima and Nagasaki. . . .

We are all searching for absolutes, however, and blame others when these persons do not share our point of view. We tell Egyptians that their newspapers and radio broadcasts are biased, as indeed they are, from our point of view; but we forget that the United Press Institute left the United States from the 1956 list of countries where full freedom prevails, on the grounds that a growing tendency on the part of government to suppress and manipulate the news is an indirect form of control. It is hard to be objective with respect to our own case.

Paul Tillich asks in his book, "The Courage to Be," "What is the end of all the magnificent means provided by the productive activity of American Society? The tool as a tool is not important, but rather the tool as a result of human productivity; therefore, the question, for what? cannot be suppressed completely." I think this question "for what?"--what is our individual purpose? what is our national purpose?--still remains to be answered. In the meantime, let us not over-idealize our own situation.

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