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THE INFLUENCE OF SOIL COMPACTION UPON THE
THERMODYNAMICS OF SOIL MOISTURE

by

James E. Box, Jr.

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

of

DOCTOR OF PHILOSOPHY

in

Soils and Irrigation

UTAH STATE UNIVERSITY
Logan, Utah

1961

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James E. Box, Jr.

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INTRODUCTION

The retention of water in soils is a very interesting subject. Soil-water research presents a great challenge to research workers. The challenge is broad in scope and extends from the field problems of large irrigation projects to the atomic scale of the solid-liquid interface.

If scientists are going to describe scientifically soil-water relations, they must ultimately utilize the instruments of science and the language of mathematics. To the end of the latter the mathematics of thermodynamics has been applied in these studies of water retention in soils.

Through the process of theory, experimental studies, and scientific debate thermodynamic expressions have evolved which describe, or attempt to describe, the soil's affinity for water.

The number and definition of the independent variables in such an expression has not been agreed upon. Part of the disagreements are probably due to the complexity of soils and soil materials. However, not only were these variables not fully understood, but often their existence was not even recognized. The result has been some confusion in the literature.

Utilization of the wrong scientific tool may have also resulted in inadequate concepts. For many years the laws of mechanics have been applied to soil moisture studies. There are many references in the

literature where discrepancies between the laws of mechanics and experimental data have been circumvented by adding correction manipulations to satisfy the experimental results. The result has been a lack of unifying concepts which can be applied in all systems. It is possible that the perspective of mechanics has guided many soils researchers down "blind alleys" and left them in positions too narrow in which to turn around. It is presently felt that thermodynamics is general enough to be applied to soils systems, but closely enough associated with microscopic details so one does not lose perspective of what is happening on the atomic level.

Bulk density changes associated with shrinking and swelling have been observed many years. Changing moisture content is generally associated with the bulk density changes. There is also an interrelation with hysteresis. Little thought has been given in the past to the influences of bulk density changes at constant moisture content on the activity of soil water.

This research consists of testing the validity of including a variable of state in a thermodynamic expression which would account for changes in the activity of soil water upon changes in bulk density.

CHAPTER I

HISTORICAL DEVELOPMENT OF THE PROBLEM

The affinity of the soil for moisture has long been recognized as a fact. An attempt to explain factors influencing such an affinity was described by Buckingham (18) in 1907. Buckingham referred to this affinity as the capillary potential, ψ . An explanation of the potential ψ , was made on the basis of mechanics:

$$\psi = \rho gh \quad [1]$$

where ρ is the density of water, g the acceleration due to gravity, and h is the height of rise of water in the capillaries above a free water surface.

It was soon found that the "Buckingham equation," did not completely express all of the variables associated with the soils' affinity for water.

Gardner in 1919 (31), and later Gardner and Gardner in 1953 (35) explained the capillary attraction of the soil particle for water in an ideal case. These developments considered the curved interface formed between two spheres as the principal source of the affinity of the soil for water in an unsaturated system. According to this development pressure under the air-water interface may be expressed by

$$p = 2\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad [2]$$

where p is the pressure, γ is the surface tension, and r_1 and r_2 are the

two principal radii of curvature. The inherent implication is that the pressure, p , in the water at constant temperature is dependent on the two principal radii of curvature. It becomes immediately obvious if moisture content is held constant that any displacement of the soil particles, one with respect to the other, will cause a change in the radii of curvature and thus the water pressure at the air-water interface, if this concept is valid.

Richards in 1928 (77) refined Gardner's concept by recognizing that both adhesive and cohesive forces were associated with the soil's affinity for water.

As studies have developed it has become increasingly apparent that Buckingham's expression of capillary potential was not, although an important start, adequate to express the complete relation of the soil's affinity for water. Richards (77) favored using potential functions similar to electro-static, gravitational, or hydrostatic potentials. Actually, he made an application of Bernouilli's equation and produced the expression

$$\Phi = \phi + \pi \quad [3]$$

where Φ is the total potential, ϕ is the gravitational potential, and π was a pressure term or pressure potential which when taken with reference to "pure free water"¹ and the free atmosphere actually gave a negative value. This pressure term, π , was to represent the "stress" under which the soil moisture was being put as a result of the soil's affinity for water. Actually, Richards related this π term to the

¹Pure free water is taken as a datum in which the water is pure, the air-water interface is flat, and the gravitational force field is acting on it.

capillary portion of the total potential and said that the term was interchangeable with the "hydrostatic potential."

In 1937 Veihmeyer and Edlefsen (92) defined the capillary potential as

$$\psi = \int_A^B f \cos\theta ds \quad [4]$$

in which f represents the force field acting per unit mass of moisture, ds is an element of distance acting along the path, A is a reference point usually taken as a free water surface, B is the point in question, while θ is the angle between f and s . They called this the moisture potential because they apparently realized that the previous uses of "capillary potential" were not entirely correct since other effects were involved. Babcock (3) pointed out that there are logical objections to this definition of ψ .

It is tacitly assumed that the integral on the right represents the mechanical work of transferring water from A to B In addition, the definition does not indicate that ψ is independent of the path chosen, that is, if f is a cohesive force.

In Veihmeyer and Edlefsen's paper they state that the effects of dissolved salt are included in their definition of ψ . Babcock pointed out that, "This would hardly seem the case since the 'osmotic work' of dilution cannot be represented by an integral of the above type."

Day in 1942 (24) realized that the "osmotic" effect must be expressed more explicitly. However, Day chose to use the methods of thermodynamics and defined the total potential or moisture potential according to Gibbs¹ as

$$\mu_1 = \left(\frac{\partial G}{\partial N_1} \right)_{T,P,N_j} \quad [5]$$

¹The thermodynamic symbols of Gibbs (43) will be used throughout this work.

where G is the Gibbs' free energy and N_j is the amount of constituent in the system. (Day's utilization of thermodynamics was probably among the earliest "clear-cut" application of thermodynamics, rather than mechanics and osmotic effects, to an expression of soil moisture potential.) Day expressed the total differential as

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_{P,N_j} dT + \left(\frac{\partial\mu}{\partial P}\right)_{T,N_j} dP + \left(\frac{\partial\mu}{\partial N_j}\right)_{T,P} dN_j \quad [6]$$

where T is absolute temperature, P is pressure, and N_j is the "osmotic effect" as a result of dissolved salts. Day called this "osmotic variable" $d\omega$, and it became known as the omega term.

Edlefsen and Anderson, 1943 (27) presented a thermodynamic treatment of soil moisture and interpreted the results in terms of the effect of adsorptive force fields on the properties of soil moisture. Their thermodynamic expression for the Gibbs' free energy of soil moisture, dG_s , became

$$dG_s = dG_{ps} + dG_{os} + dG_{fs} \quad [7]$$

in which dG_{ps} was given as the component due to pressure and is numerically equal to the hydrostatic pressure. The meaning of the term dG_{ps} was clarified by stating that "The water at the air-water interface (at a particular point) is under a hydrostatic pressure, dP_{ps} , because of the pressure exerted by the atmosphere." The value of the free energy

$$dG_{ps} = VdP_{ps} \quad [8]$$

where V equals the specific volume of water and dP_{ps} equals the total pressure acting on the water at the point in question. We have

$$dG_{ps} = 1 dP_{ps} \quad [9]$$

Edlefsen and Anderson noted that "At the point in question dP_{ps} is only 1 atmosphere and no other external forces are acting upon the interface." The conclusion was that for a particular point in question

$$dG_{ps} = 0 \quad [10]$$

Since the atmospheric pressure does not vary greatly, or measurably, over the length of a soil profile, or column, it is not expected that this term would be of any significance, except for academic considerations, when the soil pores are all open to a free atmosphere.

The second term of equation [7] is that portion of the soil moisture's free energy due to dissolved salts. This becomes the "osmotic" expression and is identical with Day's " ω " term in equation [6]. This term would be absent in a salt-free soil and may be of only minor significance in the usual agricultural soil.

The last term of equation [7] is the component due to the gravitational potential of a particle above the earth's surface. Also, included in this last term of equation [7] is the free energy possessed by water by virtue of its position in the force field of the soil particle. At this point it appears that Edlefsen and Anderson moved from microscopic considerations, which thermodynamics so vigorously requires, to microcopic quantities which are impossible to evaluate in an absolute manner.

In 1955 Babcock and Overstreet (4) gave added impetus to the use of thermodynamics in soil moisture studies. The results produced what seemed more like a supplement to Day's earlier work. The expression developed is identical to Day's shown in equation [6] except a variable has been added for the concentration of water in the system. The concentration

of water is expressed in grams of water per 100 grams of oven-dry soil.

This variable is known as the P_w term and is given in equation [11].

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_{P_w, N_j} dT + \left(\frac{\partial\mu}{\partial P}\right)_{T, P_w, N_j} dP + \left(\frac{\partial\mu}{\partial P_w}\right)_{T, P, N_j} dP_w + d\omega \quad [11]$$

Babcock also stated that "If force fields external to the whole system are present which require consideration, an additional term must be included for each."

More recently Bolt and Frissel (12) have prepared a short treatise on the thermodynamics of soil moisture and have presented two basic perspectives, both of which differ somewhat from those previously presented. They consider both macro and micro analyses. Basic thermodynamic expressions have been employed for both approaches and the final expressions are altered according to the perspective assumed. The basic thermodynamic expression employed is

$$d\mu = -SdT + VdP + d\phi \quad [12]$$

where μ is the chemical potential of water, S is the partial molal entropy, V is the partial molal volume, and $d\phi$ is the influence of the earth's gravitational field on the chemical potential of water.

In their macro approach the water phase is considered as a system by itself, being a body of water with a definite surface, thus separating the water phase from the other phases. In making the consideration the adsorptive forces existing between the solid-liquid interface and the surface tension forces of the air-water interface are added to equation [12], along with Day's ω term for a soil containing salt, such that

$$d\mu = -SdT + VdP_e + d\omega + d\phi + \sigma d\bar{O} + d\alpha \quad [13]$$

in which σ equals surface tension of water against air, \bar{O} equals surface area of the air-water interface permole of water, and α equals energy of adsorption of the water by the solid. P_e is the external pressure on the system as a whole. The last three terms have been referred to as the work terms by Bolt and Frissel. Their micro approach is essentially the same except the mass of water considered is selected in such a manner that it lies "outside the region of influence of all interfaces." The thermodynamic expression is

$$d\mu = VdP - SdT + dw + d\phi + d\alpha \quad [14]$$

and in this case $P = P_e + p$, where p is the internal pressure of the water and, thus, in effect the term $d\bar{O}$ has been incorporated in the VdP term, and the last two terms are regarded as the work term.

After expressing themselves on the semi-idealized case, Bolt and Frissel proceeded to make an application of thermodynamics to the soil and expressed the results as

$$d\mu = VdP - SdT + \left(\frac{\partial\mu}{\partial P_w}\right) dP_w + \left(\frac{\partial\mu}{\partial X}\right) dX + d\phi + dw \quad [15]$$

the only new variable being the X term which represented a "geometry" factor, being further specified as pore size distribution related.¹

In the foregoing synopsis of some of the more important thermodynamic applications to soil moisture studies it can be seen that there is still not unanimity on a thermodynamic expression of the soil's affinity for water.

In certain areas there is general agreement, and in others controversy. It seems to be commonly accepted that the general equations [1],

¹The parenthesis henceforth indicates that all variables except the one represented in the term are to be held constant.

[3], and [4] show major discrepancies when applied to soil-water systems.

The general equations [6], [7], [11], and [15] are related, but have either conflicting interpretations of the variables used and/or variables the other does not have.

It is not difficult to draw the conclusion that there is a good deal of disagreement on the thermodynamic expression for the chemical potential of soil moisture.

The advancement of fundamental soil-water research is dependent on a clearer thermodynamic definition for the total differential of the chemical potential of soil water. The variables to be included as well as the definition for such variables must be more clearly defined.

Before this is attempted it will be expedient to examine the microscopic considerations which may help in formulating any thermodynamic expression for soil moisture. These microscopic expressions are presented in the following chapter.

CHAPTER II

MICROSCOPIC CONSIDERATIONS

In the previous chapter the development of expressions relating to the retention of soil moisture have been presented on a chronological basis with little or a minimum of comment on their validity. Many of these expressions appear to apply to the isolated case for which they were developed, but were later questioned, or disproved, or added to, until the present concepts have evolved.

The approach of Buckingham in which mechanics was utilized was found to be lacking when applied to experimental data. The limitations of mechanics became obvious as it was realized that the forces emanating from the soil particles themselves as well as the gravitational forces were associated with soil moisture retention. As increasing attention was focused on the curved air-water interface, it became convenient to combine mechanics and thermodynamics to describe the observed phenomenon as Richards (77) did in equation [2]. Day (24) later added the effect of salts in the system which is conveniently expressed in a thermodynamic manner. Then in 1943 Edlefsen and Anderson (27) presented an entire treatise on the application of thermodynamics to soil moisture, and the mechanical approach was well on its way out as an accepted expression for the energy of retention of soil moisture. Edlefsen and Anderson seemed to transfer thermodynamics straight from the field of chemical thermodynamics to an application in soil studies without completely reflecting on the implication involved.

A better evaluation of soil moisture relations may be had by examining the microscopic phenomena involved. The study of microscopic phenomena should give a better basis for formulating macroscopic considerations. Swelling of clays will be used as a starting point for these considerations.

It is generally accepted that the compression and swelling of a clay saturated with sodium ions is described by the theory of swelling (11, 13, 50, 56, 96). This theory is based on osmotic effects associated with the adsorbed layer of ions on clays (11).

Hemwall and Low (46) have also examined clay swelling pressure, both theoretically and experimentally. They placed a saturated soil sample in a chamber, allowed the expressed water to flow out, and measured the resulting change in soil water volume. The quantity of water and clay used gave particle spacings of approximately 200 Å. A dilatometer was used in these studies to determine unfrozen water at various swelling pressures. It was found that the unfrozen water increased with swelling and they assumed that this was apparently because of a distribution away from the clay surface of adsorbed ions, and/or force field intensity changes with increases in interplate distance. The study also indicated that external surfaces appeared to be more effective than internal surfaces in preventing the freezing of water.

To bear out the importance of external surfaces, a paper has been presented by Barshad (7) in which he considered the relative importance of water adsorption on the external and internal surfaces of clay particles. From the data he presented he concluded that

. . . the large macroscopic swelling . . . is mainly a manifestation of intermicellar swelling rather than intra micellar swelling, and that the exterior surfaces of the particles rather than the interior surfaces make the macroscopic swelling possible.

Others who have indicated that hydration of the exterior surfaces of the particle is the cause for macroscopic swelling are Bayer and Winterkorn (8), Winterkorn and Bayer (99), Mattson (66), and Barshad (6).

Low and Deming (58) concluded that the hydrostatic pressure in the soil solution depended on the salt concentration in the intermicellar solution, the electrostatic potential in the micella solution, and the distance from the particle. Salt concentration and ions present have been found to influence swelling pressure (13, 46, 96).

The conclusion that there is a definite interrelationship between forces arising from the clay surfaces, clay-water interaction, cations present, water, and air-water interface on the activity of the water in a soil water system is not difficult to arrive at from the work presented. Therefore, it is expedient to consider these interactions individually.

Clay-clay interactions

The diffused double layer will be assumed for clay plates as described by the Gouy-Chapman theory (52, 93), and will be used as a first approximation.

A model can be chosen such that we have two flat parallel clay plates immersed in an electrolyte solution, at such a distance that the double layers interact and influence each other. Verwey and Overbeek (93) have shown that the distribution of the charges and the electric potential function in the liquid between the two plates is altered as the plates are forced together. Their work shows that the double layer

decreases as the plates are forced together; in fact, they stated that ". . . this decrease of the double layer charge may well be considered to be the most important feature in the interaction of two double layers." Their work also shows that the free energy of the double layer increases (becomes less negative) with decreasing charge. To cause this increase in free energy work must have been performed on the system, or in other words: The interaction of double layers give rise to a repulsion between the two surfaces bearing them. That these forces do exist in a clay system has been shown by Bolt and Miller (13), and Warkentin, et al. (96).

Clay-water interaction

There is considerable evidence that forces extending from the clay particle into water have an influence of making the water behave like a rigid material.

Deryagin (25) pointed out that water was influenced by the forces from the surface of mica as far as 1500 Å.

Terzaghi (91) found the viscosity of water to be many times the bulk value in the passage between glass plates 1000 Å apart. Macauley (60) found a tenfold increase in the viscosity of water between glass plates 2500 Å apart.

The resistance of clays to the pressure of a water permeable piston was used as further evidence of the rigidity of layers of water; Norton and Johnson (71) found that the rigid water film in plastic clay averaged 50 Å in thickness under a pressure of 200 pounds per square inch. At zero pressure the water film thickness was estimated to be 300 Å.

Several investigations have reported anomalies in the vapor pressure

of liquids resulting from condensation on solid surfaces, in all cases the anomaly could not be explained satisfactorily in terms of surface tension effects or monomolecular layers. Shereshefsky (82) found that the Kelvin equation for vapor pressure lowering did not account for the decrease in vapor pressure in glass and silica capillaries 2 to 5 microns in radius. The liquids used were water and toluene. If the results were explained on the basis of surface tension, a 23-fold change in surface tension would have been required. Henniker (48) has recalculated the data, using the Kelvin equation, assuming the surface tension and molal volume to be normal. The effective radii were found to be from one-half to one-eighth the true value for silica, and one-seventeenth for glass.

Similarly, Wildson et al. (98) found that the Kelvin equation did not agree with the values of adsorption of water in clays and sands found by hydrostatic tension methods. Wildson et al. (98) accounted for their results by Hardy's (45) concept of the oriented surface layer.

Henniker (48) summarized by saying that, "The surface zone of a liquid is not merely a monomolecular layer with unaltered liquid immediately underneath it, but it is a region in which orientation extends effectively to many molecular lengths.

Gregg (41) did some work on adsorbed surface films and related this to a possible origin of hysteresis. He said that, "It seems reasonable to regard many, at any rate, of the hysteresis effects . . . as having a similar origin, and thus representing a kind of suspended phase transformation." Similar results have been noted by Cassell (19).

Evidence for some regular orientation of the water held on the surface of clay mineral particles is available. The characteristics of

water molecules themselves, according to the work of Bernal and Fowler (9), Bernal and Megaw (10) and Cross et al. (22), indicate that the water molecules would tend to group into a definite network. Forslind (30) has presented diffraction data which seem to provide direct evidence for orientation in the adsorbed water layers on the clay minerals surfaces.

Cationic relations

There seems to be little doubt that the clay particle is hydrated and that the properties of the water of hydration can be altered. There also seems to be little doubt that cations may also be hydrated in a salt solution. However, there seems to be much controversy as to whether cations in the diffuse double layer are hydrated or not.

Hendricks et al. (47) using an X-ray technique and monoionic clays saturated with six different cations concluded that in the magnesium and alkaline earth salts, the first step of water sorption is the hydration of the cation with six molecules of water which is followed by completion of a water layer having a hexagonal type structure. Similar results were obtained for lithium salt except that only three molecules of water were required for hydration of the lithium ion. In sodium, potassium, and cesium salts the cation apparently was not hydrated. This was also true for the hydrogen ion in the clay acid.

Keenan et al. (51) studied the relation between exchangeable ions and water adsorption on kaolinite, and concluded that the cations are not hydrated. The mechanism of equilibrium between a hydrated ion in the bulk and the unhydrated ion on the clay particle was suggested. They

presented the idea that when water is present, the exchangeable ions presumably take up a position determined by the equilibrium between forces of hydration tending to pull the ion out of the lattice and the forces tending to pull the ion into the surface layer of the lattice. They indicated that the divalent ions with their double charge, are more strongly hydrated and will tend to be pulled out of the lattice, this effect decreasing with increasing size. More weight has been added to the work of Keenan et al. by Mooney et al. (69, 70). Cornet (20) believes that the total free energy change between any two states of the lattice may include free energy changes due to hydration of cations, orientation of solvent molecules between the planes, and polarization of molecules between the lattice planes.

Grahame (39) has rather extensively examined the pro's and con's of cation hydration in the diffuse double layer, and has concluded that it does not occur. He feels that the energy required to remove the solvent sheath of the ion is supplied by the approach of the ion to its oppositely charged image.

Grim (42) has developed the idea that adsorbed cations have a special influence on water at the solid-liquid interface which recognizes the lack of cationic hydration in this zone. The cation may determine the actual geometry of the water net, and of very great importance, determine whether the oriented water grades gradually into liquid water or is abruptly separated from liquid water. A slight change in the adsorbed cation composition might cause a destruction of the orientation of some water molecules because the replacing cation would not permit the same maximum amount of oriented water as the replaced cation.

Water

The following is a condensation of some pertinent points from a paper entitled, "Properties of Water Substance," by Rodebush and Buswell (80). The hydrogen atom is capable of forming but one primary valence bond. When this is formed between hydrogen and oxygen, the oxygen atom appears to accumulate an excess of electronic charge and the hydrogen, with a deficiency of electrons, appears to have a positive charge. The positively charged hydrogen is capable of attracting an oxygen atom from another molecule, forming the so-called hydrogen bond which is, compared to the primary valence bond, a weak bond. The hydrogen atom in this bond lies between the two oxygen atoms, but not at equal distance from the two. It is much closer to the oxygen atom to which it is attached by a primary valence bond and to which it may be considered to belong.

Water is one of the few substances which shows a greater density as a liquid than as a solid, and it is perhaps the only substance that exhibits a maximum density a few degrees above the freezing point.

The greater viscosity of ice is due to the fact that each hydrogen is firmly bonded to a single oxygen atom from another molecule; this bond must be completely broken before any movement can occur. The temperature coefficient of viscosity indicates that the energy required to break the bond between water molecules is about 15,070 joules per mole. This is much smaller than that required for a normal hydrogen bond and supports the theory of the partial or multiple hydrogen bond, where each hydrogen is bonded to two or more oxygen of adjacent water molecules. It

is only necessary to break one of the partial bonds at a time in order to permit movement of molecules past each other.

A striking fact is that the heat capacity of liquid water corresponds to the Dulong and Petit value of 25.08 joules per atom. This is the value to be expected when the frequencies of vibration of the atom, which occur at the rate of three per atom, corresponding to the degrees of freedom, are low enough to be excited at the temperature prevailing. The significance of this is that the atoms must be more loosely bound than ice where the structure is rigid. Part of this freedom of motion may arise from the bending of the water molecule from the normal configuration of approximately 105 degree angle. It is possible to accumulate energy in the hydrogen bonds without dissociation.

The picture of water as a largely associated structure of high dielectric constant accounts very well for the extraordinary ability to act as a solvent for electrolytes. Ice has no space in its lattice to permit ions to dissolve but the water molecules can arrange themselves in such a way as to largely neutralize the forces between ions, the hydrogen surrounding the anion and the oxygen the cation.

Water is thought to be a highly associated liquid with a semi-ionic structure. When ions are dissolved because of the powerful electrostatic forces which surround them, the structure of the liquid is broken down and undergoes modification.

The hydration of the cations is explained as due to a cage of water molecules being formed around the cation. The cation, which is positively charged, attracts the oxygens of two water molecules quite strongly. If the cation is small enough (smaller than the potassium ion) so that the

volume of the ion plus two water molecules is comparable to the methane molecule, then a cage of water molecules forms around this group as a nucleus. The attraction of the ion for oxygen atoms polarizes the central water molecules and increases the hydrogen bonding tendency so that a second layer of water molecules is attached in a symmetrical rigid shell. The number of molecules bound may be very large. If the cation is too large, the shell cannot form. Anions may attach one or more water molecules by hydrogen bonding; but the hydrogen bond does not propagate through adjacent water molecules and the shell does not form.

Air-water interface

Briggs (15), in trying to develop a concept of the mechanics of soil moisture, conceived the idea that capillary water existed as a continuous and tightly stretched film around the particles. The forces arising from the curvature of these capillary water surfaces (air-water interface) were visualized as the principal cause of the retention of soil moisture. Naturally, this retention would then be dependent upon the number and size of the capillary spaces. According to this concept, water movement takes place from the thicker to the thinner films; and the rate of movement is related to the difference in curvature of the films, the surface tension, and the viscosity of the liquid. No doubt Buckingham (18) had this concept in mind when he described his capillary potential.

It was from Briggs' concept that many early soil moisture concepts arose, and possibly the loci of many present misconceptions concerning

soil moisture. Briggs and McLane (16) developed the moisture equivalent expression, Briggs and Shantz (17) introduced the idea of the wilting coefficient, Widtsoe and McLaughlin (97) differentiated three phases of soil water, and Zunker (100) and Lebedeff (55) proposed classification of soil water, all of which were based primarily on the capillary-tube hypothesis. Gardner (32,33), along with his associates (36, 37, 77, 78, 79) did much to extend the capillary-tube concept into the present day. The concept became so extensive that a full size treatise could be written on this subject alone. The present presentation is by no means complete.

Bouyoucos (14) made an early criticism of the "capillary-tube" concept as a result of work studying the movement of water under thermal gradients where a maximum movement at a specific moisture content was found. Being unable to explain the change in flow by changes in surface tension or viscosity, he assumed that the soil had a great adhesive force for water.

Donat (26) found some inconsistencies in the capillary concept when he tried to calculate pore size distribution from soil moisture suction. He reported pore sizes that were 1.92 to 2.21 times as large as the actual pores, but failed to recognize the inconsistencies and tried to explain them on the basis of pore geometry.

Keen (50) and Parker (25) both criticized the capillary concept of soil moisture to some extent, principally on the basis of experimental data. Keen showed that the amount of unfree water varies with the moisture content. Parker proved that the soil does not render this unfree water

from functioning as a solvent. He also pointed out that the relation of vapor pressure, evaporation, freezing point depression, and the adsorbing power of seeds for moisture all show similar phenomena when compared as functions of moisture content. Although Parker's curves showed definite energy relations he apparently succumbed to the prevailing ideas and concluded that the capillary concept was satisfactory.

Stewart (83) compared the change in suction with temperature, and showed that it was greatly different from that predicted from surface tension changes.

From the literature presented in this section and the section on clay-water interaction, it is felt that theory and experimental facts completely antiquate the capillary concept; and that further use of this concept can only mislead researchers.

The concept seems to be one born of necessity, used to the limit by vigorous advocates, and which must ultimately be discarded because of theoretical and experimental facts which not even its strongest proponents can deny.

Temperature and the clay-water system

The fact that temperature influences the activity of soil water is easily established. Some of the more recent work is that of Gardner (34) in which he placed a tensiometer in a moist soil sample, fluctuated the temperature, and observed a change in soil moisture suction. Taylor and Stewart (89) repeated the study by Gardner and examined it using thermodynamic expressions (86). Their examinations showed that the energy changes which resulted from heating were the result of entropy and enthalpy changes of the soil water.

Soil moisture movement may also result from temperature gradients in the soil. Taylor and Cavazza (88) showed that flow of moisture in the soils from warm to cold regions might occur largely in the vapor phase. Subsequent to the work of Taylor and Cavazza, Taylor¹ designed an experiment in this laboratory to demonstrate that in an unsaturated system where a thermal gradient was established along a horizontal moist unsaturated soil column, liquid water moved from the cold to the warm end of the column. Such an apparent anomaly proves to be strikingly interesting. These relations are undoubtedly associated, at least in part, with surface phenomena.

Verwey and Overbeek (93) have given a relation for the change in electrical potential, ψ , of the colloids as a function of distance from the colloid, x , and absolute temperature, T , to be

$$\psi = \frac{4 kT}{ve} e^{-Kx} \quad [16]$$

where v is the valency of the positive ion present, e is the elementary charge of an electron, and k is the Boltzman constant. Kappa, K , is a constant which is also temperature dependent and is given by the equation

$$K = \sqrt{\frac{8 \pi n e^2 v^2}{\epsilon k T}} \quad [17]$$

where ϵ equals dielectric constant of the medium and n is the number of ions per cm^3 far from the colloid surface.

Assuming a homoionic aqueous system equation [16] and [17] may be effectively simplified to equation [18] :

¹This experiment has been demonstrated repeatedly in the Soil Physics Laboratory at Utah State University since 1954.

$$\psi = c_1 T \frac{1}{e^{c_2 x \left(\frac{1}{T}\right)^{\frac{1}{2}}}} \quad [18]$$

From equation [18] it is seen that as the temperature increases, ψ increases at any position of x . It is also seen that as x increases, ψ decreases for any particular temperature.

Schalek and Szecevari (see Kruyt, 52, p. 366) have shown that on increasing the temperature of a hydrophobic colloid suspension the time required for thixotropy to occur was shortened.

Henniker (48) feels that thixotropy in suspension of solids may well be a manifestation of long-range forces extending out from or between solid particles; but the possibility of a skeleton of particles being present prevents the general phenomenon of thixotropy being included as evidence of deep surface orientation. However, if thixotropy is a phenomenon associated with the electrostatic surface forces you would expect the thixotropy to be more apparent as these forces are effectively increased. This is what happens as the temperature is increased.

Temperature changes may also influence the cation concentration at the solid-liquid interface. According to Verwey and Overbeek (93) this relationship is given by equation [19] for a negative surface as

$$N_+ = N \exp(V_+ e \psi / kT) \quad [19]$$

From this relation it is seen that the cation concentration decreases in the diffuse double layer as the temperature increases.

CHAPTER III

THEORY

As was pointed out in Chapter I, there is disagreement in the definitions and inclusion of some of the variables contributing to the thermodynamic description of soil moisture. However, it should also be pointed out that the disagreements are not so much ones of a fixed position by any individual or group of individuals, but rather disagreements generally incurred during the evolution of any important concept. Therefore, it is not the intention of this chapter to "tear apart" any one concept for the mere sake of destruction, but rather to critically examine each of what is felt to be the more important concepts; and formulate a new concept which is more descriptive of soil moisture. It is felt that each concept mentioned here is an important step in the evolution of describing the thermodynamics of soil moisture.

In Chapter I attention was focused on expressions of Day, Edlefsen and Anderson, Babcock and Overstreet, and Bolt and Frissel. These are equations [6], [7], [11], and [15], respectively.

There is at least one variable which the equations all have in common and the interpretation of which seems to be in good agreement. This is the variable for the influence of temperature on the chemical potential of water.

The pressure variable is one which is now included in all expressions, but lacks unanimity in agreement as to exactly what pressure to

which reference is being made. Day does not discriminate and merely calls it the pressure term; Edlefsen and Anderson call it the atmospheric pressure; and Babcock and Overstreet first indicated it to be the atmospheric pressure (4), but later (5) added the hydrostatic pressure gradient which included "the gravitational field and the walls of the container of the soil."

Babcock and Overstreet (5) thought that they had conclusive proof of their external pressure implications which they used in the pressure term of equation [11]. They cited the data of Luthin and Miller (59) who studied the moisture distribution in a soil column, when the bottom of the column was placed in a free water surface. According to the "Buckingham" equation [1] the capillary potential increases with height above the water table. If equation [1] holds, ψ goes to zero as h goes to zero; therefore, it is expected that the soil would become more nearly saturated as the free water surface is approached. However, this was not the case in Luthin and Miller's data in which the moisture content, P_w , actually increased from right above the free water surface to about 30 cm, after which it began to decrease. Similar results have been observed by Wadsworth and Smith (94), Lambe (53), and Croney and Coleman (21).

Babcock and Overstreet's theory (5) was that the pressure distribution along the height of the soil column was sufficiently great on the soil water, between 30 and 0 cm. to actually cause a decrease in moisture content in the soil as the free water surface was approached. The resulting equation was

$$\frac{dP_w}{dh} = \frac{-Mg + V \frac{dP}{dh}}{(\partial\mu / \partial P_w)} \quad [20]$$

where V is the partial molar volume of water and dP is the change in external pressure along an element of the soil column dh . Thus "Buckingham's equation" would apply only when $dP/dh = 0$, the implied assumption being that this pressure of the surroundings was being transmitted directly to the soil water, even though the system was not completely saturated and was open to a free atmosphere. This assumption is undoubtedly true for the saturated case (84) but appears to fail in the unsaturated case. If one visualizes a capillary open at both ends and partially filled with water, and a pressure is applied to the capillary which uniformly reduces its diameter, it can readily be seen that the water will be displaced along the length of the capillary. Any change in water vapor pressure results from the change in curvature of the meniscus caused by a decrease in capillary diameter at constant temperature.

It is concluded then that the only pressure which should be included in Babcock's pressure variable is that of the atmospheric pressure acting on the soil water at the air water interface, all mechanical pressure being excluded except possibly in the saturated case.

Equation [7] has a variable in it which none of the other equations include. Edlefsen and Anderson have included a term which relates the influence of the soil particle's force field upon the chemical potential of soil water.

Just recently a paper has been written by Waldron et al. (95) which emphasizes the importance of these force fields on soil water. They studied water retention in homogeneous packs of known size glass beads and moisture suction. The suction range from 0 to 20 bars was studied. Fisher's method (29) for theoretically calculating the capillary pressure

of the water for given moisture contents was used. The experimental values of moisture content and corresponding suction were obtained. It was found that a large difference existed between the experimental and theoretical values. For any given suction there was a greater amount of water retained under experimental conditions than could be accounted for theoretically on the basis of capillarity. They concluded that:

The theory thus excludes the adsorptive mechanism as a contributor to the energy status of soil water. Then the departure of the experimental data from the Fisher theoretical curve might be interpreted as a measure of the adsorptive potential, which would be dependent, evidently on water content. It seems conceivable that the Fisher theory might provide a correct evaluation of the hydrostatic tension of the water in the bead systems, and by difference between experimental and theoretical data, an estimate of the adsorptive potential. (29)

There is little doubt that this does occur. However, these force fields are microscopic and not macroscopic in nature. Because of this, the validity of including the force fields about the soil particle, which might influence the free energy of soil water, is questioned from the standpoint of a thermodynamic application to soil moisture over the growth range of plants.

There is little doubt that the force fields extending from the surface of soil particles influence water molecules in the close proximity of the soil particles. Anderson and Low, 1958 (1, 57) studied the density of water at distances between 10 \AA and 84 \AA of the clay surface and found that the density of water decreased as the clay surface was approached. In addition to this, they also found that the cation adsorbed on the surface of the clay had an influence on the density of water. The influence of the adsorbed cation and water adsorbed by the soil particle has also

been observed by others. Mooney et al. 1952 (69, 72) found from the desorption isotherm of water vapor at 20° C., on homoionic mono- and divalent montmorillonite, that the exchangeable ion influences the amount of water adsorbed at a given pressure. Other investigators have found this same response (23, 38, 51, 72, 73, 74). It appears that if the force fields extending from the surface of the soil particle is to be considered as influencing the free energy of soil moisture, as has been done in equation [7], then this variable includes other microscopic effects such as that of adsorbed ions which must be separated out. To do such would completely ignore the macroscopic approach of thermodynamics, and introduce so many interacting variables that a sound conclusion would be prohibited.

Equations [11] and [15] have separated a composition variable for the influence of moisture content from the composite summation of all composition variables common to all equations. Equations [6] and [7] do not contain this variable explicitly. There seems to be little disagreement at present that a variable to express the influence of moisture content must be included.

Examination of Babcock and Overstreet's moisture content variable proves interesting. It was recognized that as the concentration of soil moisture in the system changed, the curved interfaces of the moisture films also changed; and thus the pressure in the liquid phase was a function of moisture content. Apparently Babcock assumed the soil system to be a porous, rigid mass because no reference is made to shrinking and swelling. When the occurrence of shrinking and swelling is considered along with changes in moisture content, the curvature of the air-water

interfaces becomes not only a function of moisture content, but also a function of the resulting displacement of the soil particles with respect to each other. Shrinking and swelling, or bulk density variation, with soil moisture content has been commonly observed for some time, a few of many references to such are (23, 49, 54, 76, 90).

To evaluate the possible influence of overburden pressure on the soil bulk density and water retention, it is necessary to examine the various experimental techniques used. Babcock and Overstreet made an attempt to collect their own experimental data; however, their data did not give the desired experimental results and they resolved the problem by using Luthin and Miller's data (59), as previously mentioned.

Luthin and Miller's method (59) used a soil column 122 cm. long and was assembled by fastening brass cylinder sections together. Each section was 5.08 cm. long with a 7.32 cm. inside diameter. Special plastic sections were made to accommodate tensiometers. A brass screen was placed in the bottom section and covered with a layer of glass wool to hold the soil in the column. The columns were packed in place by allowing the soil to fall from a funnel into the column. During the filling of the columns they were tapped to settle the soil.

Fireman, 1944 (28) using the Yalo fine sandy loam (Luthin and Miller used the Yalo loam) found that a continual composition response to impaction occurred. According to Fireman, soil placed in the soil columns by the method used by Luthin and Miller would be more dense on the bottom of the column than the top. As the soil texture becomes increasingly coarser, the influence of compaction by impaction is not continual, according to Fireman. Therefore, sands would reach the maximum density

to which they could be brought by a particular compaction method fairly quickly. Then, instead of the sand at the lower end of a column as described by Luthin and Miller, getting more dense, the density would reach a maximum and this zone of maximum density would increase in length from bottom to top of the column upon continued compaction.

Lambe (53) conducted a drainage study almost identical to that of Luthin and Miller using sand instead of loam soil. Lambe found that, just as Luthin and Miller did, the percentage saturation of moisture in the column increased as column height decreased until about 25 cm. above the free water surface when the percentage saturation decreased to the free water surface. However, the decrease in percentage saturation of the sand was of the order of only 8 to 9 percent, while that of the loam was approximately 25 percent, the slope of the curve being much greater in the case of the loam than that of the sand.

Babcock (3) was extremely careful in obtaining a uniform bulk density in his soil columns. After filling the column with soil, investigations of bulk densities within the column were made and a "nearly uniform pack was obtained . . . which showed only random variations from top to bottom."

It is interesting to note that an investigation of Babcock's (3) data shows that there was only a small difference in moisture distribution over the vertical length of the two-foot columns and no such condition as a decreasing moisture content to the free water surface from any point along the column, as described by Luthin and Miller (59).

It may be concluded, then, that changes in water vapor pressure can be a function of change in atmospheric pressure, and/or a change in

effective sizes of the capillaries in which the soil water is being retained. It seems to make little difference that the size of the capillary in which the water exists is due to a drying or wetting of the soil, or to shrinking and swelling of the soil. In fact, it seems more logical to include an expression in equation [11] which would allow for bulk density changes. From this point of view the change in curvature of the meniscus upon drying or wetting is not only a function of changes in moisture content of the sample, but also of the resulting changes in bulk density of the sample, and only becomes a singular function of moisture content when a rigid porous mass is considered. In the event of the latter case, the air-water interface retreats into smaller pores upon drying and vice versa for wetting. This "retreat" is apparently somewhat curtailed in soils within the plant growth range because shrinking and swelling occurs.

To solve the dilemmas of equations [6], [7], [11], and [15], an additional variable is proposed which circumvents the above contradictions. The new variable to be included in the expression for the chemical potential of soil moisture in an unsaturated soil open to the free atmosphere at a particular point in the earth's gravitational field is shown in equation [21].

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right) dT + \left(\frac{\partial\mu}{\partial P}\right) dP + \left(\frac{\partial\mu}{\partial P_w}\right) dP_w + \left(\frac{\partial\mu}{\partial \rho_B}\right) d\rho_B + \sum_j \left(\frac{\partial\mu}{\partial N_j}\right) dN_j \quad [21]$$

where T is the absolute temperature, P external pressure, P_w is moisture content, ρ_B bulk density, and N_j a composition variable.

All of the variables included in equation [21] are independent variables of state, i.e., each can be varied independent of the other.

The first four variables on the right-hand side of equation $[21]$ must be included in all porous, non-rigid, and unsaturated soil systems at a fixed position in the earth's gravitational field. The fifth variable on the right-hand side of equation $[21]$ is a composition variable, and may or may not be included, depending on whether the system's composition is dynamic or static, or contains additional variables of state which influence the chemical potential of soil moisture.

Temperature

The variable for temperature is generally accepted as being one which influences the soil moisture. The exact influences of temperature on soil moisture are not clearly understood in every case. Experimental results demonstrating that temperature does influence the chemical potential of soil water have been given by Taylor and Cavazza (88), Taylor (85), Gardner (34), and Taylor and Stewart (89).

A few of the far-reaching implications of the temperature influence on the soil system are given in Chapter II. Not only may temperature influence the activity of the water, but it may also have other influences on the system. Equation $[16]$ demonstrates the influence of temperature on the electrostatic field of the soil particle.

The exact nature or extent of these temperature influences on the chemical potential of soil water are not known. However, as pointed out in the clay-water section of Chapter II, the soil particle does have a definite influence on the soil water. It is anticipated that much additional fundamental research is needed in this area.

Pressure

The pressure term in equation [21] is defined as the external pressure on the water in the system. In the event that the system is open to the free atmosphere, the term would be the atmospheric pressure to which the system is subjected.

In many fields of chemical thermodynamics it is often the policy to correct all expressions to sea level, i.e., an atmospheric pressure of one bar; although, ideally the change in pressure (dP) may be considered as the change in pressure along the vertical profile of the soil system. For all practical purposes this will be zero in soil moisture studies.

Bulk density

The fourth term on the right-hand side of equation [21] is one which has not been included explicitly in the other expressions, although Bolt and Frissel approached it in equation [15]. They introduced a displacement, χ , variable for soil geometry and they related it to pore size distribution. However, they give no hint as to how this variable is to be measured.

When considering the water held in the soil system, it is necessary to consider not only the capillary concept, but also the influence due to the adhesive forces between clay and water, force fields arising from the clay particles, and the interaction of these clay particle forces with each other on the chemical potential of soil water. The relations are complex.

The macroscopic quantity, bulk density, is possibly an index to the

manifestation of these complex relations. Bulk density is a quantity which is measurable and can be varied independently of the other variables in equation [21].

It has been proposed in a paper by Taylor and Box (87) that the anomalies observed in the distribution of moisture in a soil column are due to bulk density changes.¹ The expression is given in equation

$$[22]: \quad - \frac{dP_w}{dh} = \frac{V dP/dh + M_E + \beta dR_B/dh}{(\partial\mu/\partial P_w)} \quad [22]$$

where V is the partial molar volume of water and β is $\partial\mu / \partial R_B$.

Equation [22] will describe the anomalies of moisture distribution in a soil column on the basis of bulk density changes in the column. This approach also justifies the elimination of the perplexing definition Babcock and Overstreet gave their pressure term in equation [11].

The inclusion of bulk density as a variable in the equation for soil moisture potential requires proof which the study reported here is designed to provide.

Composition

The fifth variable on the right-hand side of equation [21] is one for composition. This variable has been recognized, at least in part, by several of the previous workers. The recognition is principally centered around dissolved solutes.

Day (24) was probably the first to formally recognize the effect of dissolved salts on the chemical potential of soil water. Day called this his omega term. The omega term is included in equation [6].

¹The paper was prepared from research done for this thesis.

Edlefsen and Anderson (27) recognized the effect of dissolved solutes and merely included it as the osmotic effect, which is shown in equation [7].

Bolt and Frissel (12) expanded Day's omega term to include the influence of adsorbed salts and salts in the bulk solution. They correctly recognized that changes in moisture content may alter the relationship between adsorbed salts and salts in the bulk solution. It is felt that Bolt and Frissel have projected, to a limited extent, the perspective of Verwey and Overbeek (93). There is probably a need to more fully expand the concepts of Verwey and Overbeek in the area of the solid-liquid-solute interactions. Such has been done to a limited degree in Chapter II of this thesis. There is little doubt that more fundamental soil-water research needs to be done in this area which incorporates temperature relations. It may be possible to incorporate Marshall's (61, 62, 63, 64, 65, 67) clay membranes to an advantage. However, a very critical evaluation of clay membranes may limit their usefulness.

Babcock and Overstreet (4) have also included Day's omega term per se in their expression. This is shown as the fourth variable in equation [11]. They referred to this term as a composition variable for ions in solution. In addition to this effect of ions in solution it was also recognized that any change in the composition of the soil during the course of a study such as microbial population, organic matter, and the aggregation state, would have to be included. There was no variable explicitly recognized for this purpose.

In the equation proposed in this thesis for the total differential of the chemical potential of soil moisture, there is included a variable

merely defined as to include all composition variables not described by the first four terms on the right side of equation [21]. Conceivably, there is a large number of relatively minor variables which are normally held constant during the course of an experiment which could be included in this term.

Conclusions

The term soil geometry seems to carry with it the connotation of meaning only the arrangement of clay particles. However, in a normal soil many substances may be present which effectively contribute to determining the activity of soil water. In addition to the clay particles there may be present oxides, adsorbed and dissolved solutes, organic matter, microbes, etc., all of which contribute as the enveloping environment or matrix which influences the activity of soil water.

We suggest, then, that the portion of the matrix potential which may be altered by bulk density changes be referred to as structure potential. Structure is a word which has a clear and fully established meaning in soil research.

The objective of the experimental study conducted here is to evaluate the influence of bulk density changes on the matrix potential of soil water.

CHAPTER IV

EXPERIMENTAL APPARATUS AND PROCEDURE

The objective of the experimental apparatus used in this study was to allow mechanical pressure to be applied to a soil sample while the air pressure within the sample remained the same pressure as that of the free atmosphere, and at the same time permit measurements of changes of soil volume and moisture status.

Both saturated and unsaturated soils were used in this study; therefore, equipment was designed to make the desired measurements under both conditions. The apparatus used for study of the saturated soil was of different design to that used for the unsaturated soil. Each, along with their procedures, will be discussed independently in the following portions of this chapter.

Experimental apparatus for saturated soil

The apparatus designed to squeeze saturated soil is shown in Figure 1. The design is such that when the sample is squeezed the air pressure in the chamber will remain the same as that of the free atmosphere, water can freely exit the sample and run into a calibrated capillary tube, and then water may re-enter unimpeded as the squeeze pressure is released from the sample. By this method only mechanical pressure is applied to the sample.

The chamber in which the sample is placed is composed of a lucite cylinder, a lucite ring, a rubber membrane, a cylinder head, and a cylinder base.

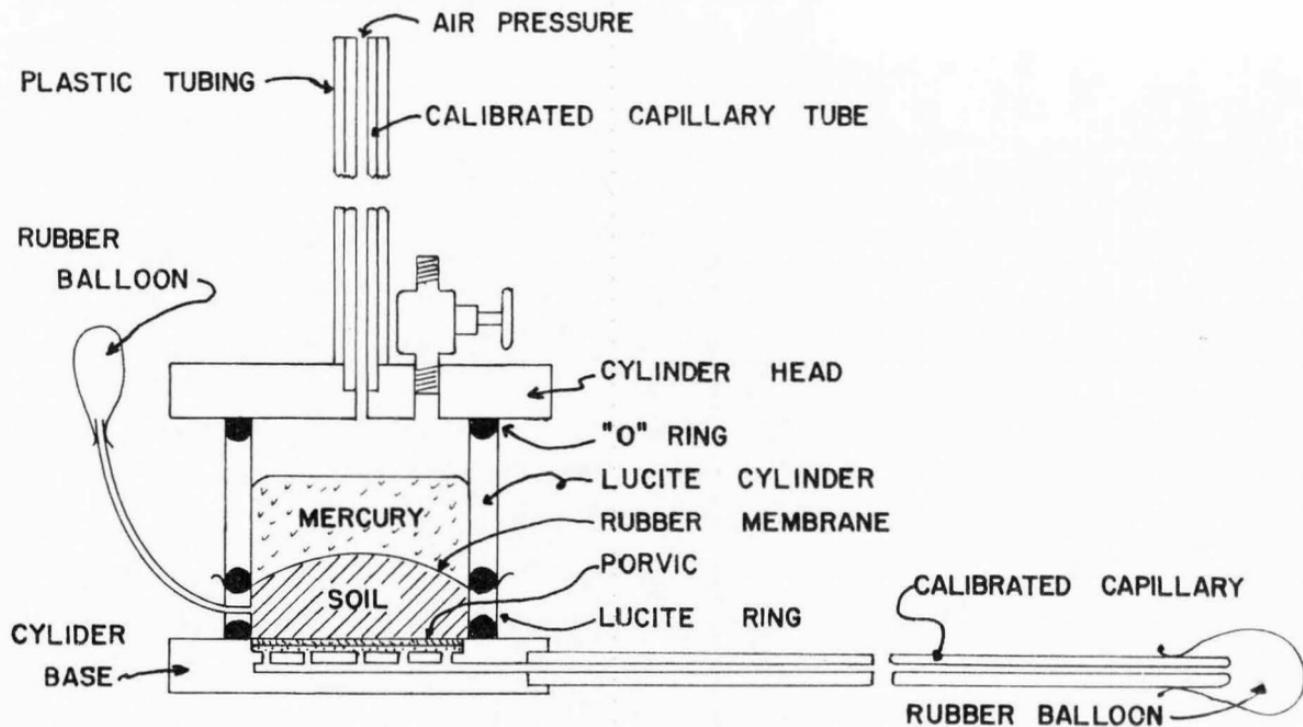


Figure 1. Apparatus for squeezing saturated soil samples and measuring resulting fluxes of soil and water volumes after successive compression and decompression cycles

The lucite cylinder and ring are made of a plastic tube which had an outside diameter of approximately 5 cm. and a wall thickness of 0.7 cm. The lucite cylinder is approximately 3 cm. long and the ring 0.75 cm. long. The ring had an air port hole drilled in it which had a very small plastic tube cemented into it. The air port tube was covered with a rubber balloon to prevent evaporation of water from the soil sample.

The cylinder head and base were made of lucite plastic which was approximately 2 cm. thick and 7 cm. square. The cylinder head had a hole in the center. A capillary tube was cemented in this hole with epoxy resin. The cylinder base was fixed so that water could run through it and into a calibrated tube which was cemented into the base. The base had a recess machined in it which was the same diameter as the inside diameter of the lucite plastic cylinder. Small water ports were drilled in this recess which emptied into the calibrated tube. To prevent the soil sample from being forced through the water ports, a fine mesh screen covered by porvic was placed in the recess. The soil sample was positioned upon the porvic. A rubber balloon covered the end of the calibrated tube to prevent the evaporation of water and at the same time allow the air pressure in the tube to be the same as the free atmosphere at all times.

The entire unit was held together by the use of four steel bolts. Holes had been previously drilled near the four corners of the cylinder head and base. A rubber "O" ring was used to seal each joint.

Experimental procedure for saturated soil

A saturated soil sample of approximately 25 grams (oven dry basis) was placed in the squeeze chamber. The sample had been treated with 1 gram of bichloride of mercury to 100 grams of oven-dry soil.

The soil sample was confined into the bottom portion of the chamber and against the porous porvic by a rubber membrane. The rubber membrane was just covered with mercury. Water was placed on top of the mercury until the calibrated capillary tube was filled to the desired height. Care was taken to remove all air from the system and the compression cycles were started.

The soil sample was maintained at constant temperature with 0.01° C. for temperatures of 10° C., 20° C., and 30° C.

The soil sample was successively compressed and decompressed in increments up to a total pressure of 5 bars. The compressive force was supplied from air pressure applied to the free end of the capillary tube cemented in the cylinder head. Each increment of pressure was applied until no further change in bulk volume or moisture flux could be recorded and then decompression was accomplished by releasing all of the mechanical pressure on the soil sample. Again, the status of decompression was permitted until equilibrium had been recorded.

The change in bulk volume was measured by recording the change in height of a colored water column in the calibrated capillary tube.

Water flux was measured by a change in water level in the calibrated tube which was cemented to the cylinder base and connected to the water ports.

Experimental apparatus for unsaturated soil

The experimental apparatus is basically designed to squeeze a moist soil sample, and in such a manner that the change in soil moisture suction and bulk volume can be measured. The experimental apparatus consists of a squeeze apparatus (Figure 2), a null point tensiometer (Figure 3), and a constant temperature air bath (Figure 4).

The squeeze apparatus consists of five basic components: a) a compression cylinder and piston, b) a null point tensiometer and brass cylinder head with tensiometer plate, c) pneumatic press, d) a steel frame for support of the unit, and e) an air bath for maintaining constant temperature. A diagram of the unit is shown in Figure 2.

A Carver press cylinder and piston was employed for squeezing the moist soil sample. The cylinder had an inside diameter of 2.88 cm. and length of 7.63 cm. Although the results obtained were satisfactory, it is felt that a stainless steel cylinder and piston would have been more desirable. There was a tendency for the soil material to react with the cylinder walls which resulted in the piston "freezing" at times.

The null point tensiometer is, in principal, similar to the one described by Miller (68) and is shown in Figure 3. The purpose of a null point tensiometer is to prevent water flux between the tensiometer system and the soil system upon a change in the soil matric potential. A reduction in water flux is accomplished by incorporating two sylphon bellows and an optical lever in the tensiometer system. The sylphon bellows are used for two purposes. One of the bellows is used to change the volume of the tensiometer system to compensate for changes in activity

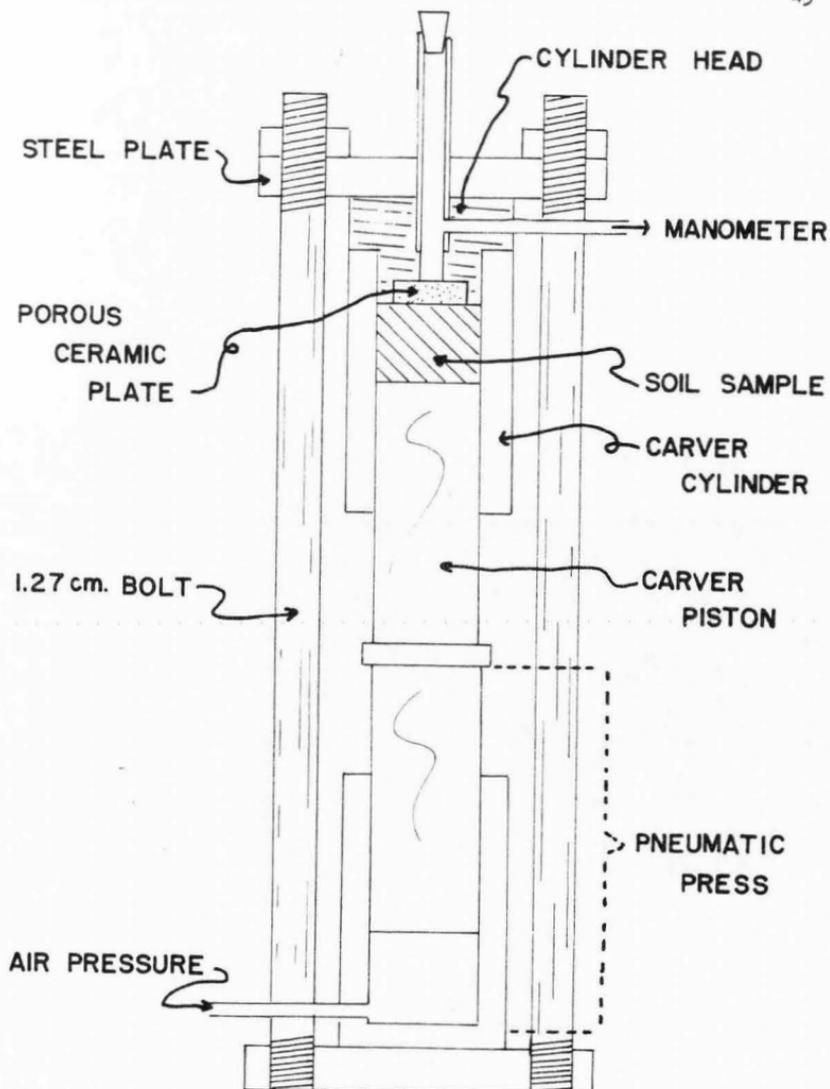


Figure 2. Sectional view of compression apparatus used for compressing unsaturated soil samples

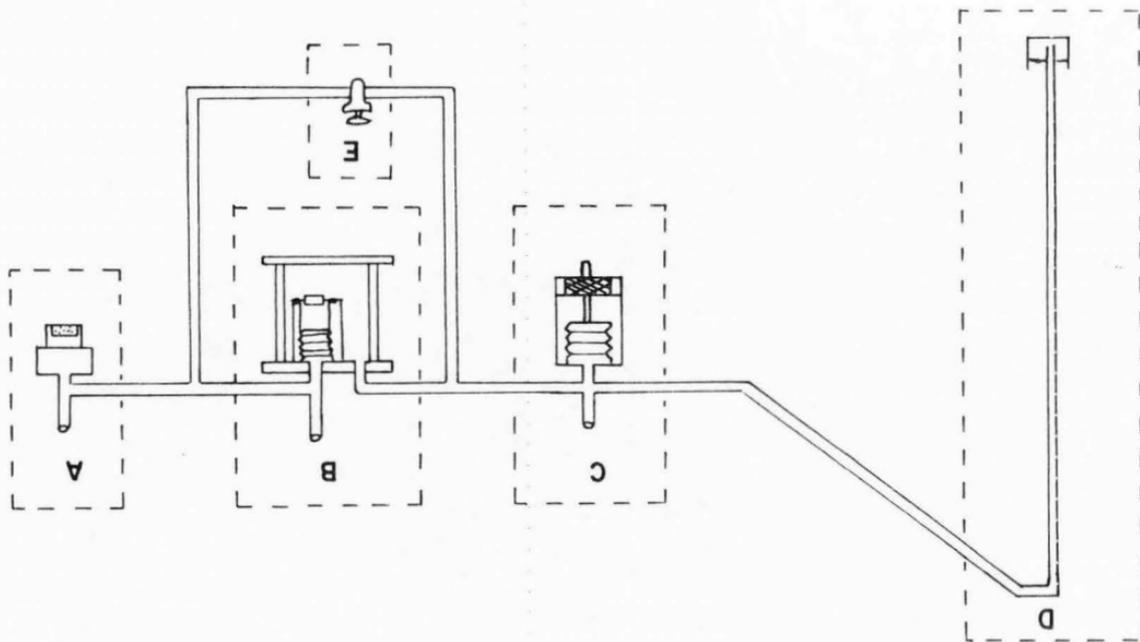


Figure 3. Null point tensiometer system used to detect changes in matric potential of the unsaturated soil

of the soil water. In this way the mercury in the manometer capillary was manually adjusted to the proper differential height before there could be a flux of water between the two systems.

Details of the null point tensiometer used in this study are shown in Figure 3. A porous ceramic tensiometer plate approximately 1.5 cm. diameter and 0.5 cm. thick is located in the cylinder head at (A), an optical lever and associated bellows are shown at (B), compensating bellows at (C), mercury manometer at (D), and high vacuum stopcock with mercury seal at (E).¹

The tensiometer plate was attached into a recess 0.6 cm. deep and 1.7 cm. in diameter machined into the face of the brass cylinder head with epoxy resin.²

The optical lever (B) used for finding the null point was included in an air-tight chamber of lucite plastic and a metal plate which bolted over the only open end of the chamber. There were two ports of entry into the chamber and they were through the metal plate. One port located in the center of the plate had a syphon bellows fused over it in such a manner so that the bellows extended into the chamber. An optical lever was attached to this bellows in the manner of Miller (68).

The air-tight chamber was constructed from a lucite cylinder having an inside diameter of 5 cm. and length of 10 cm. A lucite plate 0.7 cm.

¹Two-way stopcock with mercury seal and made of pyrex brand glass, obtained from Fisher Scientific Company.

²Armstrong's A-1 epoxy resin with activator A was used with a high degree of success. Manufactured and sold by Armstrong Products Company, Argone Road, Warsaw, Indiana.

thick was laminated to the bottom of the cylinder. Sufficient overlap of the brass and plastic plates from the lucite cylinder was left to permit the using of four 0.64 cm. x 10 cm. steel bolts; synthetic rubber gaskets were used to make the system air-tight.

A test of the sensitivity of the optical lever to changes in volume of water in the tensiometer system was made. The image from the optical lever was cast on a chalk board, a distance of 2.25 m. away. A change in suction of 1.0 cm. of water displaced the image on the chalk board by 1.54 cm. The image could be adjusted to approximately 0.1 cm., or 0.065 cm. of water suction. The scale on the mercury manometer could be read to 1 cm. of water. The capacity of the capillary tubes used for the mercury manometer was calibrated. It was found that a flux of 0.1 cm.³ of water represented a displacement in the capillary manometer tube equivalent to 114 cm. of water suction. An image displacement of 0.1 cm. was calculated to correspond to a flux of 5.56×10^{-5} cm.³ of water. The permeability of the ceramic tensiometer plate was checked and found to be 2.85×10^{-3} cm.³ min.⁻¹, or a flux of 5.65×10^{-5} cm.³ per 1.2 sec.

The influence of the detectable flux of water given above on the soil sample equivalent in size to 20 grams of oven dry soil was evaluated. A water flux of 2.82×10^{-4} percent or greater would have been detected. According to work reported by Ashcroft and Taylor (2), using the same soil as used in this study, a change in soil moisture suction from 0.3 to 0.4 bars represented a change in moisture of 2.03 percent. A flux of 2.82×10^{-4} percent of soil moisture represents a change in

suction of 1.39×10^{-5} bars for the soil used. Therefore, the null detector was adequate for the study being conducted since suction measurements could not be read closer than 1×10^{-4} bars.

The compensating bellows (C) was obtained from an automobile radiator thermostat, was 4 cm. in outside diameter, and would extend approximately 3 cm. in length.

The bellows arrangement, tensiometer plate, and manometer were all connected with copper tubing. All joints of metal to metal were fused with silver solder. Above each bellows and at the cylinder head a glass tube was attached to the tensiometer system with tygon tubing for purposes of removing air. The glass tube fit snugly against a copper tube of the same diameter, 1.0 cm., and was stoppered with a synthetic rubber stopper. The high vacuum stopcock was also joined to the copper tubing with two pieces of tygon tubing. In all cases, the glassware was fitted snugly against copper tubing of the same diameter. In this way, it was impossible for the tygon tubing to contract a significant amount when a differential pressure existed between the inside and outside of the tensiometer system.

The high vacuum stopcock (E) was used in adjusting the optical lever to the desired initial position. Air removal from the system was facilitated by the use of the stopcock. It may be noted that air removal from the system was further facilitated by alternately flushing the system with cold and hot degassed water.

The air bath, as shown in Figure 4, employed for maintaining constant temperature, was constructed of styrofoam (a solid plastic foam

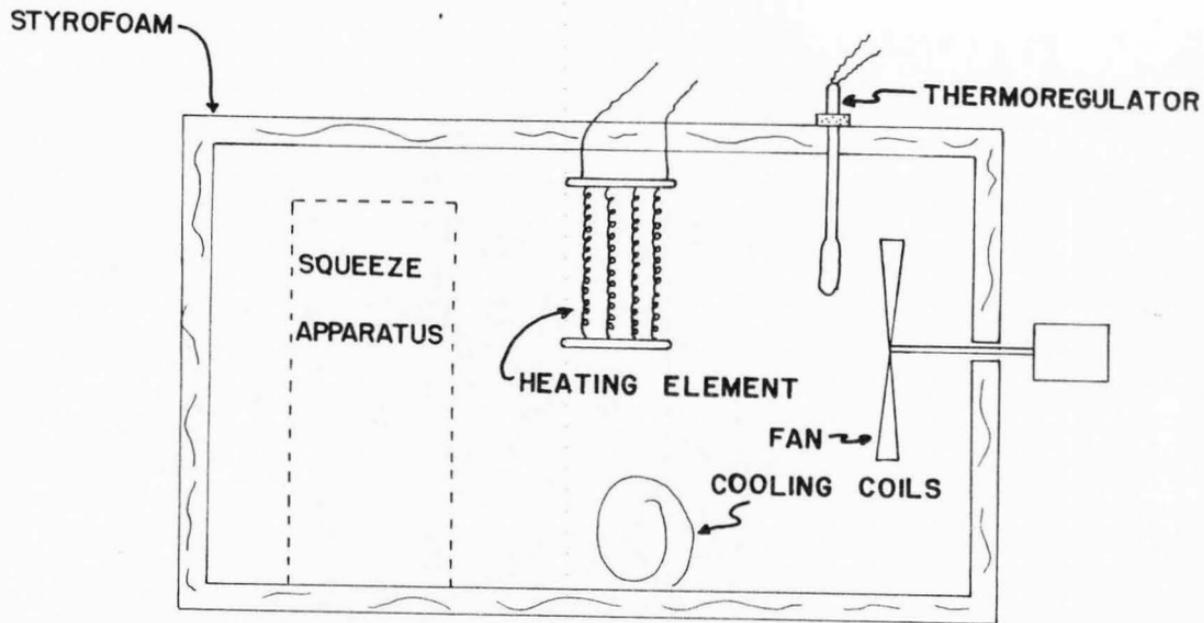


Figure 4. Air bath for controlling temperature of the compression apparatus

impermeable to air) and aluminum foil. The styrofoam walls of the air bath were 5 cm. thick. Both sides of the six walls were covered with aluminum foil. The styrofoam was cemented together by using Elmer's glue, a white liquid plastic which does not solvate the styrofoam.

By using the styrofoam to restrict flux of conductive heat energy and the aluminum to restrict radiant energy exchange through the walls, a good constant temperature bath was obtained.

The temperature in the air bath was maintained by using a constant cooling coil which cooled to a temperature slightly below that which was desired, and heating coil which could be activated and deactivated by a thermoregulator, sensitive to $\pm .005$ degrees centigrade, connected to a super sensitive relay. Observations of a thermometer in the air bath sensitive to $\pm 0.05^\circ$ C. revealed no observable temperature variations. The soil samples were encased in heavy metal cylinders; therefore, it is reasonable to expect that soil sample temperature variations were much less than $\pm 0.05^\circ$ C. A small fan was used to circulate air in the air bath.

Experimental procedure for unsaturated soil

Soil samples of known moisture content were weighed, placed in a Carver press cylinder which was assembled in the compression unit. The soil sample was subjected to alternate compression and decompression cycles.

Soil samples of the Millville loam were taken from the Greenville experimental farm in the vicinity of North Logan, Utah. Soil samples were obtained in the southwest field and about 30 yards south of the

large wooden barn. Whole soil was used which was taken from the top 15 cm. of the surface. The soil was stored at constant temperature in a 105 mm. artillery powder can and the top securely fitted. The sample was about 10 kilograms in size and at a moisture content corresponding to approximately one-half bar of suction.

Three samples of approximately 500 grams each were extracted, water added to bring the moisture content to that desired, and stored in covered desiccators to allow for equilibrium. Moisture contents of approximately 19 percent, 17 percent, and 15 percent, were used in this study. At the time the 500 gram samples were taken, bichloride of mercury was added to each sample at the rate of 1 percent by weight. The purpose of the bichloride of mercury was to inhibit or eliminate microbial activity in the soil sample both prior to and during the squeezing process.

From the 500 gram sample, a moist subsample was taken containing soil material approximately equivalent to 20 grams of oven dry soil. The subsample was placed in a Carver press cylinder, the cylinder affixed to the cylinder head and mounted in the unit frame. A check was made to assure that the soil was in good contact with the tensiometer plate by gently applying pressure with the fingers to the Carver cylinder piston. After good contact between the soil and the tensiometer plate was assured, the unit located in the air bath was first brought to 25° C. and the compensating bellows manually adjusted to maintain the image from the optical level at a predetermined position. These adjustments were made until equilibrium had been reached and no more displacement of the image could be observed. After equilibrium at 25° C. had been reached, the readings

of bulk volume and suction were recorded, the bath temperature adjusted to the desired new temperature, and the manual adjustments repeated until equilibrium had been reached once again. After readings had been made at the new temperature, a pressure increment was applied and the manual adjustment process repeated. This procedure was repeated until a maximum of 27 bars of pressure had been applied to the sample.

The experiment was done in triplicate for three moisture contents, at three different temperatures.

It should be noted that only mechanical pressure was applied to the soil sample. The cylinder head was machined to fit loosely in order that the air pressure in the soil sample would be in equilibrium with that of the free atmosphere.

Moisture evaporation from the sample was eliminated by placing stopcock grease on the cylinder piston, a thin film of stopcock grease on the inside cylinder walls, and a thin film of stopcock grease over the external joint between the cylinder head and cylinder.

CHAPTER V

RESULTS

The results show the influence of confining pressure on bulk density for both saturated and unsaturated soil. In the unsaturated soil relations between soil matric potential, moisture content, temperature, and bulk density are shown. Data are presented in graphic form.

Thermodynamic relations were used to calculate relative partial specific entropy, ΔS_w , and enthalpy ΔH_w . The thermodynamic data were calculated for only the soil sample containing 19 percent moisture.

Results for the saturated soil

Figures 5 and 6 show the influence of alternate compression and decompression on the bulk density of saturated soil. The data are given for 10° C. in Figure 5 and 30° C. in Figure 6. It can be seen that in all cases compression decreased the soil's ability to hold water. The bulk density upon decompression was always less than that of the associated previous compression. However, each decompression bulk density was greater than that of the previous decompression bulk density.

Results for unsaturated soil

The results are shown in Figures 7, 8, and 9. It may be noted that in all cases compression had a definite influence on soil moisture matric potential. The influence of compression was not the same in all cases. The changes in soil matric potential upon compression may be altered by temperature also.

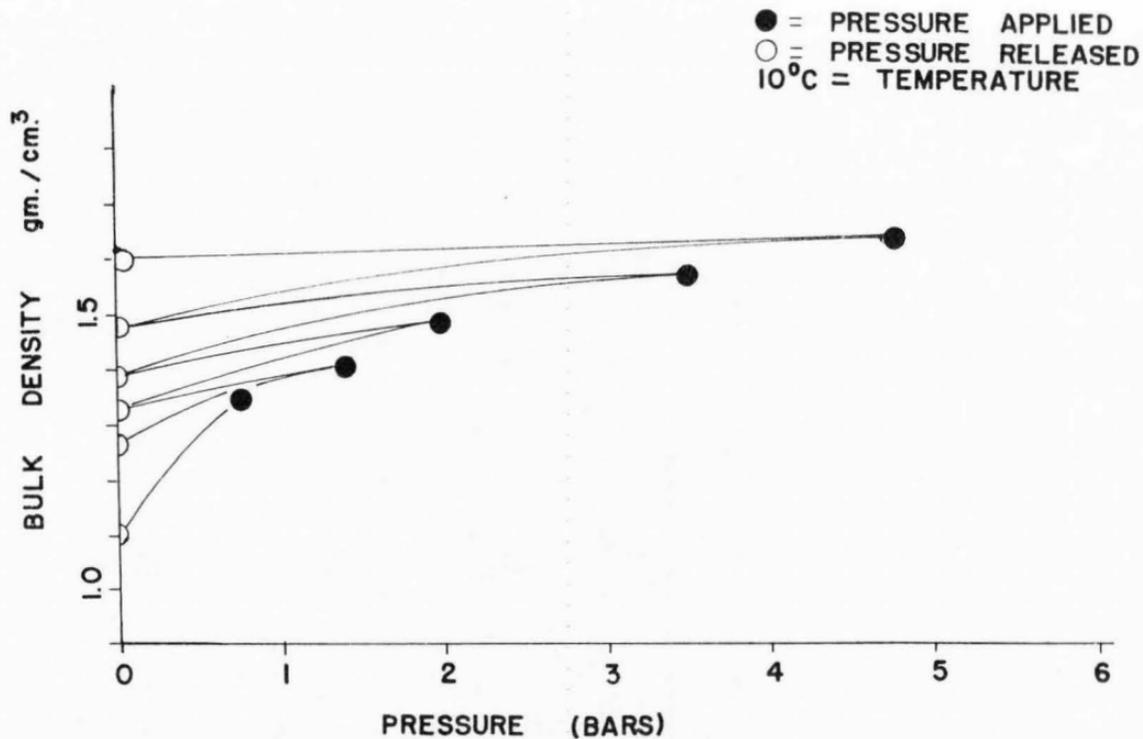


Figure 5. The influence of alternate compression and decompression on saturated soil at 10° C.

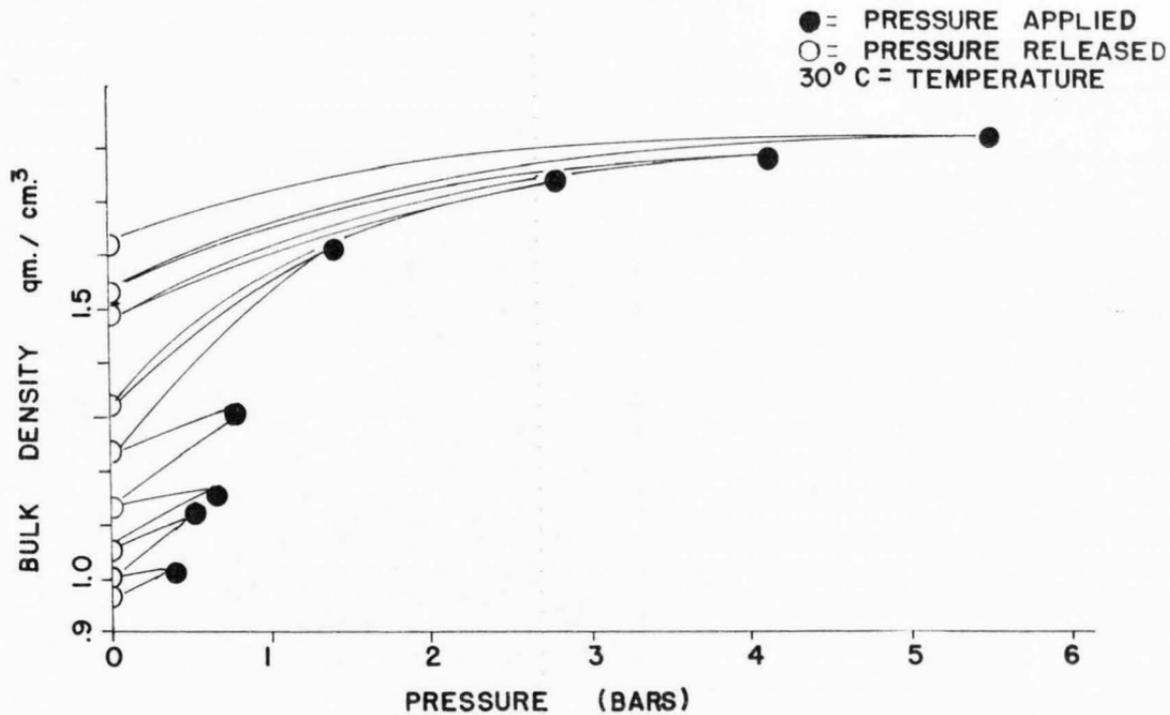


Figure 6. The influence of alternate compression and decompression on saturated soil at 30° C.

The results for compression of a sample at 19 percent moisture content are shown in Figure 7. From this figure it can be seen that the principal influence is one of temperature. The displacement of the curves for the various temperatures is the most obvious influence. It can also be seen that compression had the greatest influence on matric potential at 10° C., and least at 40° C. over the range studied. There seem to be no abrupt changes over the range studied.

Figure 8 gives compression results for a soil sample at 17.2 percent moisture content. The results in this case are more apparent above bulk densities of 1.50. The influence of compression is greatest at 40° C. and least at 10° C. The 25° C. sample occupies an intermediate position.

Figure 9 shows results very similar to those of Figure 8. The sample compressed at 40° C. gave a curve which was much the same general shape as that at the same temperature and 17.2 percent moisture.

The influence of compression on the 10° C. and 25° C. was not as drastic as that of the 40° C. sample. All of the samples in this figure appear to initially show a decrease in matric potential upon compression, after which continued compression shows an increase in matric potential

Figure 10 is essentially identical with Figure 8, except that the sample compressed at 10° C. shows a peculiar response in that the curve crosses over the 40° C. and 25° C. curve. The results are felt to be real; however, no explanation is readily apparent. Taylor (86) has shown similar relations. In Taylor's study the activity of soil water was plotted as a function of moisture content at two temperatures (7° C.

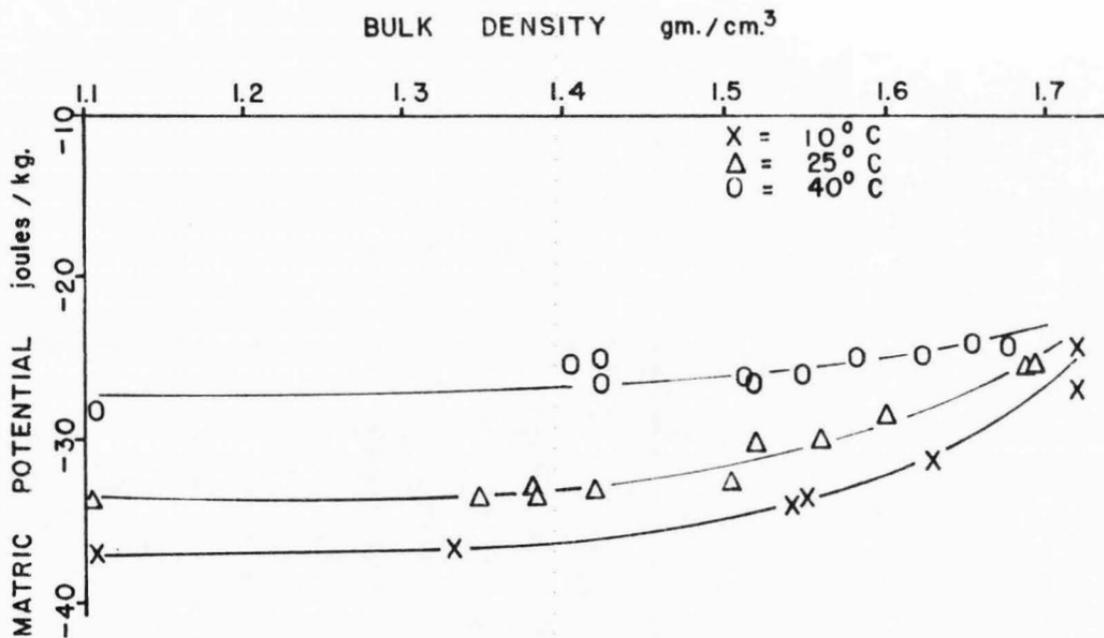


Figure 7. The relationship between soil water matric potential, bulk density, and temperature for a soil moisture content of 19 percent

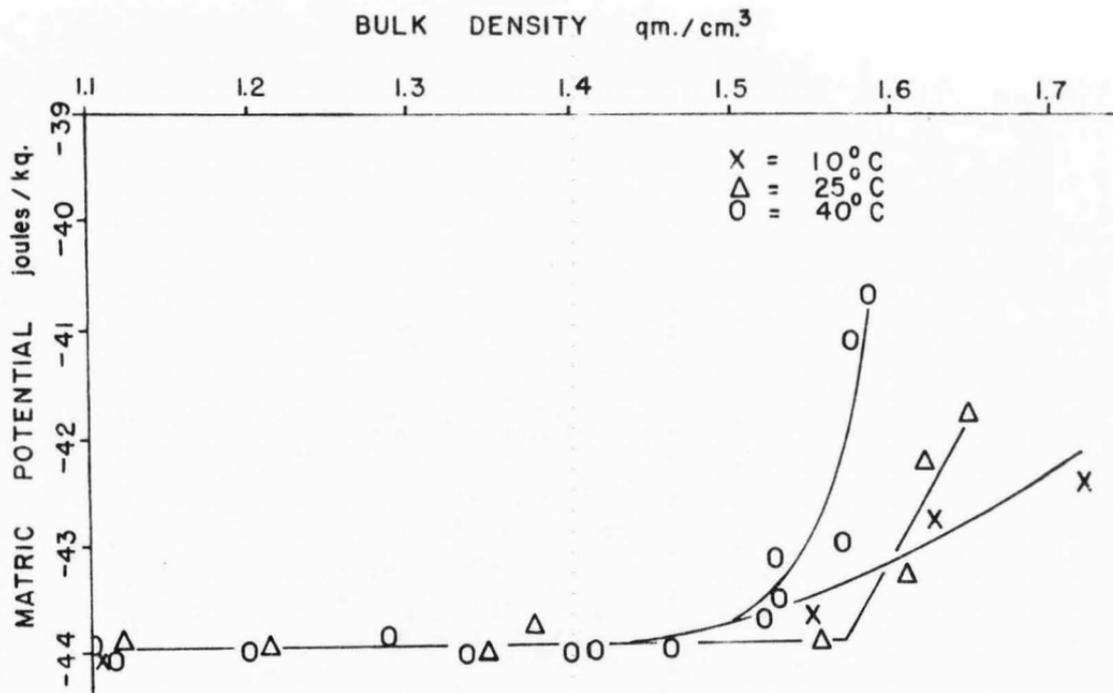


Figure 8. The relationship between soil water matric potential, bulk density, and temperature for a soil moisture content of 17.2 percent

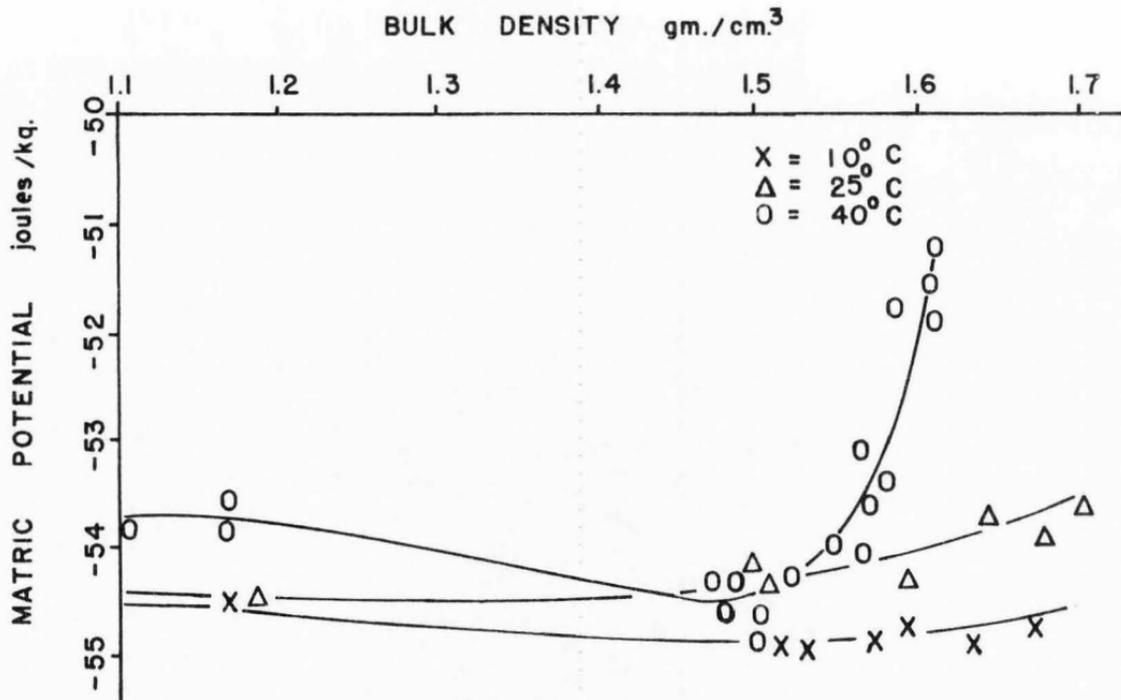


Figure 9. The relationship between soil moisture potential, bulk density, and temperature for a soil moisture content of 15.5 percent

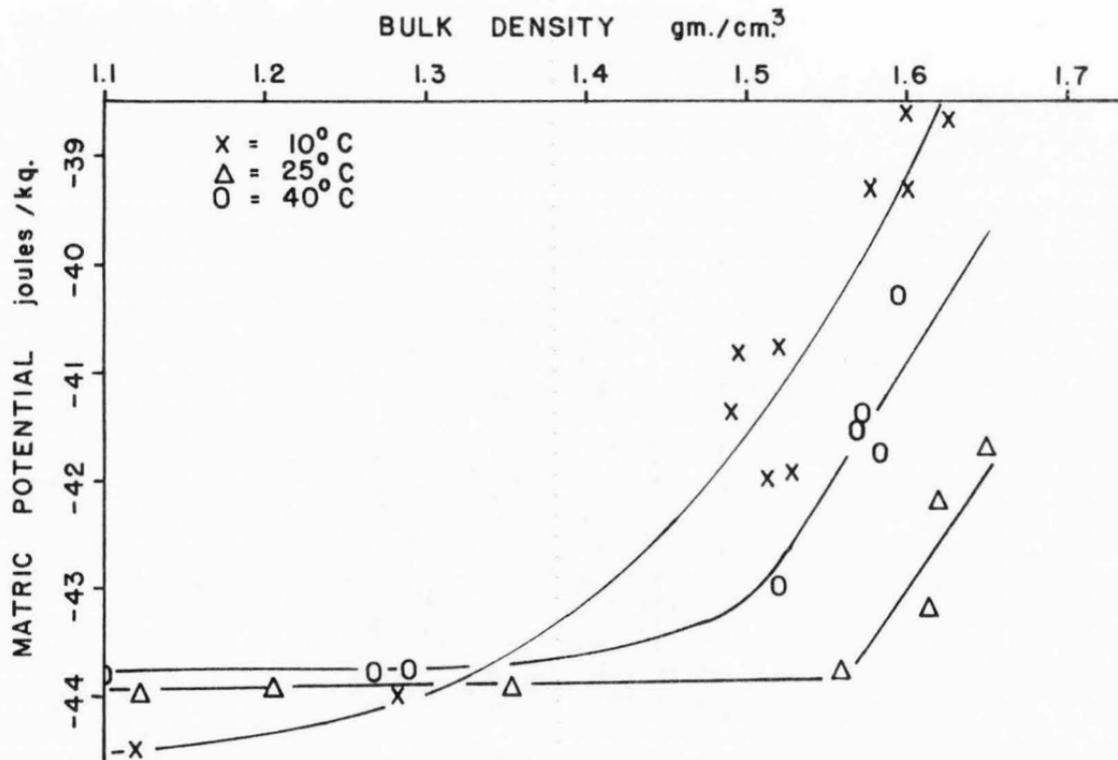


Figure 10. The relationship between soil moisture potential, bulk density, and temperature for a soil moisture content of 17.2 percent

and 15° C.) for a Benjamin silty clay loam. The plot included a moisture range from approximately saturation to a matric potential of 16 bars. Generally the matric potential for the 7° C. sample is smaller than the 15° C. sample at equal concentration of soil moisture. However, in the region of approximately 0.5 bars the matric potential for the 7° C. sample becomes larger than that of the 15° C. sample.

Soan (81), studying a Millville loam, found that for water flow from a soil sample there was a sharp decrease in the mobility coefficient at a relative activity of 0.5 bars. The data were collected at 14° C., 25° C., and 35° C. All of the data show the phenomena. The sharp decrease in mobility for the 25° C. data is not as distinct and occurs at a lower matric potential than either the 14° C. or 35° C. data. Soan had no explanation for this apparently erratic phenomenon.

From the data presented in this thesis, the work of Taylor (80) and Soan (81), it appears that a detailed study is justified which would examine the interrelationships among soil moisture matric potential, soil temperature, bulk density, and the mobility of soil moisture. It is felt that with slight modification of the apparatus used in this study such an experiment could be performed very easily. The compression apparatus shown in Figure 2 could be modified to include a null point tensiometer in the piston face. The optical levers of both tensiometers could be calibrated for flow, the matric potential differential established across the sample, and data collected for flow, temperature, bulk density, and matric potential. Such a study should yield valuable information concerning the status of soil moisture within the tensiometer range.

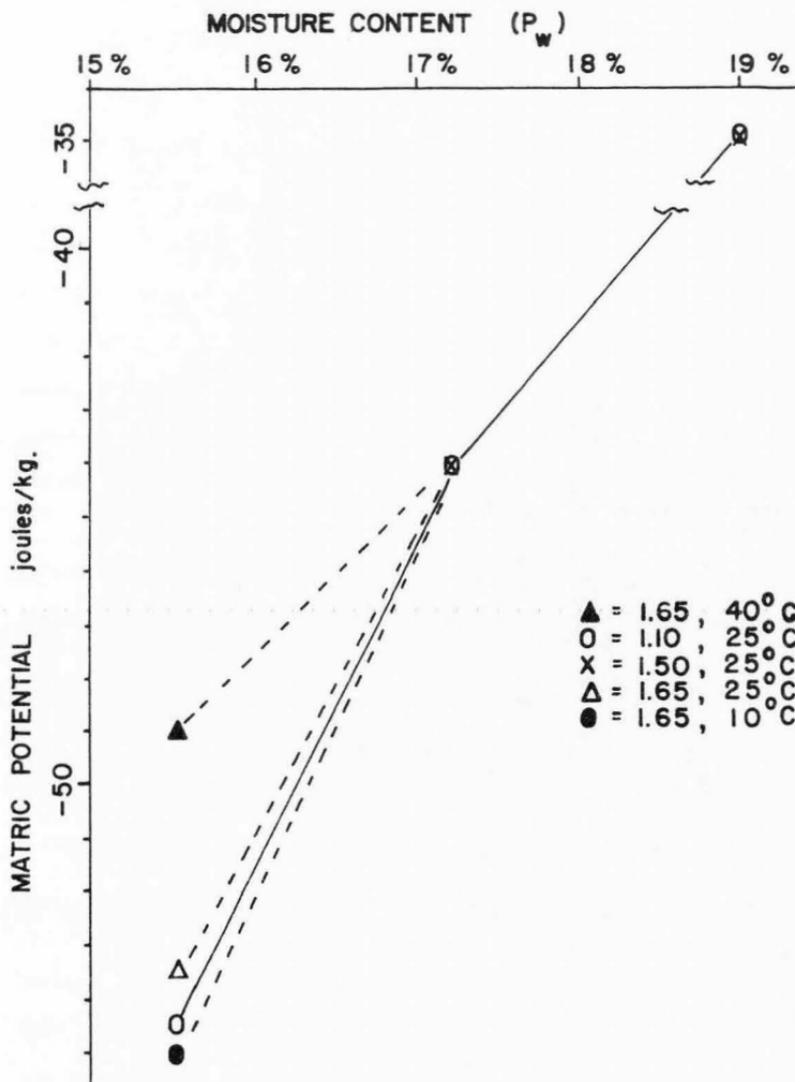


Figure 11. The influence of bulk density and temperature on the moisture characteristic curve

Correlation of thermodynamics with the mobility coefficients might prove interesting.

Figure 11 is a plot of matric potential as a function of soil moisture content for various bulk densities. The plot shows a soil moisture characteristic curve when the bulk density is held constant at 1.10 and 25° C. The effect on matric potential of increasing the bulk density to 1.65 at 25° C. is plotted. If, as in the case of a clod or similar soil mass, the soil bulk density increases as moisture content decreases the moisture characteristic curve would be a function of bulk density in addition to moisture changes.

The same effect has been compounded with temperature changes and it can be seen that a change in temperature from 25° C. to either 10° C. or 40° C. drastically alters the matric potential.

Figure 7 has been treated to yield relative partial specific entropies and enthalpies for changing bulk densities. Soan (81) has shown how mobility data could be calculated. The relative partial specific entropy, ΔS_w , and enthalpy ΔH_w , may be calculated similar to that of Taylor and Stewart (89).¹

In their application of thermodynamics to soil moisture, Taylor and Stewart have displayed graphical techniques of obtaining the relative partial specific entropy, ΔS_w and enthalpy ΔH_w . In their development they have shown that the relative partial specific entropy is given by the equation:

¹The symbols S and H are used here largely to apply to the entropy and enthalpy per 1000 grams of water rather than the molar quantities as are sometimes used.

$$\left[\frac{\partial(\mu_w - \mu_w^o)}{\partial T} \right]_{P_o, P_w, N_j} = \frac{\partial \psi}{\partial T} = -(\Delta S_w) P_o \quad [23]$$

where μ_w is the chemical potential of soil water, μ_w^o is the chemical potential of pure free water, T is the absolute temperature in degrees Kelvin, P_o is atmospheric pressure, P_w is the moisture content, ψ the soil moisture potential, and N_j is the solute content of the system. From equation [23] it can be seen that the relative partial specific entropy can be calculated by plotting the soil moisture potential, ψ , as a function of temperature.

The relative partial specific enthalpy can be obtained from the Gibbs-Helmholtz relationship:

$$\psi = \Delta \mu_w = \Delta H_w - T \Delta S_w \quad [24]$$

There are other approaches which may be taken for arriving at the desired thermodynamic data (89); however, application of equations [23] and [24] prove most desirable in this approach.

The entropy relations for the 19 percent moisture content samples have been calculated. It is felt that additional data are needed before the thermodynamic relations for the 17.2 percent and 15.5 percent moisture samples could be calculated.

Figure 12 shows the soil moisture matric potential as a function of temperature and bulk density. The slope of the lines were taken to satisfy equation [23] which resulted in values for the relative partial specific entropy. This was combined with the associated soil moisture matric potential in equation [24]. From these data the relative partial specific enthalpy could be obtained.

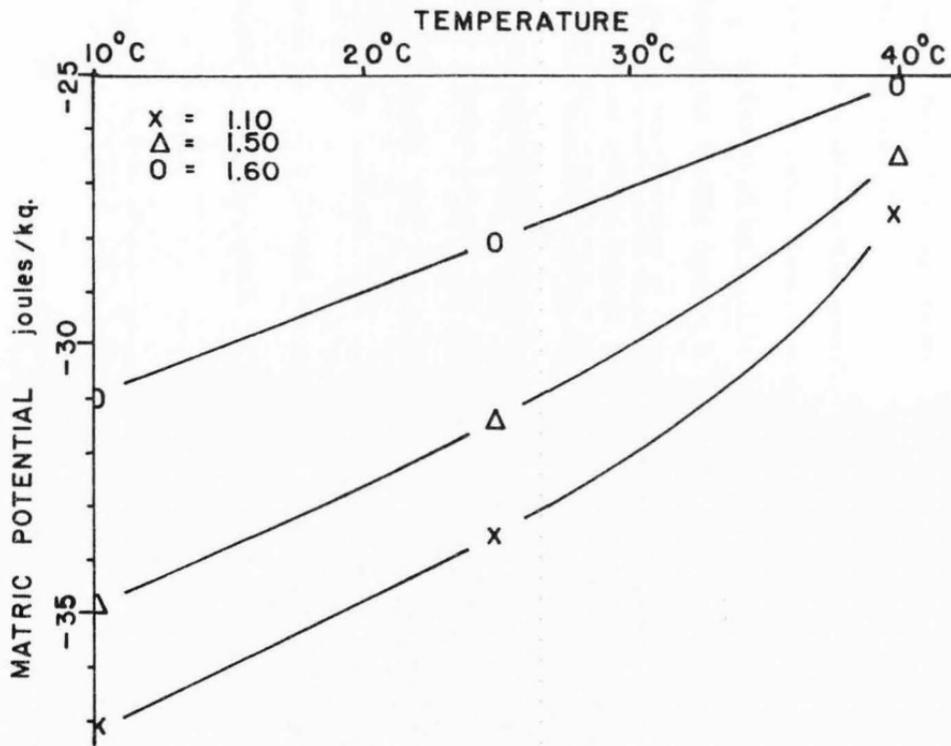


Figure 12. Soil moisture matric potential as a function of temperature and bulk density

Figure 13 shows the relative partial specific entropy as a function of temperature for bulk densities of 1.10, 1.50, and 1.65. It is seen that at a bulk density of 1.65 the relative partial specific entropy is not changed. However, as the bulk density decreases to 1.10 the relative partial specific entropy becomes increasingly more negative upon increasing temperature.

The relative partial specific enthalpy is identical in nature to the relative partial specific entropy.

In Figures 13 and 14 it is shown that relative partial specific entropy and enthalpy increase in a negative sense with increasing temperature at bulk densities of 1.10 and 1.50. However, it is noted that this entropy and enthalpy decrease becomes smaller as bulk density increases, and at a bulk density of 1.65 temperature has no influence on either entropy or enthalpy.

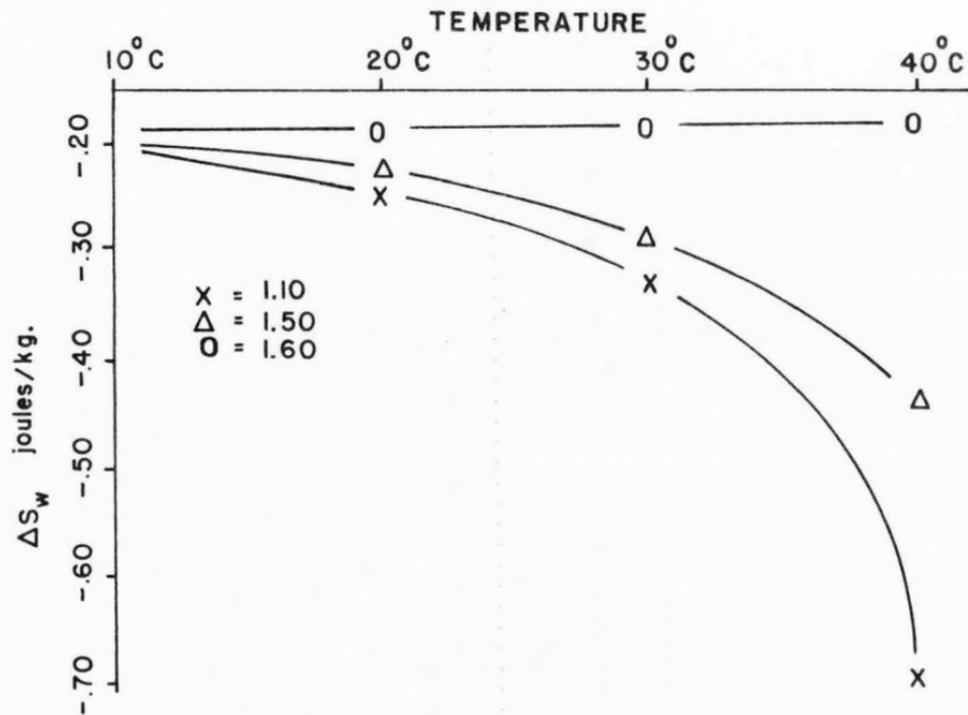


Figure 13. Relative partial specific enthalpy as a function of temperature and bulk density

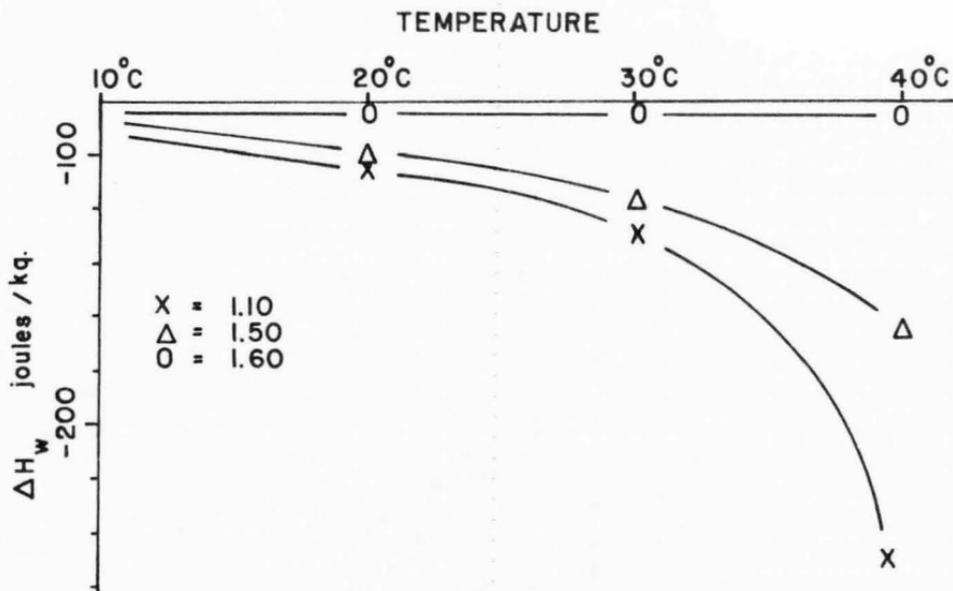


Figure 14. Relative partial specific entropy as a function of temperature and bulk density

CHAPTER VI

DISCUSSION

The fact that soil bulk density changes have an influence on soil matric potential can be very important in field and laboratory studies.

There are also important theoretical implications. Bolt and Frissel (12) in their application of thermodynamics to soil moisture have expressed the total differential of the chemical potential of soil water in any given position of the gravitational field as

$$d\mu = VdP_e - SdT + \left(\frac{\partial\mu}{\partial P_w}\right) dP_w + \left(\frac{\partial\mu}{\partial X}\right) dX + dw \quad [15]$$

where P_e is external pressure, T is temperature, P_w is moisture content, and X is a geometry factor. Bolt and Frissel's geometry concept seems to be built around the capillary concept and apparently ignores the force fields associated with the soil matrix. Although thermodynamics requires that all variables be macroscopically measurable, Bolt and Frissel give no hint as to how one should measure their geometry factor.

If Bolt and Frissel's geometry factor is centered around the capillary concept, it has the same inherent errors as previous developments of the capillary concept. Certainly, as pointed out earlier, there have been many experimental discrepancies found in applying the capillary concept. Generally, the experimentalists have reconciled these discrepancies by correction factors or mathematical manipulation. Application of the capillary concept in this study would probably require such "manipulations." The capillary concept might feasibly be applied to data in

Figure 7. Figures 8 and 9 would require a good deal of manipulation to make capillarity fit. It would prove difficult to show the matric potential changed differently for similar bulk densities and different temperatures using capillarity. Figures 8 and 9 show changes which would be difficult to be accounted for by temperature influences on surface tension. One would not expect changes in surface tensions or pore radii to be so abrupt as shown for the samples at 40° C. and 25° C. in Figure 8, and 40° C. in Figure 9.

Therefore, if Bolt and Frissel intended for their geometry factor to be related purely to pore size distribution relations it appears that serious errors would result. Measurements of pore size distribution to obtain the geometry factor would only incur difficulty.

To go a step further, it has been shown that the clay particle has a definite influence on soil moisture, and that this influence can possibly be altered by clay-clay, clay-water, and clay-ion-water interactions. None of these can be directly incorporated into the capillary concept.

We proposed here that bulk density be used as a measure of the geometry factor. The equation then becomes

$$d\mu = \bar{V}dP - \bar{S}dT + \left(-\frac{\partial\mu}{\partial P_w}\right) dP_w + \left(-\frac{\partial\mu}{\partial \rho_B}\right) d\rho_B + \sum_j \left(\frac{\partial\mu}{\partial N_j}\right) dN_j \quad [25]$$

where ρ_B is bulk density. Bulk density is a macroscopic variable of state which can be measured.

The expression now includes external pressure P, temperature T, moisture content P_w , bulk density ρ_B , and a composition variable N_j which are all variables of state. Each can be altered independently without altering the other.

Bolt and Frissel have not included a variable for changing composition except for the osmotic influence of salts. It is obvious that changes in species of exchangeable cations, organic matter, microbiology and clay size fraction, etc., may influence the soil matric potential. It is felt that this is a major omission in equation [15].

The results reported here require that an additional variable to account for changes in the affinity of the matrix for water as a result of compression should be included explicitly in the thermodynamic equation for the state of water in the soil under conditions where such changes in structure or bulk density might occur. It has been shown that changes in bulk density in both the saturated and unsaturated case alter the soil's affinity for water. Other variables that are now hidden in the composition term may also need to be explicitly recognized when changes in composition of the soil are considered. Such changes are usually of insignificant proportions and it is only under special conditions that they would need to be included.

CHAPTER VII

CONCLUSION

1. The thermodynamic equations for retention of moisture in a soil have been examined and have generally been found lacking in a variable which adequately describes the effects of changing bulk density on soil matric potential.

2. It has been experimentally demonstrated that soil bulk density changes influence the moisture retention in soils for both saturated and unsaturated cases.

3. There is a temperature relationship between soil matric potential, bulk density, and soil moisture content.

4. All variables in the thermodynamic expression have been clearly defined in such a manner as to be consistent with the requirements of thermodynamics.

5. Relative partial specific entropy and enthalpy changes are altered by bulk density changes. Increases in bulk density decreases the initial values and rates of change of the values for increasing temperature.

6. There is a need to set apart that portion of the soil matric potential related to bulk density. We propose that this be designated as the structure potential. Structure is a noun which is well accepted in soils research.

CHAPTER VIII

SUMMARY

It has been shown that a variable relating the influence of changing bulk density of soil on soil matric potential needs to be explicitly included in the present thermodynamic expressions of the chemical potential of water in soils.

Variables used in the thermodynamic expression of soil matric potential have been defined in such a manner as to be constant with criterion of thermodynamics.

It has been shown that relative partial specific entropy and enthalpy are altered with bulk density. At the maximum bulk density of 1.65 it was found that temperature did not influence either relative partial specific entropy or enthalpy. At lower bulk densities the values became more negative with increasing temperature.

The experimental data collected in this study utilized a Millville loam soil at temperatures of 10° C., 25° C., and 40° C. for an unsaturated soil; and 10° C. and 30° C. for a saturated soil. The unsaturated soil was studied at matric potentials between 0.3 and 0.6 bars suction. Three different suctions were studied at each temperature.

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APPENDIX A

$$P_w = 19\%$$

 $t = 10^\circ \text{C.}$

| Pressure applied | | Pressure released | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -34.3 | 1.51 | -34.8 | 1.46 |
| -31.5 | 1.59 | -32.2 | 1.58 |
| -26.8 | 1.64 | -29.6 | 1.62 |
| -26.3 | 1.69 | -27.4 | 1.66 |
| -22.9 | 1.72 | -25.4 | 1.67 |
| -33.0 | 1.61 | -34.4 | 1.32 |
| -28.4 | 1.61 | -31.3 | 1.52 |
| -25.1 | 1.70 | -31.5 | 1.61 |
| -22.4 | 1.72 | -30.0 | 1.65 |
| -20.0 | 1.74 | -27.1 | 1.70 |
| -34.0 | 1.30 | -26.6 | 1.70 |

 $t = 25^\circ \text{C.}$

| Pressure applied | | Pressure released | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -34.0 | 1.44 | -34.0 | 1.41 |
| -34.2 | 1.52 | -34.4 | 1.48 |
| -33.0 | 1.49 | -32.5 | 1.47 |
| -32.4 | 1.54 | -30.0 | 1.62 |
| -32.0 | 1.59 | -30.5 | 1.64 |
| -31.3 | 1.59 | -24.8 | 1.69 |
| -24.0 | 1.66 | -32.5 | 1.37 |
| -19.3 | 1.69 | -32.8 | 1.38 |
| -14.2 | 1.73 | -29.6 | 1.41 |
| -33.4 | 1.39 | -30.0 | 1.56 |
| -33.5 | 1.39 | -25.5 | 1.70 |
| -31.7 | 1.41 | -23.2 | 1.70 |
| -31.5 | 1.45 | | |
| -27.0 | 1.65 | | |
| -24.0 | 1.71 | | |
| -21.5 | 1.72 | | |
| -21.5 | 1.73 | | |

$$P_w = 19\%$$

t = 40° C.

| <u>Pressure applied</u> | | <u>Pressure released</u> | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| - 26.8 | 1.39 | - 26.5 | 1.38 |
| - 28.0 | 1.48 | - 26.5 | 1.38 |
| - 27.3 | 1.56 | - 27.3 | 1.47 |
| - 26.1 | 1.59 | - 27.7 | 1.55 |
| - 25.0 | 1.62 | - 26.7 | 1.58 |
| - 24.5 | 1.66 | - 26.3 | 1.61 |
| - 27.0 | 1.41 | - 24.5 | 1.63 |
| - 27.2 | 1.48 | - 26.2 | 1.41 |
| - 27.3 | 1.51 | - 26.7 | 1.40 |
| - 25.2 | 1.59 | - 24.6 | 1.47 |
| - 23.8 | 1.62 | - 26.7 | 1.50 |
| - 22.5 | 1.63 | - 26.0 | 1.58 |
| - 26.2 | 1.40 | - 24.2 | 1.60 |
| - 27.0 | 1.42 | - 21.0 | 1.62 |
| - 27.7 | 1.51 | - 26.2 | 1.40 |
| - 26.7 | 1.58 | - 26.0 | 1.40 |
| - 24.7 | 1.63 | - 24.8 | 1.42 |
| - 24.7 | 1.66 | - 27.5 | 1.58 |
| | | - 27.2 | 1.55 |
| | | - 25.4 | 1.62 |
| | | - 23.5 | 1.66 |

$$P_w = 17.2\%$$

t = 10° C.

| Pressure applied | | Pressure released | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -39.3 | 1.61 | -44.5 | 1.28 |
| -39.3 | 1.61 | -44.0 | 1.28 |
| -38.5 | 1.63 | -40.8 | 1.52 |
| -38.6 | 1.63 | -40.8 | 1.58 |
| -38.6 | 1.63 | -39.3 | 1.60 |
| -42.0 | 1.51 | -44.5 | 1.12 |
| -39.5 | 1.58 | -44.0 | 1.18 |
| -39.5 | 1.58 | -40.8 | 1.49 |
| -38.5 | 1.60 | -39.3 | 1.58 |
| -38.6 | 1.60 | | |
| -38.6 | 1.60 | | |

t = 25° C.

| Pressure applied | | Pressure released | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -43.0 | 1.27 | -43.8 | 1.20 |
| -43.3 | 1.68 | -43.2 | 1.27 |
| -43.0 | 1.68 | -43.6 | 1.55 |
| -42.4 | 1.72 | -42.6 | 1.63 |
| -43.8 | 1.34 | -44.0 | 1.21 |
| -42.7 | 1.61 | -44.0 | 1.36 |
| -43.2 | 1.61 | -43.8 | 1.57 |
| -41.7 | 1.66 | -42.2 | 1.62 |

$$P_w = 17.2\%$$

t = 40° C.

| <u>Pressure applied</u> | | <u>Pressure released</u> | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -44.4 | 1.04 | -43.0 | 1.12 |
| -42.8 | 1.10 | -43.5 | 1.33 |
| -43.1 | 1.17 | -44.0 | 1.40 |
| -43.9 | 1.34 | -43.1 | 1.41 |
| -43.7 | 1.34 | -43.8 | 1.28 |
| -43.7 | 1.34 | -43.5 | 1.52 |
| -43.6 | 1.41 | -43.0 | 1.57 |
| -43.5 | 1.41 | -41.1 | 1.58 |
| -43.2 | 1.21 | -44.3 | 1.23 |
| -44.5 | 1.21 | -44.4 | 1.39 |
| -43.9 | 1.29 | 44.5 | 1.46 |
| -44.2 | 1.54 | 44.1 | 1.49 |
| -43.9 | 1.58 | | |
| -42.9 | 1.58 | | |
| -40.7 | 1.60 | | |
| -44.3 | 1.23 | | |
| -44.3 | 1.23 | | |
| -44.5 | 1.40 | | |
| -44.2 | 1.46 | | |
| -44.2 | 1.46 | | |
| -44.3 | 1.50 | | |
| -44.3 | 1.50 | | |
| -44.1 | 1.50 | | |
| -44.1 | 1.50 | | |

$$P_w = 15.5\%$$

t = 10° C.

| Pressure applied | | Pressure released | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -54.3 | 1.18 | -54.3 | 1.18 |
| -55.0 | 1.53 | -55.0 | 1.51 |
| -55.0 | 1.52 | -54.8 | 1.58 |
| -54.7 | 1.59 | -55.0 | 1.58 |
| -54.7 | 1.68 | -55.0 | 1.58 |

t = 25° C.

| Pressure applied | | Pressure released | |
|--------------------------------|--------------------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. | Bulk density gm./cm. ³ | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -54.5 | 1.18 | -54.0 | 1.49 |
| -54.3 | 1.51 | -54.3 | 1.59 |
| -53.8 | 1.64 | -54.0 | 1.69 |
| -53.8 | 1.70 | | |

t = 40° C.

| Pressure applied | | Pressure released | |
|---|-------------------------|--------------------------------|--------------------------------------|
| Matric potential joules/kg. ³ | Bulk density gm./cm. | Matric potential joules/kg. | Bulk density gm./cm. ³ |
| -53.7 | 1.51 | - 52.9 | 1.19 |
| -53.7 | 1.51 | - 54.9 | 1.50 |
| -53.1 | 1.57 | - 53.1 | 1.56 |
| -51.9 | 1.62 | - 52.9 | 1.56 |
| -51.5 | 1.62 | - 51.7 | 1.59 |
| -51.4 | 1.62 | - 53.5 | 1.18 |
| -55.0 | 1.48 | - 55.0 | 1.48 |
| -54.9 | 1.48 | - 54.5 | 1.52 |
| -55.1 | 1.54 | - 53.5 | 1.57 |
| -55.0 | 1.54 | - 53.5 | 1.57 |
| -55.1 | 1.54 | | |
| -53.5 | 1.58 | | |

APPENDIX B

PROPOSITION #1¹

The American and European systems of education need to be systematically combined at the graduate level to produce better and more independent thinking.

Introduction

There is probably one mental characteristic which unifies the majority of successful scientists--open-mindedness. It is doubtful that anyone can understand the miracle of modern life without understanding that not superior mental ability, but merely a difference in mental habits has made it possible. These mental habits constitute the essence of education.

The marvelous inventions and discoveries are probably due not to our having more ingenious minds than men of former ages, even the men of the Stone Age, but merely to the fact that we use our minds in a different way; to the fact that at least a few men have achieved a new sort of spiritual existence, a habit of deciding things only on evidence.

It is of value to examine the origin of this open-mindedness and new way of thinking. Men had been going along for ages--living, fighting, loving, dying, building civilizations and tearing them down, without ever developing either the interest or the will that is necessary for the mental habit, when rather suddenly it laid hold of a number of men and not only began to produce rather astonishing practical results, but revolutionized the whole outlook of men upon the universe.

Science has been defined as a "systematized positive knowledge." To be able to systematize knowledge into positive, constructive thought constitutes the difference between a man of large information who never gets anywhere with what he knows, and the man who can combine his knowledge into a logical synthetic whole and who does get somewhere. It was just when this habit of synthetic constructive thinking about nature entered the world that there occurred what will always be known as the "Greek miracle."

Greek philosophy and philosophical thinking was the origin of scientific thinking; however, our present scientific thinking also incorporates motivations from the Romans and their utilitarian concept of power, law, social organizations, teamwork, and regimentation.

The Greek and Roman concepts of life are ever present in our present educational systems. All too often an educational system tends to go either to one of philosophy or utility. Maintaining a proper balance between the two is not always achieved. It is the author's feeling that the American system of education comes more nearly to this balance than the European system. However, it is possible that the European system can contribute to the American education at the graduate level. Before this can be decided it will be necessary to explore the philosophy of both systems.

¹The propositions #1 through 4 in this Appendix were submitted to the author's graduate committee in partial fulfillment of his final exam.

The American System of Education

Since most of us are familiar with the American system of education, it will not be dealt with in detail. The American system of education at the graduate level is a combination of course work and research. It is an approach at a balance between a philosophical and utilitarian approach. In this approach a combination of research and intensive course work studies are combined.

It is the feeling of the author that all too often the philosophical way of development is not given an equal opportunity. More often than not, course work seems to take precedence and development of the individual's ability beyond that of being able to take a group of data, assimilate the data with formulas, and produce an answer seems non-existent. In effect, the advanced student often becomes a well-trained machine that operates very smoothly as long as data are poured into the "hopper." It is not felt that this is the result of too much course work, but rather a lopsided development.

The European System of Higher Education

The European system of education at the graduate level seems to be at exactly, or nearly so, opposite poles from that of the American system. Oxford University in England will be used as an example. Oxford seems to follow along the Greek lines of education

Though lectures and classes are given at Oxford, the center of the educational system is still the ancient tutorial hour in which a student once a week privately reads an essay to his tutor and discusses it with him. This survival of the medieval "reading with a master," is the ark of the academic covenant, and the university still revolves, as it always has, around the tutor.

Unlike students of the United States, Oxford students are not expected to troop obediently from one required lecture to another. They are free from this sort of routine and may spend or waste their time as they please. Emphasis is placed on the student's outside reading. Indications are that a few minute's reading is more valuable than an hour of lecture. Probably the emphasis on outside reading and preparation of papers are one of the most outstanding differences in the American and European systems.

Another area in which the European scientist's education differs from the American scientist is in his training in philosophy. The importance in a scientist studying the Greek philosophers is cited by Dr. Werner Heisenberg¹ who is a Nobel prize winner for physics. Dr. Heisenberg points out that "Our whole cultural life, our actions, our thoughts, and our feelings are steeped in the spiritual roots of the West--in that attitude of mind which in ancient times was brought into being by Greek

¹Werner Heisenberg, A Scientist's Case for the Classics. Harpers Magazine 216:25-29. 1958.

art, Greek poetry, and Greek philosophy." Secondly, he feels that, "We must stress the fact that the whole strength of our western civilization is derived, and always has been, from the close relationship between the way in which we pose our questions and our practical actions. Other people were just as experienced as the Greeks in the sphere of practical action, but what always distinguished Greek thought from that of all others was its ability to change the questions it asked into questions of principle. Thus it could arrive at new points of view which impose order of the experience and makes it accessible to human thought."

"It is this which made Greek thought unique. . Even during the rise of the West at the time of the Renaissance, this habit of mind stood at the mid-point of our history, and produced modern science and technology. Whoever delves into the philosophy of the Greeks will encounter at every step this ability to pose questions of principle; in this way he can learn to command the strongest tool produced by western thought."

Conclusions

It is concluded that the American system of education in which the Roman philosophy of regimentation and utilitarianism is predominate is very good for the area it covers. However, it is felt that the system is lacking in two major points: 1) the student does not do or is not required to do enough outside reading in all of the areas of his course work; 2) the development of philosophical thinking is all too often left to chance.

The following suggestions are made in which European educational philosophy may be systematically combined with the American system to promote better and more independent thinking.

1. That all graduate level classes require outside reading and reporting in an associated area on a weekly basis and that at least a portion of the student's grade be derived from this reading. Ideally, these reports should be criticized and returned. The criticisms should not be so much on attention to details and content as to thought.

2. Graduate students should be required to complete at least some courses in philosophy. The important thing to be obtained in this area is not an extensive knowledge of the "great classics," but rather a way of thinking.

Summary

In summary, it may be said that the American technical training should not be severely altered and that the European methods of developing thought should have more emphasis.

PROPOSITION #2

The energy barrier referred to in soil moisture movement could possibly be associated with the solid-liquid interface and the cations present.

Biggar (3) has established that an activation energy is associated with the wetting front. The energy of activation was found to be of the order of 4180 joules/mol/deg. to 8360 joules/mol/deg. Biggar gave the physical interpretation of this with regard to water moving in the unsaturated soil as that of free energy barriers in the form of roughness as well as impurities such as organic matter, prevent laminar flow of the liquid. He indicated that the phenomena of shrinking and swelling may also contribute to increases in free energy of the system.

Biggar makes the statement that "As the system becomes drier, this phenomenon of energy barriers becomes more pronounced."

Keenan et al. (6) studied the relation between exchangeable ions and water adsorbed on kaolinite and concluded that the cations are not hydrated. The mechanism of equilibrium between a hydrated ion in the bulk and the unhydrated ion on the clay particle was suggested. They presented the idea that when water is present, the exchangeable ions presumably take up a position determined by the equilibrium between forces of hydration tending to pull the ion out of the lattice and the forces tending to pull the ion into the surface layer of the lattice. They indicate that the divalent ions, moreover, with their double charge, are more strongly hydrated and will tend to be pulled out of the lattice, their effect decreasing with increasing size.

Razouk et al. (8) has shown the relation between energy of cation hydration and energy of wetting in clays saturated with various cations. The results are shown in Figure 1. From this data there can be no question that the energy of hydration of clay is related to that of the cations. It was also concluded that the clay content of a soil has a more pronounced effect than that of silt on the heat of wetting by water. The higher the percentage of clay, the more will be the heat evolved.

Grim (5) has developed the idea that adsorbed cations have special influence on water at the solid-liquid interface which recognizes the lack of cationic hydration in this zone. The cation may determine the actual geometry of the water net, and of very great importance, determine whether the oriented water grades gradually into liquid water or is abruptly separated from liquid water. A slight change in the adsorbed cation composition might cause a destruction of the orientation of some water molecules because the replacing cation would not permit the same maximum amount of oriented water as the replaced cation.

Such cationic influence on the structure of water could cause the formation of water structures which could in effect repel an approaching air-water interface. The occurrence of such phenomenon is described by Bernal and Fowler (2), and Weyl (4). An activation energy associated with the cation could thus cause an energy of activation for wetting.

Low (7) has demonstrated the presence of an activation energy for ionic movement. He feels that the activation energy for ionic movement is equal to the sum of the energies expended by the ion in pushing back molecules to form a hole and in breaking bonds with the clay and neighboring water molecules so that it can move into the hole formed. Therefore, one would expect the activation energy to go up with an increase in the cohesion of the water structure. Evidently, this is what happened, as indicated by the data in Table 1.

The importance of cations adsorbed on clay in the process of wetting has been clearly established by Weyl (10). By treating montmorillonite with different salts, suspension of various heavy metal clays were obtained. These clay slips were sprayed on unglazed ceramic tiles and allowed to dry in a drying oven. The Na^+ -clay was found to adsorb a drop of water immediately. The Ca^{2+} -clay adsorbed a drop of water within 4 to 5 seconds. Pb^{2+} -clay and clay treated with other highly polarizable cations showed contact angles of about 70° , and the water was not absorbed until up to 15 minutes had elapsed.

Weyl describes the different wetting by the polarizability of the various cations present. He feels that the more polarizable the cations are the more the electron cloud of the cation will tend to be away from the surface of the solid. This, in effect, gives a more negative charge presentation to the approaching wetting front of the water. Weyl (10) and Bernal and Fowler (2) have shown that the approaching wetting front of water is also negative and thus water is repelled. The result is that a force must be exerted which forces the two negative charges together to induce wetting. This represents an energy barrier which must be overcome by an activation energy.

Weyl demonstrated the importance of these polarizable cations in wetting. He feels that the phenomenon of wetting is the result of the forces acting between the surface of a solid and a liquid, but it is not connected with the thermodynamic equilibrium of the system. Anhydrous chromic chloride and water are not in equilibrium at room temperature. CrCl_3 is soluble in water and forms crystalline hydrate. Nevertheless, chromic chloride in its anhydrous state is hydrophobic because its surface consists of strongly deformed Cl^- ions. Its layer lattice causes these surface anions to be in the asymmetric field where the electron cloud is pulled toward the cation to such an extent that the surface forces are too weak to overcome the cohesive forces of water. In spite of the fact that chromium chloride is quite soluble in water, it may float on water for many hours without being wetted. If a drop of water is placed

on a little pile of these crystals, it does not wet the solid but remains like a drop of mercury on a glass surface. No interaction can be observed.

However, if the same dry CrCl_3 crystals are pressed in a mold to a little disk, they react with water instantaneously. A drop of water placed on the disk turns green within a few minutes, thus indicating that Cr^{3+} ions have gone into solution.

The molding and pressing operation has strained some of these crystals so that some of the cations are less screened and, therefore, in an "activated state." This experiment proves that mechanical stresses affect the chemical reactivity of ionic substances just as they affect that of metals.

The repulsion of the liquid interface from that of the solid as described above depends on the negative surface charge of the liquid. Weyl (10) has examined the possibility of the negative surface charge of water. This possibility is presented in the following discussion.

Liquid water and ice have atomic structures which show a close resemblance as far as their geometry is concerned. Liquid water, like other liquids, lacks the long range order, but in the short range order of its atoms, there is a far-reaching similarity between water and the various forms of silicon. Bernal and Fowler (2) have given us a great deal of detail on the structure of water. However, Bernal and Fowler's model of the structure of water applies to the bulk structure only and cannot be used for describing the atomic arrangements within their films or minute droplets. In accordance with his ideas concerning the surface structure of crystals, Weyl postulates that the extreme outer layer of liquid water or ice does not contain protons.

According to this concept, a droplet of water therefore has its O^{2-} ions in the exterior layer, followed by a second layer which contains the nonpolarizable H^+ ions. A particle which contains OH^- or O^{2-} ions in the surface, followed by a layer which is preferentially positive, can be considered as being covered with dipoles, the negative parts of which point into space; whereas the positive parts are directed toward the interior.

As a result of the electrical double layer, two water droplets repel one another when in close proximity in spite of being electrically neutral. Large droplets unite on collision because of their greater inertia which overcomes the repulsion forces; small droplets may remain separated (fogs, clouds) over long periods of time.

Weyl has pointed out that several phenomena which could not be explained previously were traced to the influence of the polarizability of ions. The hysteresis of the contact angle, the hydrophobicity of water-soluble salts, the chemical properties of adsorbed ions, etc., can be understood only if one considers that electron distribution

probability of surface ions is highly asymmetrical. By changing the electron distribution of the surface, ions lower surface energy and with it, the free energy of the system.

Changes in surface tension have been observed which proceed so slowly that they cannot be accounted for by diffusion. Addison (1) has observed such changes in the surface tension of solutions of decolic acid and considers them to be caused by rearrangements in adsorbed layers when the changes require hours or days. Ward and Tordai (9) have analyzed the time dependence of boundary tensions of solutions and concluded that they are not accounted for by diffusion and must be due to an activation barrier that determines the rate of adsorption.

In more practical terms, the foregoing can be summarized in the following manner: The energy barrier to wetting of soil will increase with increasing polarizability of the adsorbed cations, ability of the clay particle to polarize ions, thinness of the advancing water film, and alteration of the structure of the "rigid" water in the diffused double layer by the cation present.

It may be said, then, that the reduction of the energy barrier to movement of the wetting front is dependent on at least two factors: a) on the increase in water film thickness to the point that the surface negative nature of the water is sufficiently reduced; and b) the negative surface of the adsorbed "rigid" water is a function of the cations present, and cationic removal from the adsorbed surface may be accomplished by contact exchange between the interface associated with the solid and that of the water, which in effect may have to take place before wetting can occur.

It may be noted that the increase in film thickness is a diffusion or flow phenomenon associated with time. Therefore, it is plausible that any rate equation could be expressed as a function of time, but that the constants in such an equation are related to a function of the energy barriers as well as to the porosity of the material.

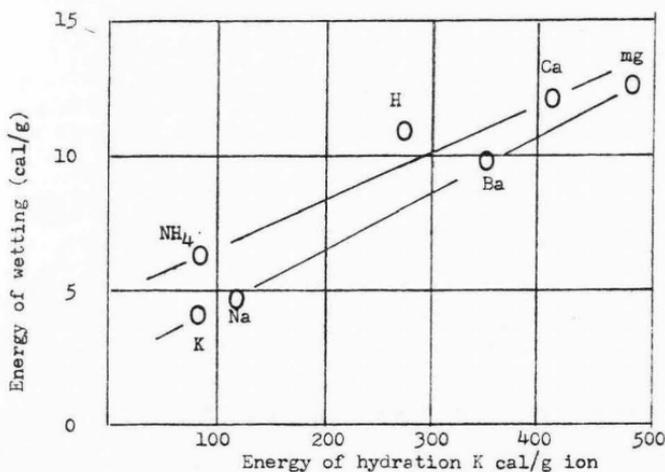


Figure 1. Relation between the energy of wetting and the energy of hydration of ions

Table 1. Nature of water adsorbed on clays in relation to the electrochemical properties of the exchangeable ions

| Clay | Ionic mobility at 25° C. Sq.cm./volt/sec. | Ionic activation energy Cal./gm. ion | Ionic dissociation (Relative) | Density of adsorbed water at 25° C. Gm./cc. | Structural development of water (relative) |
|---------|---|--------------------------------------|-------------------------------|---|--|
| K-clay | 0.000051 | 4037 | ++ | 0.981 | + |
| Na-clay | 0.000069 | 4486 | +++ | 0.972 | +++ |
| Li-clay | 0.000057 | 4358 | ++ | 0.975 | ++ |
| Na-clay | 0.000132 | 5157 | ++++ | — | — |

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PROPOSITION #3

The necessary and sufficient condition that the activity of soil water is associated predominantly with the solid-liquid interface and colligative properties of the soil colloids rather than the properties of the air-water interface is that the activity of soil water first increases and then decreases with increasing salt concentration.

There is considerable evidence that forces extending from the clay particle into water have an influence of making the water behave like a rigid material. The resistance of clays to the pressure of a water permeable piston was used as evidence of the rigidity of layers of water. Norton and Johnson (5) found that the rigid water film in plastic clay averaged 50 Å in thickness under pressure of 200 lbs. per sq. inch. At zero pressure the water film thickness was estimated to be 300 Å. Deryaguin (2) indicates that water is influenced by forces from the surfaces of mica as far as 1500 Å.

A number of investigators have reported irregularities in the vapor pressure of liquids resulting from condensation on solid surfaces, in all of which cases the irregularity could not be explained satisfactorily in terms of surface tension effects or monomolecular layers. Shereshefsky (6) found that the Kelvin equation for vapor pressure lowering did not account for the decrease in vapor pressure in glass and silica capillaries 2 to 5 microns in radius. If the results were explained on the basis of surface tension a 23-fold change in surface tension would have been required.

The only conclusion which can be drawn from the above is that the solid-liquid interface has a profound influence on the adsorbed water film.

Considerable evidence exists that the clay particle is hydrated and that the properties of the water of hydration can be altered. Cornet (1) believes that the total free energy change between any two states of the lattice may include free energy changes due to hydration of cations, orientation of solvent molecules between the planes, and polarization of molecules between the lattice planes.

Grahame (3) feels that the cation is not hydrated at the solid-liquid interface and that the energy required to remove the solvent sheath of the ion is supplied by the approach of the ion to its oppositely charged image.

Keenan et al. (4) studied the relation between exchangeable ions and water adsorption on kaolinite and concluded that the cations are not hydrated.

The effect of cation adsorption on the diffused double layer with increasing adsorption of cations at the solid-liquid interface is a decrease

in zeta potential. The decrease of the zeta potential, or the effective colloid charge, will decrease the force field intensity which is acting to orient the water molecules associated with the colloids. As the water molecules become oriented they become less free to move and thus the activity of the water is reduced.

Therefore, if there is an increase in cation concentration at the solid-liquid interface the zeta potential will decrease and the activity of the water in the bulk will increase by virtue of the fact that the force field from the clay particle has a less tendency to orient the water molecules. However, this increase in water activity on adsorption of cations at the solid-liquid interface is countered by an increase in salt concentration in the bulk. As salt concentration in the bulk increases, the activity of the water decreases. It can be seen from equation [1] how the concentration of cations at the solid-liquid interface increases with increasing concentration in the bulk.

$$C = C_0 \exp (v e \psi / kT) \quad [1]$$

where C and C_0 are the concentration of the cations in the solid-liquid interface and bulk solution respectively, v is the valence of the cation, e is the elementary charge, ψ is the electrical potential, k the Boltzmann constant, and T the absolute temperature. The "exp." indicates that everything in the brackets is an exponent of the natural logarithm 2.718.

The effective electrical potential as a function of cation concentration is given by equation [2]:

$$\psi = \frac{kT}{ve} \ln \frac{C}{C_0} \quad [2]$$

The relationship between the effective electrical potential (zeta potential) and cation concentration can be seen in Figure 1.

For very dilute solutions the osmotic pressure of a solution is given by equation [5] as:

$$\pi = \frac{RT}{\bar{V}} \left[-\ln (1-N_2) \right] \quad [5]$$

where π is the osmotic pressure, R is the gas constant \bar{V} the partial molar volume of water, T the absolute temperature, and N_2 is the mole fraction of the solute. For small values of a number the natural log of a number is approximately equal to the number; therefore, small concentrations of salt equation [5] becomes:

$$\pi = C \left[1-N_2 \right] \quad [6]$$

π as a function of concentration of salt is plotted in Figure 1. From Figure 1 it may be seen that as salt concentration is increased in a

colloidal system, the activity of the water must first increase and then decrease. The magnitude of this increase before a decrease which is incurred, is left to experiment.

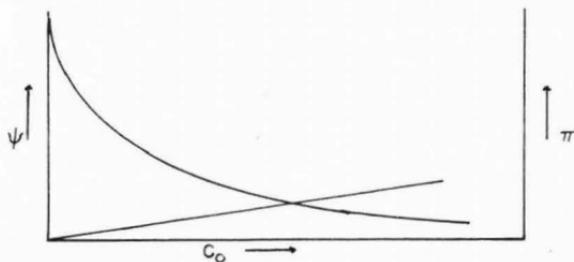


Figure 1. Electrical potential (zeta) and osmotic pressure as a function of concentration of cations for a clay water system.

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PROPOSITION #4

It is proposed that an inexpensive portable voltage amplifier can be constructed which can be used with the psychrometer.

Recent developments (1), (2), (3), (4) using the vapor pressure technique for measuring relative humidities of water between 98 percent and 100 percent makes it desirable to have an inexpensive portable amplifier which will measure voltages to 0.1 microvolts.

Teele and Schumann (5) have designed a potentiometer circuit for measuring voltages of 10 microvolts to an accuracy of 0.01 microvolt. However, the construction of this unit is difficult and its utilization requires an auxiliary potentiometer.

The circuit to be utilized is given in Figure 1. It consists of a .01 ohm resistor, 100 ohm resistor, a null detector, reversing switch, Dewar flask, a 10,000 ohm variable resistor, and millivolt meter. All of the circuit shown within the dotted lines must be constructed so that it can be housed in a Dewar flask. The same system of thermal grounding should be used as described by Teele and Schumann (5).

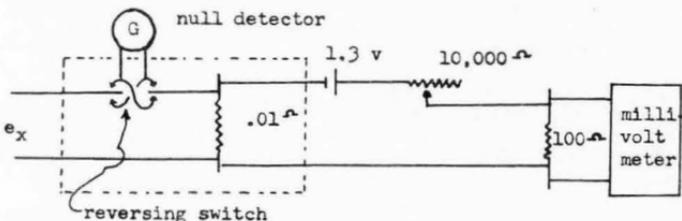


Figure 1. Amplifier circuit

The circuit may be supported on an aluminum chassis which will fit into the Dewar flask. Low thermal solder should be used for all junctions within the dotted line. Bobbin resistors may be used for the 0.01 and 100 ohm resistors. The 10,000 ohm variable resistor may be a potentiometer type commonly used in radio electronics. The reversing switch is a two-position, single gang, rotary switch. The millivolt meter is one which reads from 0 to 100. Each millivolt represents approximately 0.1 microvolt after amplification. The 1.3 volt battery is a mercury cell type battery. The null detector may be either a

galvanometer or electronic detector and must be sensitive to within .05 microvolts. All of the components not enclosed in the dotted line may be mounted on a panel.

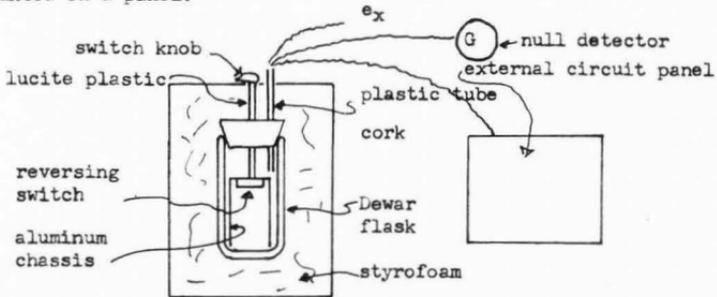


Figure 2. Cross-sectional view of amplifier

Using the psychrometer described by Richards (3) the above amplifier should be adequate to detect changes in suction equivalent to 100 cm. of water. The unknown e.m.f. is applied at e_x . The amplifier shown in Figure 2 is inexpensive, portable, and compact.

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