Pressure Dependence of Soil Water Metric Potential

Bozorg Bahrani

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\[
\pi = \sum_{j} \left( \frac{\partial \mu}{\partial n_j} \right)
\]

\[
\tau = \left( \frac{\partial \mu}{\partial \theta} \right)
\]
INTRODUCTION

The partial specific Gibbs\textsuperscript{1} free energy or the chemical potential has been shown to be the most desirable thermodynamic function for describing soil-water systems. The absolute value of the chemical potential of soil water cannot be determined. If pure water at standard temperature and pressure is taken as the reference, the difference between the chemical potential of soil water and that of the reference can be measured and is called "soil water potential," which has the dimension of energy per unit mass.

The barometric pressure at the sea level has been accepted as the standard reference pressure. Thus, any device that measures a certain property with respect to local barometric pressure should be standardized to the pressure at sea level. In case of a tensiometer, a device for measuring soil water potential operating at different locations with varying altitudes, the reference pressure changes from place to place and time to time. In pressure plate or pressure membrane apparatus, on the other hand, the soil water potential is measured at a pressure several times greater than standard reference pressure. If pressure has an appreciable influence on the soil water potential, there would be a problem with respect to pressure in evaluation of water potential.

The effect of external pressure on soil water potential has been neglected by most workers in the past. That is, they have assumed that

\textsuperscript{1}The thermodynamic symbols of Guggenheim (19) will be used throughout this dissertation.
soil water behaves the same way toward pressure as pure free water.
The main objective of this investigation is to evaluate the validity of this assumption and to determine the nature of the pressure dependence of soil water potential.
The effect of pressure on soil water potential has usually been assumed by soil physicists to be negligible. Richards (34), in evaluating the pressure membrane method for measuring matric potential maintained that:

The rate of change of matric potential with pressure is seldom mentioned and is generally assumed to be negligible. It is just another of those soil effects awaiting investigation.

Richards and Ogata (36) made the statement that the effect of pressure on matric potential is assumed to be of the same order of magnitude as the compressibility of liquid water in bulk, and therefore it is probably negligible for most purposes. However, it will be seen later that this assumption is theoretically and experimentally invalid.

Taylor (41), in introducing the concept of activity of water, pointed out clearly that the results obtained by the pressure membrane method for determining moisture potential would be different than those obtained by the tensiometer method because the activity of soil water is different at a pressure greater than standard reference pressure. Collis-George (12) explained that if pressure is constant over the length of a vertical soil column standing in free water, the moisture content variation with height may not coincide with the moisture-content variation with suction obtained by conventional pressure-membrane techniques.
Peck (31) assumed that the effect of air pressure on soil water potential was caused by the effect of air that is entrapped in the soil by the water. Based on this assumption and after many other approximations, he developed the mathematical relation

\[
\frac{\partial \psi'}{\partial P_e} = \frac{V'}{P \frac{\partial \theta'}{\partial \psi'} - V'}
\]

where \( \psi' \) is the pressure difference across the air-water interface (equivalent to matric suction), \( P_e \) is air pressure, \( \theta' \) is the volume function of water, \( V' \) is the relative volume of entrapped air, and \( P \) is hydrostatic pressure of soil water defined as \( P = P + \psi' \). The author did not present any experimental data or verification in support of his theory.

Experimental data which have been reported by various authors (43, 34) have always given positive values for \( \frac{\partial \theta'}{\partial \psi} \) for several different soils. If this is generally true, one can see clearly that Peck's equation contains a discontinuity point when \( P \frac{\partial \theta'}{\partial \psi} = V' \). The limit for this discontinuity is when \( P \) approaches zero in the region of \( P_e > P > 0 \) where \( P_e^o \) is atmospheric pressure. This limit corresponds to the value of \( \psi' \) approaching \(-P_e \) in the region of \( 0 > \psi' > -P_e^o \).

Peck (31) did not point out that such a discontinuity point exists nor did he propose any explanation with regard to its significance in soil water systems. There seems to be no physical nor theoretical reason to believe that such a discontinuity actually exists in soil-water systems. Consequently, Peck's theory seems to have no valid application.
Richards et al. (35) have reported recently that measurements of total water potential as measured by the method of vapor pressure showed no significant difference as air pressure changed. The accuracy of their measurements was 0.03 bars which corresponds to 3 joules per kilogram (30 cm. of water). Therefore, it is possible that the magnitude of pressure dependence of water potential, in the water content range in which they were working was below their accuracy of measurements.

**Pressure as an Independent Variable in Thermodynamic Equations**

The use of energetics of soil water has occupied the attention of soil and irrigation scientists for many years. Buckingham (11) was the first to introduce the concept of "capillary potential" in 1907. He defined it as "the work required per centigram to pull the water away from the mass of soil" when the soil is at some definite water content. Later use and development of this concept led the investigators in the 1940's to shift from mechanics to the direct application of thermodynamics. The main reason for this shift is the fact that energy relations of soil water are strongly temperature dependent, and therefore the use of thermodynamics is more accurate.

There is some ambiguity about the nature of the pressure that is used as an independent variable in thermodynamic equations presented by different workers. This has led to controversial ideas, most of which deal with whether this pressure is the hydrostatic pressure of the soil water or the external pressure on the system.
Day (15) was among the earliest who utilized the method of thermodynamics separate from mechanics for describing soil water systems. He defined the chemical potential, or, as he called it, "moisture potential $\mu$, as

$$\mu = \left( \frac{\partial G}{\partial n_j} \right)_T, P, n_j \quad \ldots \ldots \quad [2]$$

where $G$ is the Gibbs free energy, $n_j$ is the amount of the constituent $j$ in the system. Then he considered $\mu$ to be a function of only three variables, namely pressure $P$, temperature $T$, and solute concentration $n_j$. Thus he expressed the total differential as

$$d\mu = \left( \frac{\partial \mu}{\partial T} \right)_P dT + \left( \frac{\partial \mu}{\partial P} \right)_T dP + \sum \left( \frac{\partial \mu}{\partial n_j} \right)_P dn_j \quad \ldots \ldots \quad [3]$$

The last term which was designated by Day as $d\omega$ became known as the "osmotic effect." There is no specification about the nature of the pressure term in Day's equation, and water content's effect is not included. However, Babcock and Overstreet (5) interpreted Day's as the hydrostatic pressure of water film in the soil.

Edlefsen and Anderson (17) presented a thermodynamic treatment of soil water in which pressure, solute concentration, and gravity were considered to be independent variables. Here again water content is not included, and was most probably considered to be implicit in the pressure term.

Babcock and Overstreet (5) pointed out clearly the difference between the hydrostatic pressure and external pressure and presented the parentheses indicate that all variables except the one represented in the term are to be held constant.
a discussion as to which one should be used as an independent variable in thermodynamic equations. They stated:

Thermodynamics demands that the state variables which are selected be macroscopic, experimentally measurable quantities. The microhydrostatic pressure within a moisture film or the radius of curvature of the film do not meet this demand, and it is improper to define the pressure term in a thermodynamic foundation in terms of these quantities.

They defined the pressure term as the pressure exerted on the soil system by the surroundings. An additional variable was introduced to be added to Day's equation which is as they called it the "relative amount of water to soil" under unsaturated conditions. They indicated that any appropriate relative quantity can be used in place of this variable. However, they preferred to use water content on the dry weight basis, which will also be used throughout this dissertation and is denoted by $\Theta$. The effect of the radius of the curvature or of the hydrostatic pressure, as Babcock and Overstreet (5) held, on the chemical potential is included in $\Theta$. Then Babcock and Overstreet's equation in the absence of external fields can be represented as

$$d\mu = \left(\frac{\partial \mu}{\partial \rho_e}\right) d\rho_e + \left(\frac{\partial \mu}{\partial T}\right) dT + \left(\frac{\partial \mu}{\partial \theta}\right) d\theta + \sum \left(\frac{\partial \mu}{\partial n_j}\right) d n_j \quad \ldots \quad (4)$$

By definition where $\left(\frac{\partial \mu}{\partial T}\right) = -\frac{S_w}{\rho_w}$ and $\left(\frac{\partial \mu}{\partial \rho_e}\right) = \frac{V_w}{\rho_w}$ where $S_w$ and $V_w$ are the partial specific entropy and partial specific volume of soil water respectively (18, 19). Then equation (4) becomes

$$d\mu = -\frac{S_w}{\rho_w} dT + \frac{V_w}{\rho_w} d\rho_e + \left(\frac{\partial \mu}{\partial \theta}\right) d\theta + \sum \left(\frac{\partial \mu}{\partial n_j}\right) d n_j \quad \ldots \quad (5)$$

It is interesting to note that although Babcock and Overstreet (5)

---

$^3$The unsaturated condition is assumed for soil throughout this dissertation.
cleared the confusion about the use of pressure in thermodynamic
equations, surprisingly they introduced the same kind of confusion
in their later paper (7) for interpreting the Buckingham equation (11).
Takagi (40), Collis-George (12), and Taylor (38, 42) have drawn atten-
tion to this ambiguous usage of by Babcock and Overstreet (7) and
have confirmed that the pressure term in thermodynamic equations should
be external pressure.

Bolt and Frissel (8) have reviewed the literature dealing with
the thermodynamics of soil moisture and their point of view is that
Day's equation is correct with the exception that the pressure term
consists of two parts, $P + P_e$, where $P$ is the hydrostatic pressure in
the water film. Thus equation $\int^3_2$ becomes

$$d\mu = (\frac{\partial \mu}{\partial T})dT + (\frac{\partial \mu}{\partial P_e})dP_e + (\frac{\partial \mu}{\partial P})dP + \sum (\frac{\partial \mu}{\partial n_j})dn_j \cdot \int^6_3$$

Comparison of equations $\int^6_3$ and $\int^4_4$ shows that they are basically the
same with little difference, that is, the water content of equation $\int^4_4$
is being replaced by hydrostatic pressure in equation $\int^6_3$. Inasmuch
as the hydrostatic pressure of water is not a macroscopic quantity, the
equation of Babcock and Overstreet (5) seems to be more practical.

Box and Taylor (10), in studying the effect of soil compaction on
soil moisture potential, introduced another variable of state, soil bulk
density, the effect of which, as they showed, cannot be neglected. Addition
of this variable to equation $\int^5_5$ would result in a new equation as

$$d\mu = -\sum_{w} \overline{\nu} d\theta + \sum_{w} (\frac{\partial \mu}{\partial \theta})d\theta + \sum (\frac{\partial \mu}{\partial n_j})dn_j + (\frac{\partial \mu}{\partial \rho_B})d\rho_B \cdot \int^7_5$$
where \( \rho_B \) is soil bulk density.

At this point it should be pointed out that some workers, mainly in the field of soil mechanics and soil engineering, have used the confined or mechanical pressure on the soil for the pressure term in thermodynamic equations (13). However, this effect has usually been included with the bulk density change (9, 10, 42), and it is considered to be independent of the external atmospheric pressure.

**Evaluation of Soil Water Potentials**

The absolute value of the chemical potential of soil water cannot be determined in soil moisture studies; but rather the difference with respect to a reference, in this case pure free water, is of importance and can be measured. For conditions of constant temperature (isothermal), bulk density, and pressure, equation \( \int \) becomes

\[
d\mu = \left( \frac{\partial \mu}{\partial \theta} \right)d\theta + \sum \left( \frac{\partial \mu}{\partial n_j} \right)dn_j
\]

In this equation the terms \( \left( \frac{\partial \mu}{\partial \theta} \right) \) and \( \sum \left( \frac{\partial \mu}{\partial n_j} \right) \) can be denoted by \( \tau \) and \( \pi \), respectively. However, Taylor et al. (43) considered the integrated form of \( \tau \) as the matric potential, \( \psi_m \)

\[
\int_{\theta_0}^{\theta} \tau d\theta = \psi_m
\]

and the integrated form of \( \pi \) as the solute potential,

\[
\int_{0}^{n_j} \pi d\pi_j = \psi_s
\]

---

This term was first proposed by T. J. Marshall in the interim report of the International Committee of Horticultural Congress, March 1958 (34). Taylor et al. (43) defined it as that portion of water potential that can be attributed to the attraction of soil matrix for water.
The limits of integration in equation $L-9$ is from water content at saturation to any given water content, and for equation $L-10$ is from zero solute concentration to any given concentration.

The integrated form of the left side of equation $L-8$ is called the moisture or the water potential, $\psi$.

$$\mu - \mu_0 = \psi \quad \ldots \ldots \quad [11]$$

where $\mu_0$ is chemical potential of pure free water and $\mu$ is the chemical potential of soil water at any given moisture content and salt concentration. The term "total potential" as used by Richards (34, 36) is the same term as in equation [11]. Both equations $L-9$ and $L-10$ can be expressed in terms of chemical potential difference if the limits are appropriate. For instance, matric potential can be written as

$$\mu - \mu_0' = \psi_m \quad \ldots \ldots \quad [12]$$

where $\mu_0'$ is the chemical potential of soil water at saturation and

$$\mu_0' - \mu_0 = \psi_s \quad \ldots \ldots \quad [13]$$

where $\mu_0$ is the chemical potential of pure free water as in the case of equation [11]; addition of equations [12] and [13] results in

$$\psi = \psi_m + \psi_s \quad \ldots \ldots \quad [14]$$

An equation of type [14] has been presented by Babcock and Overstreet (6), Taylor et al. (43) and Richards (34, 37).
A difficulty presents itself in connection with equation \( L_8 \) and integration of its various components. To begin with, water content and salt concentration are assumed to be independent of each other. In reality, there are instances when this is not the case. Kemper (23) stated that successive increments of solution coming out of a pressure membrane have increasingly higher salt concentration due to what he called "salt sieving effect." The same result was reported by Reitemeyer and Richards (33). This would cause an error in determination of matric potential by the pressure plate or pressure membrane methods as discussed in Appendix A. In the case of the tensiometer, as will be seen later, this difficulty is minimized, especially in the case of low salt concentration.

Each one of the terms in equation \( L_4 \) can be determined experimentally. The relationship between water potential and relative vapor pressure of water at equilibrium with soil water (36, 43, 37), provides a tool for measurement of \( \psi \) and \( \psi_s \). This relationship is

\[
\psi = \mu - \mu_o = RT \ln \frac{p}{p_o}
\]

where \( R \) is the specific gas constant and \( p/p_o \) is the relative vapor pressure of soil water. Apparatus are now in use that will measure \( p/p_o \) with a precision of six significant figures (36, 24). In this method the gas phase acts like a semi-permeable membrane across which water vapor can move but not soil matrix nor solutes.

The evaluation of matric potential will be discussed in detail in later sections.
Effect of Pressure on Thermodynamic Properties

Water activity

The absolute activity, $\lambda_i$, of a component $i$ in a mixed system containing gas, liquid, and solid phases is related to chemical potential (18, 19) by the equation

$$\mu_i = RT \ln \lambda_i \quad \ldots \ldots \quad [16]$$

This equation provides the possibility of taking absolute activity rather than chemical potential as the dependent variable of state whenever it is more convenient to do so. Taylor (41) has applied this concept to soil-water systems.

Applying equation [16] to soil water and differentiating with respect to $P_e$, while holding other variables constant, would result in

$$\left( \frac{\partial \mu}{\partial P_e} \right) = RT \frac{d \ln \lambda_w}{d P_e} \quad \ldots \ldots \quad [17]$$

Substituting $\overline{V_w}$ for $\left( \frac{\partial \mu}{\partial P_e} \right)$ in equation [17] and rearranging gives

$$\frac{d \ln \lambda_w}{d P_e} = \frac{\overline{V_w}}{RT} \quad \ldots \ldots \quad [18]$$

If equation [18] is applied to a single component system of pure free water, a different equation is obtained as

$$\frac{d \ln \lambda_w^o}{d P_e} = \frac{\overline{V_w^o}}{RT} \quad \ldots \ldots \quad [19]$$

where $\lambda_w^o$ and $\overline{V_w^o}$ are activity and specific volume of pure free water, respectively. Subtraction of equation [19] from [18] gives
If water vapor is treated as an ideal gas the term $\frac{\lambda_w}{\lambda_w^0}$ is called relative activity and is equal to relative vapor pressure, $p/p_o$.

Thus equation [20] becomes

$$\frac{d\ln \frac{\lambda_w}{\lambda_w^0}}{dP_e} = \frac{V_w - V_w^0}{RT} \ldots \ldots \ [21]$$

Equation [21] shows that the pressure relationship to relative vapor pressure depends upon the difference between the partial specific volume of water in the mixture and that in the pure free state. Equations similar to [21] have been used to determine the volume difference in a phase change process. For example, Glasstone (18) suggests equation

$$\left( \frac{\partial \ln N_2}{\partial P_e} \right) = \frac{-\Delta V_f}{RT} \ldots \ldots \ldots \ [22]$$

where $N_2$ is solubility of a pure solid forming an ideal solution in a liquid and $\Delta V_f$ is the volume change accompanying the fusion of 1 mole or 1 gram of solid solute at constant temperature.

**Entropy and enthalpy**

Pressure dependence of entropy is related to the coefficient of thermal expansion by means of Maxwell's equation as is derived by Guggenheim (19):

$$\left( \frac{\partial S}{\partial P_e} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_{P_e} = -\alpha V \ldots \ldots \ldots \ldots \ldots \ [22]$$

where $S$ and $V$ are entropy and volume of the system, respectively.
The term \( \alpha \) is the coefficient of thermal expansion and is defined as

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P_e} \quad \ldots \ldots \quad [24]
\]

Equation \([23]\) is for a closed system, but it could be modified for an open system and be applied to a soil water system as well. For this, one has to go back to the original equation from which \([23]\) is derived

\[
dG = -SdT + VdP_e \quad \ldots \ldots \quad [25]
\]

which is valid only for a closed system. Equation \([25]\) is an exact differential and \([24]\) is one of the properties associated with its exactness. Equation \([23]\) is equivalent to equation \([25]\) for an open system when applied to soil water systems. It is also supposed to be an exact differential, and therefore, an equivalent to equation \([23]\) is

\[
(\frac{\partial S_w}{\partial P}) = -(\frac{\partial V_w}{\partial T}) = -\alpha_w \overline{V_w} \quad \ldots \ldots \quad [26]
\]

where \( \alpha_w \) is the coefficient of thermal expansion of soil water. No information is available in the literature concerning \( \alpha_w \), therefore, no statement can be made at this time as to whether or not it is the same as \( \alpha \) of free water. Equation \([26]\) can be integrated with respect to pressure for soil water:

\[
\int d \overline{S_w} = -\int_{P_e}^{P} \alpha_w \overline{V_w} dP_e \quad \ldots \ldots \quad [27]
\]

where \( P \) is the hydrostatic pressure of soil water near the meniscus.

Since \( \alpha_w \) and \( \overline{V_w} \) can be considered independent of pressure, we obtain

\[
\overline{S_w} - \overline{S_w}^0 = \alpha_w \overline{V_w} (P - P_e) \quad \ldots \ldots \quad [28]
\]
Equation 28 is interesting since it provides a method for evaluating the partial specific entropy from suction, the coefficient of thermal expansion, and the partial molar volume of soil water.

The equation for the pressure dependence of enthalpy is derived by Guggenheim (19), and its modification for soil water is

\[ \frac{\partial \overline{H}_W}{\partial P_e} = \overline{V}_W (1 - a_w T) \]  \(\text{(22)}\)

where \(\overline{H}_W\) is the partial molar enthalpy of soil water. This equation can also be integrated for soil water the same way as equation 22 to give

\[ \overline{H}_W - \overline{H}_W = \overline{V}_W (1 - a_w T) (P - P_e) \]  \(\text{(23)}\)

From this equation the partial specific enthalpy change can be measured for soil water once \(\overline{V}_W\) and \(a_w\) are known.

**Surface energy**

Pressure dependence of surface energy, \(\gamma\), is shown by Adamson (1) in an equation as

\[ \left( \frac{\partial \gamma}{\partial P_e} \right) A = \left( \frac{\partial V}{\partial A} \right) P_e \]  \(\text{(24)}\)

where \(A\) is the surface area. He assumed that the right side of this equation is negative for a solid-liquid interface. Therefore, the equation shows a decrease in surface energy as pressure increases.

According to Adamson, pressure increase over the liquid surface is always associated with introducing an additional component into the system, such as some inert gas. One thus increases the density of liquid in the gas phase; and, moreover, there will be some gas adsorbed on the liquid
surface, in an amount corresponding to a volume change $\Delta V_a$. The value of $\Delta V_a$ is determined by equation

$$ V_a = -\Gamma \frac{RT}{P_e} \ldots \ldots \quad (527) $$

where $\Gamma$ denotes the moles of gas adsorbed per unit area. The total change in volume with area is the sum of $\Delta V_a$ and the volume change of the liquid. Thus

$$ \left( \frac{\partial \gamma}{\partial P_e} \right) = -\Gamma \frac{RT}{P_e} + \left( \frac{\partial V}{\partial A} \right) \ldots \ldots \quad (537) $$

Adamson reported that the first term dominates, so that the surface energy at a liquid gas interface generally decreases with increase in pressure.

**Gas Sorption by Soil Water as Affected by Pressure**

The effect of gas sorption as a result of pressure increase on a moist soil has been pointed out by Takagi (39). In considering the Gibb's free energy equations of type $\Sigma i \gamma_i$, Takagi held that the increase of pressure adds to the equation and that sorption of air has a negative effect on it. He suggested these changes are regulated by including dissolved air of the liquid phase in the $n_j$ term, which will then be the concentration of all solutes including air in soil water.

The amount of gases sorbed by liquids increases in proportion to the gas pressure according to Henry's Law, $p = KN$, where $p$ is the partial pressure of gas, $K$ is a constant, and $N$ is the mole fraction of the gas dissolved. Free water can dissolve 1.87 percent by volume of air at 20° C temperature and 1 bar pressure (21). According to Daniels
and Alberty (14), the increase in volume caused by the solution of a mole of a gas in a liquid is nearly equal to the corresponding values of \(Q_y\) in the equation of Van der Waals. This value for air is approximately 0.0376 liter/mole which corresponds to 0.156 percent of the volume of dissolved gas. The volume increase, then, would amount to 0.00156 x 0.0187 = 2.83 x 10^{-3} \text{ percent}. This means that for every 100 cm\(^3\) of water the volume increase due to solution of air is approximately 0.00283 cm\(^3\).

If air pressure is increased by 25 cm Hg, the increase in the volume of water due to solution of air would increase, according to Henry's Law, up to 0.00376 cm\(^3\) per 100 cm\(^3\) of water.

When one considers all these figures, it seems reasonable to believe that gas sorption and its pressure dependence has little effect on the volume change of soil water.

Nakayama et al. (29) and Runkles et al. (38) have made an extensive study on the sorption of oxygen by moist soils at various water contents. Their results show that the sorption of oxygen by soil water is the same as that by free water down to a very low water content corresponding to a relative vapor pressure of approximately 0.70. For lower water contents, the amount of oxygen sorption was more than the theoretical value that can be sorbed by free water. Based on the capillary concept and Kelvin's equation, a theory has been developed by the same authors (30) to explain the high sorption of oxygen at vapor pressures lower than 0.70. This region of soil water content is far below the water content range of the experiment reported in this dissertation.
Specific Volume of Soil Water

The physical structure of water in soil has been a focal point of attention of soil physicists and clay mineralogists for many years. This is due to the suspicion that the orientation and the physical properties of the absorbed water may be different in the vicinity of the solid surface than in the bulk liquid. Specific volume (reciprocal of density) is one of the physical properties that has received the most consideration.

It has been generally believed that the adsorptive forces at the clay-water interface alter the structure of the adsorbed water, but the nature of this alteration is not yet established (26). For example, some workers assume an ice type structure for adsorbed water and thus propose that adsorbed water is less dense than normal water (22, 27). Some investigators, on the other hand, believe that the high ion concentration and calculated adsorptive pressure in the interfacial region would break down the hydrogen-bonded structure and lead to closed packing, thus a more dense structure (28).

The experimental evidence to date is contradictory. De Witt and Arens (16) reported the values of 0.76, 0.73, and 0.71 cm³/g for specific volume of adsorbed water on montmorillonite with moisture contents of 28.4, 16.6, and 11.6 percent, respectively. MacKenzie (28) reported values of specific volume of water ranging from 0.725 at 9 percent water to 0.940 at 20 percent water. Low and Anderson (26) in proposing a new

---

5 Inasmuch as the pressure dependence of moisture potential, as it will be seen in the next section, leads to calculations of partial specific volume of soil water, it was found necessary to present a review of the previous works on the subject.
technique for determining partial specific volume of soil water in a clay suspension found no difference between the partial specific volume of water in Li, Na, and K-clay suspensions and that of pure water.

In a later paper Anderson and Low (3, 4) used a compression apparatus and determined the specific volume of water adsorbed on Li-, Na-, and K-bentonite to be 1.026, 1.031, and 1.021, respectively, for a distance of about 10 Å from the clay surfaces. This distance corresponds to approximately 2 molecular layers of water. They also reported a gradual increase in specific volume as the clay surface was approached.

Low and Anderson’s findings are in complete disagreement with the report of MacKenzie (28) and De Witt and Arens (16). MacKenzie (28), in criticizing Low and Anderson’s conclusion, stated that the validity of any results for the density of sorbed water are extremely difficult to assess, since every value must necessarily involve the volume of the sorbed water; and this has to be estimated on the assumption that the amount of swelling of clay mineral represents the volume of this water. He believes that this can only be true if the surface of the individual clay mineral layers are impermeable to water. He also stated that some water molecules could be adsorbed into the hexagonal holes of the clay layers, thus giving a specific volume of zero.

From the above considerations, it would appear that no very useful conclusions regarding the structure of adsorbed water can yet be drawn from specific volume measurements.

---

6 Low and Anderson (26) defined partial specific volume as the change in the volume of the suspension resulting from the addition of 1 gram of water to such a large quantity of suspension that the clay concentration remains virtually constant, thus it is the volume per gram for the last increment of water at the specified clay concentration.
THEORY

Tensiometer Equation

If one assumes no change in soil moisture, salt concentration, temperature, and bulk density, equation \( \text{-7}_7 \) becomes

\[
d\mu = \frac{V_w}{\rho} \rho P
\]

Let us consider a tensiometer cup installed in a soil connected to a mercury manometer when thermodynamic equilibrium is established. In such a system we have two phases at equilibrium with each other: one, water in the soil, denoted by \( \alpha \), and the other water in the tensiometer cup, denoted by \( \beta \). Equation \( \text{5}_7 \) can be integrated for the phase with the limits of atmospheric pressure and equilibrium pressure in the cup (measured by the manometer).

\[
\int d\mu^\beta = \int \frac{\rho}{V_w} \rho P_e
\]

The limit \( \mu^\beta_o \) corresponds to chemical potential of water in the tensiometer cup, with the same salt concentration as soil water, when \( P = P_e \). The limit \( \mu^\beta \) corresponds to chemical potential of water in the tensiometer cup at equilibrium with soil water, therefore, \( \mu^\beta = \mu^\alpha \). Since the coefficient of compressibility for water is of the order of \( 5 \times 10^{-5} \), can be considered independent of pressure (25), thus the integrated form of \( \text{5}_7 \) is

\[
\mu^\alpha - \mu^\beta_o = \frac{\rho}{V_w} (P - P_e)
\]
This equation is identical with equation \([327]\); therefore,

\[
\psi_m = \mu - \mu'_o = \overline{V}_w^B (P - P_e) \quad \ldots \quad [327]
\]

The important fact to observe in \([327]\) is that the term is the partial specific volume of water in the tensiometer cup rather than that of soil water. However, there have been some authors in the past who hold the opposite point of view \((25)\). Day \((15)\) thought that in order for the tensiometer equation to be correct, \(\overline{V}_w^a = \overline{V}_w^B\), but the equilibrium state of the system, as was just shown, does not require equality of any property other than chemical potential.

It might now be observed that because soil and tensiometer water are in equilibrium does not mean that the pressure on both sides of the cup is the same; that is, that water in the soil must be under suction. Babcock and Overstreet \((5)\) have explained this clearly by saying that it cannot be assumed that the pressure of the soil water is the same as that of water in the tensiometer cup any more than we could assume that the water in an osmometer is at the same pressure in both phases at equilibrium. This brings out the point that we cannot directly obtain the water pressure in the soil by means of a tensiometer, but we can and do obtain the matric potential as shown by \([327]\).

Taking the derivative of equation \([327]\) with respect to external pressure we get

\[
\frac{d\psi_m}{dP_e} = \frac{d\mu}{dP_e} - \frac{d\mu'_o}{dP_e} \quad \ldots \quad [328]
\]

When \(\frac{d\mu}{dP_e}\) and \(\frac{d\mu'_o}{dP_e}\) are replaced by \(\overline{V}_w\) and \(\overline{V}_w^o\) respectively,
equation \( \frac{d\Psi_m}{dP_e} = \bar{V}_w - \bar{V}_w^0 \) \( \dots \dots \) \( \text{[B27]} \)

(\( \bar{V}_w^0 \) is the specific volume of water at equilibrium with soil water that contains certain amounts of salts; nevertheless, for all practical purposes it is equal to the specific volume of pure free water, \( \bar{V}_w^0 \).)

In the four component systems of soil, water, dissolved air, and salts, the partial specific volume of soil water is defined as

\[
\left( \frac{\partial V}{\partial n_w} \right) n_j, n_a, n_s = \bar{V}_w \quad \text{[B40]}
\]

where \( V \) is the volume of the whole soil-water system, \( n_j, n_a, \) and \( n_s \) are concentration of salt, dissolved air, and soil material, respectively. Since the water fraction of the soil water on dry weight basis is the conventional way of expressing the amount of water in soil, it is dimensionally appropriate to express \( V \) in terms of volume fraction on soil dry weight basis, \( V \). Assuming \( n_j, n_a, \) and \( n_s \) stay constant as changes, and replacing \( V \) and \( n_w \) by \( V_\theta \) and \( \theta \), respectively equation \( \text{[B40]} \) becomes

\[
dV_\theta = \bar{V}_w d\theta \quad \text{[B41]}
\]

Integration of this equation between limits would give

\[
\Delta V_\theta = \int_{\theta_1}^{\theta_2} \bar{V}_w d\theta \quad \text{[B42]}
\]

\( \Delta V_\theta \) is the change in the volume of soil-water system as a result of addition of water from \( \theta_1 \) and \( \theta_2 \).

\( \frac{1}{V_\theta} \) has the dimension of \( \frac{cm^3}{g} \). \( \theta \) is dimensionless and \( \bar{V}_w \) has the dimension of \( \frac{cm^3}{g} \), thus \( \text{[B41]} \) is dimensionally correct.
Integration of the right side of equation \[ \text{[42]} \] can be made graphically; that is, is plotted as a function of and the area under the curve between the limits is determined.

Equation \[ \text{[42]} \] corresponds to the same type of equation derived by Phylip (32) for determining integrated values of thermodynamic properties from the partial specific values.

**Pressure Membrane Apparatus**

In the pressure membrane or pressure plate apparatus a saturated soil is subjected to pressure and soil solution is extracted until equilibrium is established (out-flow ceases). In this process of extraction, under salt-free conditions or negligible amounts of salt, constant bulk density and temperature, only pressure and moisture content is being varied. Thus equation \[ \text{[7]} \] becomes

\[
d\mu = \nabla \rho P_e + \tau d\theta \quad \ldots \ldots \quad \text{[42]}
\]

Integration of this equation for soil water inside the pressure cell and for the process of extraction between the appropriate limits would result in

\[
\int_{\mu'}^{\mu} d\mu = \int_{P_e}^{P_{eq}} \nabla \rho P_e + \int_{\theta}^{\theta_e} \tau d\theta \quad \ldots \ldots \quad \text{[44]}
\]

where \( \theta_o \) is water content at saturation and \( \theta \) is water content at pressure \( P_{eq} \) under equilibrium conditions. \( \mu^o \) is the chemical potential of soil water at saturation which is the same as that of out-flow water. Since at equilibrium the chemical potential of water outside and inside the pressure cell is the same, that is, \( \mu = \mu^o \), thus the left side of
equation $[44]$ is zero. Holding $\overline{V}_w$ independent of pressure and rearranging equation $[44]$ and combining it with equation $[12]$, we get

$$\psi_m = -\overline{V}_w (P_e - P) \quad \cdots \cdots \quad [45]$$

Comparison of this equation with $[32]$ shows that both relate matric potential to a pressure difference across a membrane, but not in exactly the same manner. In the case of a tensiometer, equation $[32]$, the term $-\overline{V}_w$ is partially specific volume of water in the tensiometer cup, which is the same as free water, whereas the term $\overline{V}_w$ or equation $[45]$ is partial specific volume of soil water in the pressure cell at any given moisture content. However, it was shown earlier that $\overline{V}_w$ of soil water is different than that of free water (1, 16, 27, 28). Therefore, the equilibrium gauge pressure in a pressure membrane or a pressure plate should be multiplied by the partial specific volume of soil water at equilibrium moisture content before it could be called soil water matric potential.\(^7\)

\(^7\)For further discussion, refer to Appendix A, proposition #2.
PRELIMINARY EXPERIMENT

Tensiometer

Apparatus and procedure

A schematic diagram of the apparatus is shown in Figure 1. A tensiometer (mercury gauge type) was placed in Millville silt loam soil, and the whole system was sealed in a lucite plastic cylinder. Rubber gaskets were used to help in sealing. Air was introduced into the system from a compressor, and the pressure was measured by a mercury manometer attached to the system.

The experiment was conducted in a constant temperature room with ± .50°C temperature variation. Water was added to dry soil until a desired water content was reached. After equilibrium was established, the suction reading was recorded as the water suction at atmospheric pressure. Pressure was then varied in increments of about 5 cm Hg using either compressed air for increased pressures, or vacuum for reduced pressures. The change in the tensiometer reading was recorded as a function of time for a period of 24 hours after each pressure change. The barometric pressure was also recorded from a barometer installed in the nearby constant temperature room. To prevent evaporation, the soil sample was covered by a rubber membrane which contained a very small hole to assure pressure equalization.

Results

A typical variation of suction reading with respect to time after a pressure change is shown in Figure 2. When pressure was increased, the

1The Millville silt loam soil was used throughout this study.
Figure 1. Tensiometer apparatus for preliminary experiment
Figure 2. Time variation of tensiometer reading immediately after external pressure is changed.
suction reading rapidly reached a maximum point, then immediately started to decrease toward equilibrium which was always reached in less than 24 hours. For the case of decreasing pressure, a minimum point was quickly reached followed by a gradual increase to an equilibrium condition. From the suction reading at any equilibrium state, the matric potential was plotted as a function of external pressure for two runs with different moisture contents and at different temperatures. The result is shown in Figure 3. The unit of matric potential is chosen to be joules per kilogram of water, a unit which seems to be a convenient one to use in soil water studies and was first introduced by Taylor et al. (43). A straight line seems to fit the data for both runs, showing a decrease of moisture potential with respect to pressure increase. The slope of the lines are calculated to be -0.125 and -0.127 cm$^3$/c for run 1 and 2, respectively.

Figure 4 shows the result of a run where the pressure was varied around a cycle.

The behavior of the matric potential as pressure changes around a cycle suggests the possibility of a hysteresis effect in matric potential--pressure relationship in soils. Further study along this line has been made with the improved apparatus and will be reported in the appropriate section.

**Moisture Blocks**

The objective of this experiment was to study the effect of pressure on the electrical resistance reading of moisture blocks at equilibrium with Millville silt loam soil. The idea was originated from the work of

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2 Joules/kg is equivalent to 0.01 bar of pressure 0.00987 atm. and 10.17 cm water (assuming that the density of water is unity).

3 The slope of energy function versus pressure has the dimension of specific volume according to equation $[32]$. 
EXT. PRESSURE, MILLIBARS

MATRIC POTENTIAL, J/KG

θ = 28.3 %
T = 20 ± 0.5 °C

θ = 26.5 %
T = 23 ± 0.5 °C

Figure 3. Pressure variation of soil water matric potential for two runs: run 1 with 28.3 percent water content and at 20 °C temperature; run 2 with 26.5 percent water content and at 23 °C temperature.
Figure 4. Pressure variation of soil water matric potential as pressure changes around a cycle at 22 ± 0.5° C.
Holmes (20) who found a higher resistance reading immediately after the pressure was released from a pressure membrane apparatus where the blocks were buried in soil. After a period of 7 hours, as he reported, the resistance decreased to a lower value than the initial one.

This experiment was carried out essentially the same way as that of Holmes, except that the backflow of water, from the membrane to the soil, was completely prevented.

**Experimental method and procedure**

A 15-bar ceramic plate extractor model 1500⁴ was used. The stainless steel rectangular screen-type blocks were buried in saturated soil placed on the ceramic plate. The electrical connection from the blocks to outside the pressure chamber was made through the holes already existing on the body of the apparatus. A Wheatstone bridge was used to measure the resistance. Pressure was applied by introducing compressed air into the system through a pressure control gauge that maintained a desired constant pressure. The pressure was measured by a regular pressure gauge with the sensitivity of ± 1 psi.

A desired moisture content was obtained by applying appropriate pressure on the soil until equilibrium was established (blocks resistance did not change with time). The pressure was released, the contact between the soil and the plate was broken, and the plate was taken out of the pressure chamber. The system was sealed again and the resistance reading was taken until equilibrium was reached. Then pressure was applied with increments of 5 bars. The resistance was recorded immediately after each

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⁴Soil Moisture Equipment Co., Santa Barbara, California.
pressure application, and then recorded at intervals until equilibrium point which was usually reached within 1 to 2 hours after pressure application.

In order to check the effect of pressure on the resistance of water saturated blocks, the blocks were immersed in water inside the pressure cell and the effect of pressure variation was studied the same way as mentioned above.

The experiment was conducted in a constant temperature room with a temperature variation of ±0.5° C.

Results

In Figures 5 and 6 the pressure variation of resistance is plotted for blocks at equilibrium with free water and with soil at three different moisture contents. Each point in these figures represents the average resistances of 3 blocks at equilibrium after each pressure change. The immediate resistance reading after each pressure change was always lower in the case of pressure rise and higher in the case of pressure release than the equilibrium reading. This is attributed to the immediate temperature change inside the chamber due to compression in the case of pressure rise and expansion in the case of pressure release. This temperature change is eliminated within 1 to 2 hours after which the resistance reading did not change.

The data of Figures 5 and 6 show a sharp decrease in resistance of blocks in free water and in soil with the lowest water content (7.1 percent) as the pressure increases. The reduction of resistance due to pressure rise of blocks in soil with 14.5 and 11.4 percent water content is lower than the other two cases. When the pressure was changed around a cycle
Figure 5. Average block resistance as a function of air pressure; (a) blocks in free water, (b) blocks in soil with $\theta = 14.5\%$ percent (at equilibrium with 2 bars pressure).
Figure 6. Average block resistance as a function of air pressure; (a) blocks in soil with $\theta = 11.4$ percent (at equilibrium with 5 bars pressure); (b) blocks in soil with $\theta = 7.1$ percent (at equilibrium with 15 bars pressure).
there is evidence of a hysteresis effect as shown by Figures 5b and 6a which show a closed cycle for the final round of pressure change. The significance of these results are included in the Discussion.
PRIMARY EXPERIMENT

Apparatus

The experimental apparatus used in this study was designed to allow air pressure to be varied on a soil-water system and the tensiometer with which it is in equilibrium while water content remained constant. Provision was made to allow water to be extracted from, or added to, the soil through a ceramic plate in order to bring the soil to the desirable water content for each run.

The apparatus, as shown in Figure 7, consisted of the following sections:

Pressure chamber

The sample holding chamber was composed of a cylinder, a ceramic plate, a cylinder head, a cylinder base, an out-flow tube, and two rubber "O" rings.

The two types of chambers that were used are described as follows:

(a) A cylindrical chamber made of a lucite tube which had an inside diameter of 5.3 cm, a wall thickness of 0.47 cm, and a length of 3.8 cm was used for all soils with less than 21 percent water. The cylinder head and base were also made from a lucite plastic plate approximately 2 cm thick. (b) The second type of cylindrical chamber was made of brass tubing with an inside diameter of 12 cm, a wall thickness of 0.63 cm, and a length of 6.3 cm. This chamber was used for all samples of more than 21 percent moisture.
In both chambers there was a hole near the bottom edge of the chamber through which the tensiometer cup could be inserted and the tube (B$_2$) cemented in place with epoxy resin. A ceramic plate with an air entry value of 1 bar was fixed on the cylinder base that separated the chamber from the outside so that only water and dissolved solutes could run out of the chamber. The chamber was thus air tight.

The ceramic plate was cemented to the cylinder base of the lucite chamber by Silastic.$^1$ The brass chamber was sealed with the "O" ring which sat right on the edge of the plate, thus automatically sealing the chamber.

The entire unit in both chambers was held together by the use of four metal bolts. Rubber "O" rings were used to seal both top and bottom to the system.

**Tensiometer system**

The ceramic tensiometer cup (outside diameter 0.5 cm and length 5 cm) was cemented to lucite plastic tube (B$_2$) which had an outside diameter of 0.9 cm. The connection between tube (B$_2$) and the mercury manometer was made of a tygon tubing with an inside diameter of .45 cm or copper tubing with an inside diameter of 0.15 cm for suction less or more than 250 mb.$^2$

The mercury manometer was made of a U-shaped glass capillary tube with an inside diameter of 0.1 cm. This gave a volume change of 0.079 cm$^3$

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$^1$Silastic RTV 731, Dow Corning Corporation, Midland, Michigan.

$^2$It was observed that tygon tubing does not stand suctions higher than 250 mb. At higher suctions, air leaked through it. Other tubing like Korseal and rubber were tried with no successful results, and finally copper tubing was used and was successful.
for each 13.55 millibars change in suction. A glass "T" joint was used to make the connection between the manometer and the tube \(B_2\). The joints were made of rubber or Korseal tubing 0.47 cm in diameter.

The whole tensiometer system was filled with de-aired water to establish a hydraulic connection between the tensiometer cup and with the contents of the soil and the mercury in one leg of the manometer. The other leg of the mercury manometer was connected to the pressure chamber through the rubber tubing \(D_2\) in order to provide the equality reference pressure on the soil and the mercury. The system was sealed with the clamp \(V_1\) and a rubber stopper at the top of \(B_2\).

**Pressure control**

The pressure control system consisted of a manostat, a pressure gauge, a mercury manometer, and a water trap. The air was introduced into the system from a compressor and the desired pressure difference was maintained with \(1.3\) mb. by a proper adjustment of the pressure gauge and a manostat No. 8.\(^3\) The water trap was used to remove any waters that might possibly come from the compressor and thus prevent water entry into the system.

**Extraction unit**

The outflow tube of the pressure chamber was connected to an Erlenmeyer flask where soil extract was collected. The flask was connected through \(F_2\) to a vacuum control unit where the vacuum was being controlled by a manostat similar to \(E_1\). During the process of extraction, the clamp \(V_2\) was closed and \(V_3\) was open.

\(^3\)Manostat Corporation, 20-26 N. Moore Street, New York 13, New York.
Temperature control

All experiments were carried out in a constant temperature room with temperature variations of ± 0.5° C. In addition, the pressure chamber, containing the soil sample, was suspended in a constant temperature (± 0.05° C) water bath of dimensions 76 x 38 x 38 cm. Figure 8 shows a schematic diagram of the temperature control system.

Temperature control was affected by a continuous cooling and intermittent heating arrangement. The water was stirred constantly by a small pump. When the desired bath temperature was greater than the air temperature, cooling was by evaporation and heat dissipation to the surroundings. When a bath temperature below room temperature was desired, cold tap water was circulated through coils that were immersed in the water bath.

The control circuit consisted of a mercury thermoregulator, a resistance heating coil immersed in the water bath, and an electronic relay.4 The sensitivity of the thermoregulator was ± 0.01° C. Observation of a thermometer in the water bath sensitive to ± 0.05° C revealed no observable temperature variations; therefore, it is reasonable to expect that soil sample temperature variations were less than ± 0.05° C.

Most of the experiments were conducted at 20.0° in the temperature bath and at 20 ± 0.5° in the room except for water contact of 24.1 percent for which the experiment was repeated at 11.0, 30.0, and 40.0° C.

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4American Instrument Company, Silver Spring, Maryland.
Figure E. Water bath for temperature control.
Experimental Procedure

Both pressure chambers were used simultaneously with Millville silt loam soil taken from the Greenville Experimental Farm in the vicinity of North Logan, Utah. Samples of approximately 300 and 100 grams of air-dried soils were used for brass and lucite chamber, respectively. The soil was passed through a 2 mm round-hole sieve and was allowed to become saturated from the bottom for a period of 4 to 5 hours. The saturated soil was transferred to the pressure chamber and a desired moisture potential was obtained by extraction under vacuum from the outflow tube of each chamber. After equilibrium was reached (when there was no change in tensiometer reading), the clamp \( V_3 \) was closed and \( V_2 \) opened (Figure 7), thus preventing any more outflow of water and insuring that the soil remained at constant water content.

The equilibrium water potential, obtained from the tensiometer, was taken when the soil was at atmospheric pressure. Thereafter, the pressure was increased in increments of 5 cm Hg up to a maximum of 25 cm Hg atmospheric pressure, after which the pressure was released and the dry weight moisture percentage determined for all except one sample which was taken through a pressure reduction cycle in order to study the hysteresis effect. For all pressure change the equilibrium tensiometer reading was reached within 48 hours. When the tensiometer reading did not change for a period of at least 12 hours, it was assumed that the equilibrium was reached, and from that the water potential was measured for that particular pressure.

After the series of pressures had been completed for soil at one
constant water content, $V_3$ was opened and $V_2$ closed to extract water from the soil again, and the same procedure was used at a lower soil water content. Usually the same soil was used for repeating the experiment at successively lower water contents; but sometimes it was necessary to introduce a new sample because of technical difficulties.

The wetting of air-dried soil samples was done in most cases under atmospheric pressure, except for one run in which the soil was wet under a high vacuum of approximately 2 cm Hg of absolute pressure. During this process the air-dried soil was placed in the lucite cylinder and the vacuum was applied to the chamber while water was being allowed to enter through the ceramic plate until the soil was saturated. Thereafter, a desirable water content was obtained by the extraction procedure described previously.

To compare the result of pressure plate apparatus with tensiometer for determining the soil water retention curve, a separate experiment was conducted in which the soil was extracted in a pressure plate apparatus by applying increments of pressure to the system. At each pressure the volume of outflow solution was measured with ± .02 cm$^3$ accuracy. From this outflow measurement, the water content of the soil was calculated for each pressure.

**Results**

The results show an effect of external pressure on soil water matric potential as shown in Figure 9, where soil water matric potential is plotted as a function of absolute external pressure for three water

---

5It was thought that this method of wetting would prevent or minimize entrapped air in the soil-water system.
Figure 9. Pressure variation of soil water matric potential for run a₁ at 20.0°C.
contents in one run \((a_1)\) starting from wet \((\theta = 34.3\) percent\) to drier \((\theta = 24.1\) percent\). The soil remained undisturbed in the brass chamber throughout the entire run and the temperature was at 20.0\(^\circ\) C. A straight line relation seems to adequately fit the data.

The result for run \(b_1\), in which the experiment was conducted in the lucite chamber for three lower water contents is shown in Figure 10.

Figures 9 and 10 indicate a definite trend for the slope of the lines as the soils become drier, although this is not apparent if Figure 9 is taken alone.

The results of three runs each at only one water content are plotted in Figure 11. The continuation of the runs for other water contents became impossible in runs \(a_2\) and \(b_2\) because of technical difficulties. In run \(b_3\) the soil was wetted under vacuum and then dried to \(\theta = 24.7\) percent.

The pressure dependence of soil water matric potential at four different temperatures for water content of 24.1 percent is shown in Figure 12. There is no particular trend for the change of the slope in this temperature range as shown by statistical analysis (Table 1).

The data of temperature dependence of soil water matric potential are obtained from Figure 12 and are given in Table 2, and the relation plotted in Figure 13 which shows an increase in soil water matric potential with temperature. This results in agreement with the findings of Taylor and Stewart (44), although unpublished results of the vapor pressure method have recently shown the opposite; that is, the water potential decreases with increasing temperature.\(^6\)

---

Figure 10. Pressure variation of soil water matric potential for run b at 20 ± 0.5°C.
Figure 11. Pressure variation of soil water matric potential for runs $b_2$, $b_3$, and $a_3$ at $20^\circ \text{C}$. 

$\theta = 27.1\%$

$24.7\%$

$22.8\%$
Figure 12. Pressure variation of soil water matric potential for run at a\textsubscript{1} of 24.1 percent water content and at 4 different temperatures.
Table 1. Calculated slopes ($\frac{\partial \psi_m}{\partial \text{Pe}}$) with confidence limits at 99 percent level at different temperatures for 24.1 percent water content

<table>
<thead>
<tr>
<th>Runs</th>
<th>Temperature °C</th>
<th>Slope b</th>
<th>Standard error of b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>11</td>
<td>-0.197 ± 0.046</td>
<td>0.010</td>
</tr>
<tr>
<td>$a_1$</td>
<td>20</td>
<td>-0.119 ± 0.037</td>
<td>0.008</td>
</tr>
<tr>
<td>$a_1$</td>
<td>30</td>
<td>-0.151 ± 0.051</td>
<td>0.012</td>
</tr>
<tr>
<td>$a_1$</td>
<td>40</td>
<td>-0.146 ± 0.041</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Table 2. Soil water matric potential\(^a\) at three different external pressures and four different temperatures, (obtained from Figure 12)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$P_e$ millibars</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900</td>
</tr>
<tr>
<td>11</td>
<td>-27.1</td>
</tr>
<tr>
<td>20</td>
<td>-24.2</td>
</tr>
<tr>
<td>30</td>
<td>-18.7</td>
</tr>
<tr>
<td>40</td>
<td>-16.8</td>
</tr>
</tbody>
</table>

\(^a\)In terms of joules per kilogram.
A definite hysteresis effect that depends upon which direction the pressure is changing was found and is shown in Figure 14.

Soil water matric potential is plotted as a function of water content for data obtained by pressure plate apparatus and tensiometer in Figure 15. The plot shows that the water retention curves obtained by the two methods are different, that the tensiometer curve is significantly above the other curve as soon as the water content is below saturation, and the two curves diverge as the soil gets drier.

In order to calculate the potential specific volume of soil water, the slopes of the lines \( \frac{\partial \psi_m}{\partial P_e} \) of Figures 3, 9, 10, and 11 for different water contents and temperatures, are given in Table 3. The slopes are associated with their appropriate confidence limits at 99 percent level. The tabulated values of \( \overline{V_w} \) were then calculated from equation [27] by using data for \( \overline{V_w^o} \) taken from the Handbook of Physics and Chemistry (21) and are listed in the last column of Table 3 together with their confidence limits obtained by assuming that \( \overline{V_w^o} \) was known without error.

Since temperature seems to have no significant effect on the slope of the lines (Figure 12), the condition of precise constant temperature is not necessary.

The data of Table 3 are plotted in Figure 16 which shows the partial specific volume of soil water as a function of soil water content for all runs. The data seem to be scattered around a straight line with a zero slope down to about 21 percent moisture content, which is the field capacity of Millville silt loam soil, below which a significant reduction in \( \overline{V_w} \) occurs.
Figure 13. Temperature variation of soil water matric potential for run a of 24.1 percent water content at 3 different external pressures.
Figure 14. Pressure variation of soil water matric potential as the pressure varies around cycles showing the hysteresis effect for $a_1$ at 24.1 percent water content at 20.0°C.
Figure 15. Soil water release curve as obtained by tensiometer and pressure plate apparatus.
Table 3. Computed slopes \( \frac{\partial \psi_m}{\partial P_e} \) associated with 99 percent confidence limit for different runs and water contents and temperatures

<table>
<thead>
<tr>
<th>Runs</th>
<th>Water content</th>
<th>Temperature</th>
<th>Slope</th>
<th>( \overline{V_w} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1 )</td>
<td>34.3</td>
<td>20.0</td>
<td>-0.059 ± 0.009</td>
<td>0.943 ± 0.009</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>31.2</td>
<td>20.0</td>
<td>-0.215 ± 0.050</td>
<td>0.787 ± 0.050</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>24.1</td>
<td>20.0</td>
<td>-0.119 ± 0.037</td>
<td>0.883 ± 0.037</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>20.5</td>
<td>20 ± 0.5</td>
<td>-0.204 ± 0.050</td>
<td>0.798 ± 0.050</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>18.4</td>
<td>20 ± 0.5</td>
<td>-0.399 ± 0.074</td>
<td>0.603 ± 0.074</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>16.6</td>
<td>20 ± 0.5</td>
<td>-0.450 ± 0.060</td>
<td>0.552 ± 0.060</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>17.6</td>
<td>20 ± 0.5</td>
<td>-0.464 ± 0.046</td>
<td>0.538 ± 0.046</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>27.1</td>
<td>20.0</td>
<td>-0.217 ± 0.090</td>
<td>0.785 ± 0.090</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>22.3</td>
<td>20.0</td>
<td>-0.071 ± 0.018</td>
<td>0.931 ± 0.018</td>
</tr>
<tr>
<td>( b_3 )</td>
<td>24.7</td>
<td>20 ± 0.5</td>
<td>-0.240 ± 0.060</td>
<td>0.762 ± 0.060</td>
</tr>
<tr>
<td>( x_1 )</td>
<td>28.3</td>
<td>20 ± 0.5</td>
<td>-0.125 ± 0.032</td>
<td>0.877 ± 0.032</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>26.5</td>
<td>23 ± 0.5</td>
<td>-0.127 ± 0.041</td>
<td>0.875 ± 0.041</td>
</tr>
</tbody>
</table>
Figure 16. Variation of $\bar{V}_w$ with soil water content for different runs at $20^\circ$ C temperature.
DISCUSSION

The results of both the preliminary and primary experiments show a linear decrease in soil water matric potential as pressure increases from 860 to 1,200 millibars. The potential was measured with an accuracy of ±0.13 joules per kilogram, which is approximately 25 times greater than the accuracy of the experiment reported by Richards et al. (35) in which the effect of total pressure on the vapor pressure of soil water could not be detected for a dry soil that had a water potential of -600 joules per kilogram, even though the differences reported here are large enough that they should be detectable with the practices he used. It is possible that the soil water in such a low potential region as Richards' used might be less pressure dependent and cannot be detected with his accuracy of measurement. This does not seem probable, however, since the data reported here indicate an increasing sensitivity to pressure as the soil became drier. It should also be noted that Richards' procedure using the vapor pressure technique measures all components of the soil water potential while the tensiometer, used here, measures only the matric component and not that which results from soluble materials. It seems unlikely, however, that pressure induced through insolubility of soil materials would be enough to account for the discrepancy. Consequently, the problem should be studied in more detail.

The decrease of matric potential with pressure indicates, according to equation (35), that the chemical potential of free water changes at a faster rate than that of soil water as pressure increases; that is, soil
water chemical potential is less pressure dependent than free water.

The study of pressure dependence of the soil water potential requires that other variables be kept constant. In this experiment temperature was kept constant to \( \pm 0.05^\circ C \) and water content was also kept constant (at least within the error of measurement of water content by the gravimetric method). The effect of volume change due to change of solubility of air has already been shown to be negligible (14), and salt concentration is also considered to be independent of air pressure in the pressure range of around 1 bar (18). Attention should be given to the remaining variables, soil bulk density, whose constancy as the external pressure has changed is not clear. Theoretically, air pressure should not have a compressing effect to compact an unsaturated soil. The fact that Alpan (2) found no measurable change in the bulk volume of a moist soil as air pressure was applied supports the above statements. Nevertheless, in a really wet soil near saturation, air pressure might partially have a compressing effect. But it should be expected that the compressing effect of air pressure must decrease rapidly as soil gets drier.

A look at Figures 9, 10, 11, and 16 and Table 3 shows that the wide variation of the slope of the line \( \left( \frac{\partial \psi_m}{\partial P_e} \right) \) and therefore \( \bar{V}_w \) in the water content range of 22 to 34 percent may include some bulk density changes. The bulk density changes might have occurred as a result of shrinkage as the soil dried in addition to any possible compression of the soil that might result from increased air pressure at a particular water content. The possibility of such a change is expected to be more
intense in the wet than in the drier regions as was actually found. When the water content was below 21 percent, as Figure 16 shows, there was a definite reduction in $\overline{V_W}$ which can no longer be attributed to experimental error or bulk volume change. The points in this region were taken from the same undisturbed soil sample in which water content and associated factors constituted the only known variable. The fact that the reduction in $\overline{V_W}$ takes place near 20 percent water content, and the field capacity near the same value, suggests that there might be a more rapid change taking place in the physical status of soil water in this region of water contents.

A hysteresis effect in pressure-soil water matric potential relationship is apparent in Figure 14. The fact that the curves for the first cycle do not close suggests the possibility of a change in soil structure as pressure was applied and released. Hysteresis effect has also been reported to exist in soil water potential-water content and temperature relationship (43). In the case of temperature the fact that the hysteresis curves never closed lead the authors to conclude that structural changes had occurred (43).

Temperature seems to have no significant effect on the slope of the moisture potential-pressure curves as is shown in Figure 12 and Table 1. This indicates that the temperature dependence of soil water partial specific volume and therefore, the pressure dependence of the partial specific entropy soil water according to equation $[\frac{2\sigma}{7}]$ is smaller than can be detected within the accuracy of this study.

The theory proposed by Peck (31) in which the pressure dependence of soil water potential is based only on the volume of the entrapped
air in the soil-water system, does not seem to be consistent with experimental results. This is evident by the fact that the soil sample that was wet in vacuum, a practice for eliminating the entrapped air, showed a definite pressure dependence of matric potential with no significant difference to those samples which were wet under atmospheric pressure.

**Interpretation of the Result of Moisture Blocks**

The result of moisture gypsum block experiment shows a decrease of block resistance as air pressure increases. The block resistance is a measure of the amount of dissolved gypsum in the block, and that in turn is a measure of the water content of the block. The reduction of block resistance as a result of pressure increase can be explained by the following postulates:

First, pressure might have affected the solubility of gypsum in the block according to equation [22] and then caused the resistance to be decreased. The reduction of resistance of the saturated blocks in free water can particularly be interpreted according to this postulation.

Second, considering $\mu_s$ and $\mu_b$ to be the chemical potential of water in the soil and in the block, respectively, at equilibrium and at pressure $P_1$:

$$\mu_{s_1} = \mu_{b_1}$$  \[46\]

When pressure is applied to the system, $\mu_s$ and $\mu_b$ both increase but with different rates so that

$$\frac{\partial \mu_s}{\partial P_e} > \frac{\partial \mu_b}{\partial P_e}$$

This would convert equation [46] to an inequality at pressure $P_2$, $\mu_{s_2} > \mu_{b_2}$

In order for equilibrium to be established again, some water has to move
from the soil to the block, and that reduces the resistance.

In the case of blocks in free water, the same interpretation can be applied; that is

$$\frac{\partial \mu}{\partial P_e} > \frac{\partial \mu_b}{\partial P_e}$$

Therefore, the final chemical potential of the free water will be greater than that of block water, and this will induce water to flow to the block and in turn to reduce the resistance.

**Significance of \( \bar{V}_W \)**

Before we discuss the significance of \( \bar{V}_W \), it is appropriate to review a few facts presented by Glasstone (18) concerning the behavior of some ideal mixtures.

Glasstone (15) explains that when two liquids are mixed to form an ideal solution, there will be no change in the volume, and the partial specific volume of each constituent is equal to its specific volume in the pure state. Ideal solutions obey Raoult's Law; and, therefore, there is also no change in the partial vapor pressure of each constituent. There are mixtures that exhibit a negative deviation from Raoult's Law; that is, the vapor pressure is lowered, the volume is decreased, and heat is evolved as the mixing takes place. Glasstone (18) attributes this behavior to the net attractive forces that exist between the two species. Of course, there are mixtures that show a positive deviation from Raoult's Law, and behave completely opposite to the previous group due to the fact

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1Raoult's Law is an equation that relates partial vapor pressure of a substance in a mixture to its mole fraction by a simple proportionality constant \( P_i = k N_i \) where \( P_i \) is partial vapor pressure, \( k \) a constant, and \( N_i \) is mole fraction.
that the mean attractive force between the two species in the mixture is smaller than for each one separately.

Soil-water systems can be considered as binary mixtures that exhibit a negative deviation from Raoult's Law on the basis of the following characteristics. First, it is a well-known fact that as water goes from free state to its state in unsaturated soil, its vapor pressure is reduced by an amount depending on the water content of the soil. Second, when water is mixed with dry soil, heat is evolved as the heat of wetting or heat of immersion. Finally, it is a well-known fact that there are attractive forces between soil and water which cause the retention of water in soils. In view of these points, a decrease in volume as water is mixed with soil could be expected, since this was one of the characteristic behaviors of non-ideal mixtures that shows a negative deviation from Raoult's Law. This is in agreement with the present findings that the partial specific volume of water is decreased as it goes from its free state to its state as soil water, and in disagreement with the report of Anderson and Low (3, 4) that the partial specific volume of water in a clay system was greater than that of free water. However, the evaluation of $\bar{V}_w$ in this study is based upon thermodynamic measurements that assume a two-component system of soil and water. Likewise, thermodynamics predicts a decrease in soil water partial specific volume with respect to that of water in the free state. Considering the fact that there have been other workers (16, 28) who have reported the specific volume of soil water to be less than unity (down to 0.71) we might suspect that the result of Anderson and Low's (3, 4) experiment is subject to some unknown
errors, or perhaps the changes in volume that they observed were not attributable to a difference in partial specific volume of soil water.

The results of this study assume a more dense structure for soil water which is an indication of more orderliness of the water molecules, and this, in turn, is an indication of lower entropy for soil water than free water. This conclusion is supported by the work of Taylor and Stewart (44).
CONCLUSIONS

1. It has been experimentally demonstrated that soil-water matric potential is pressure dependent, and that the potential decreases as pressure increases.

2. Temperature seems to have no measurable interaction with the pressure-matric potential relationship.

3. There is a hysteresis effect in the pressure-matric potential relationship.

4. Water content affects the pressure dependence of matric potential of Millville silt loam soil particularly in the region immediately below "field capacity."

5. The presence or absence of entrapped air in soil water systems does not seem to affect the pressure dependence of matric potential.

6. Pressure plate apparatus produces a soil-water retention curve that underestimates the potential of soil water as measured by tensiometers operating at atmospheric pressure.

7. Air pressure reduces the electrical resistance of moisture gypsum blocks buried in soil due to the effect of pressure on solubility of gypsum or perhaps due to the fact that the soil water is more pressure dependent than water in the gypsum blocks.

8. The pressure dependence of soil water matric potential as reported here, suggests that there must be a decrease in volume as water is mixed with unsaturated soil.
SUMMARY

An experiment has been developed to measure the soil water matric potential by tensiometers as the external air pressure changes. The apparatus was so designed that the pressure on the soil and on the mercury reference level of tensiometer was changed periodically, and the equilibrium matric potential was measured from the tensiometer reading.

The overall results showed a decrease in soil water matric potential as pressure increased from 500 to 1,220 millibars. The slope of the pressure-matric potential relationship did not vary significantly as soil water content decreased down to 20 percent (field capacity of the Millville loam soil) after which it dropped sharply as the water content decreased to 16 percent. Temperature in the range of 11° to 40° C showed no significant effect on the slopes. The existence of a hysteresis effect in the relationship was evident.

Study of the moisture blocks buried in soil in a pressure chamber showed that pressure reduced the electrical resistance of the blocks.

Comparison of the results of the pressure plate apparatus and tensiometer showed that the two produced different soil-water retention curves that diverged from each other as water content decreased. The pressure plate curve underestimated the matric potential in comparison with tensiometer curves at any particular water content.

A soil sample that was wet under low vacuum, therefore, had a minimum amount of entrapped air and showed no significant differences from other samples toward pressure changes.

The partial specific volume of soil water obtained from pressure dependence data was always less than that of free water.
LITERATURE CITED


APPENDIX A
Proposition #1 - Fall and winter irrigation could be practiced to reduce water need of certain crops during the growing season. This may also improve soil physical condition.

In many places in the world the cost of irrigation water during the growing season (summer in particular) is really high and sometimes it is economically unpractical to irrigate a farm. Fall and winter precipitation, on the other hand, is insufficient to keep the soil moist and prevent it from drought. In such localities water should be used with the highest possible efficiency throughout the entire year to conserve moisture in the soil for crop use.

Soil as a water reservoir

In some places storage of water in the surface reservoirs is unpractical because of high cost and lack of suitable natural facilities. In such cases it is advantageous to use the soil as a storage reservoir and to apply water whenever available as a means of storing it for future use.

A portion of the water that reaches the ground from precipitation or irrigation is wasted as run-off. The remainder that enters the soil is partly percolated from the root zone and the rest is stored in the soil which will be returned to the atmosphere either by soil surface evaporation or plant transpiration. Thus, storage of water in the soil deals with the balance amount of water application (or precipitation), run-off, deep percolation, and evaporation. In other words, run-off, evaporation and deep percolation should be minimum in order to make a maximum efficiency water storage in the soil. Run-off could be minimized by the use of proper tillage operation but evaporation is the main source of water loss and is something that cannot be prevented. Many practices have been recommended to reduce evaporation, some of which have been already proven to be of little value (3). Summer fallow has been shown to be of some value for water storage in the soil for future crop use (3). The efficiency of storage, as reported by workers in different parts of the U.S., can be from 25 to 60 percent. Self-mulching due to rapid drying of the soil surface is another means of reducing water loss from the lower depth, since the dry surface soil transmits little water to the surface to be lost in evaporation (3).

Practicability of fall and winter irrigation

Generally speaking, there is more water available for irrigation in the fall and winter, and in most cases the water is being wasted. Thus, the cost of irrigation water is practically nothing. In fact, the total operation cost was shown to be four times less than irrigation during the vegetative period (4). In the winter if the climate is mild and there is no severe soil freezing, irrigation may be practiced similarly, though a report from USSR (4) shows that winter irrigation is also practicable during the time the soil is frozen.
Effect on soil temperature

The undesirable consequences of drought are not only due to the shortage of water, but also to soil overheating. For some crops in arid and semi-arid regions the air temperature in contact with the soil and soil temperature is usually much higher than the biological optimum.

By fall and winter irrigation of the new irrigated area of the Lenin Volga-Don Carrol, USSR Shubin (4) has reported the following hydro-thermal effects:

1. A soil temperature decrease of (0-100 cm depth) 2°-4° C during the entire vegetative period.

2. Considerable cooling of the air layer (10°-12° C above the soil surface and 3°-6°C at the height of 50-100 cm) especially in spring.

3. Air humidity increase of 18-20 percent in early spring.

These results are with respect to the control plots which were not irrigated in the fall and winter. For the arid region of south Volga of USSR the soil temperature of 28°-30° C is normal for the period that tubers begin to form, and this temperature stops the growing of tubers. In fall and winter irrigated fields soil temperature does not exceed 26° C and there is no degeneration of tubers. This cooling effect plays a very important role in the early spring time, since the ground is not shaded and is being dried by hot sun rays and possibly strong winds.

Effect on yield

Fall and winter irrigation has been reported (4) to effect and increase the yield of spring wheat and potatoes at a collective farm in USSR by a significant amount with respect to control plots. The result is shown in the following table.

Table 4. Effect of Fall-Winter Irrigation on Yield

<table>
<thead>
<tr>
<th>Irrigation treatments</th>
<th>Spring wheat yield (centner/ha)</th>
<th>Tuber yield (centner/ha)</th>
<th>Potatoes Large marketing tuber percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fall-Winter only</td>
<td>14.8</td>
<td>192.0</td>
<td>80.0</td>
</tr>
<tr>
<td>2. Fall-Winter 2 vegetative</td>
<td>24.3</td>
<td>224.0</td>
<td>93.0</td>
</tr>
<tr>
<td>3. 2 vegetative only</td>
<td>21.3</td>
<td>46.0</td>
<td>30.4</td>
</tr>
<tr>
<td>4. No irrigation</td>
<td>9.1</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

1 After Shubin(4)
This table shows that fall-winter irrigation could be practiced for potatoes without any supplemental watering during the growing season, to yield a higher yield than would be obtained if the crop were irrigated only during the growing season.

It is interesting to mention at this point that in some agricultural districts in Iran (Varamin and Garmsar) where the annual precipitation is less than 10 inches with mild winters and very hot summers, fall and winter irrigation is being practiced to grow very good quality melons and watermelons. They till the land and then irrigate it by the method of basin (Kart) in the fall and winter. In early springtime the land is cultivated. The seed is planted and irrigated again; from then on no irrigation is applied throughout the entire season.

Reduction of water requirement (evapotranspiration)

Water need of a crop which is irrigated in fall and winter will be reduced for the growing season for the following reasons:

1. As was reported by Russian scientists (4) the temperature of the soil and air layer (up to 100 cm height) is reduced during the growing season for plots with irrigation in the fall and winter with respect to those with no irrigation in the fall and winter. However, air temperature is the main factor for estimating evapotranspiration by some empirical methods such as Blaney-Criddle and Thornthwaite (2). These methods are based in the mean monthly air temperature. Hence a reduction of 3°-6° C or 5°-11° F would cause a real significant reduction of water consumption.

2. Fall and winter irrigation, as was shown previously, reduces the number of irrigations during the growing season (sometimes there is no need for vegetative irrigation). This is very important point in reducing evapotranspiration during the growing season due to these possible reasons:

(a) It has been shown by many workers (2) that evapotranspiration decreases as the soil moisture suction increases. This means that during the first couple of days immediately following irrigation, evapotranspiration is only a function of evaporative demand (with no soil factor), because of lower amount of net radiation in the fall and winter. Water loss due to evapotranspiration would be much higher during the growing season after any irrigation.

(b) It has been shown experimentally (1, 2) that following any irrigation the net radiation above the irrigated field is increased, especially if the crop spacing is large (as in the case of melons and watermelons). Since evaporation is a direct function of net radiation, it is increased after any irrigation. The effect may not be as great for fall and winter irrigation.
Effect on soil physical conditions

Drought is known to have bad effects on soil physical conditions. It has been shown (4) that fall and winter irrigation could be practiced to control drought which, in a way, would be an improvement to soil physical conditions. It has been shown that fall and winter irrigation makes water penetration easier and decreases the salt concentration (4). Besides, in places where most of the rainstorms fall during the fall and winter seasons, water is usually muddy as a result of floods, and this would make the soil productive with feasible physical conditions. This is particularly true in cases of Varamin and Garmesar provinces of Iran.

References


Proposition #2 - The comparison of total moisture suction with solute and matric suction as is reported by Richards and Ogata (1961) is subject to serious errors for at least two reasons.

The concept of total, solute, and matric suction has been presented in the literature review of this dissertation. Richards and Ogata (3) made the comparison of total suction and solute and matric suction on several soil samples. They measured the total suction (TS) and solute suction (SS) by the method of vapor pressure and matric suction (MS) by pressure membrane apparatus. They put the soil samples in the pressure membrane apparatus and applied a given pressure; after equilibrium is established (the out-flow has ceased) they took the sample out and put it in vapor pressure apparatus for measurement of TS. They considered the equilibrium pressure on the sample in the pressure membrane apparatus as the matric suction (MS). The extracts for SS measurements were made from saturated paste of soil samples.

The result of Richards' and Ogata's experiment showed that the TS values were always less than (MS + SS) values for the group of samples with low SS. On the other hand, for samples of medium or high SS on the average the TS values seemed to be higher than (MS + SS) values. The authors called these discrepancies experimental error.

As for the defense of the proposition, it will be shown that the occurrence of these discrepancies was not just due to experimental error but rather that they could be interpreted.

Going back to the basic thermodynamic equation for soil water as given in the text of this dissertation for the condition of constant temperature bulk density, one can write

\[ d\mu = -\nabla_w dP_e + \tau d\theta + \Pi d\pi \]  \[ \text{[1]} \]

We can apply this equation to a pressure membrane apparatus when the soil is put under pressure and the equilibrium is established. Integration of equation [1] between the two limits of saturated soil and equilibrium state would give:

\[ \int_{\mu^0}^{\mu} d\mu = \int_{P_e}^{P_e} \nabla_w dP_e + \int_{\theta_0}^{\theta} \tau d\theta + \int_{\pi}^{\pi} \Pi d\pi \]  \[ \text{[2]} \]

for a salt free soil \( d\pi \) is zero, and the pressure membrane equation is derived as:

\[ MS = \int_{\theta_0}^{\theta} \tau d\theta = -\nabla_w (P_{e1} - P_e) \]  \[ \text{[3]} \]

1 Refer to page 24.
In the case where salt concentration is not negligible, \( \tau \) would not be zero due to salt sieving effect as was introduced by Kemper (2). The difference between the two chemical potentials of water outside and inside the pressure cell is no longer zero. Also, according to definition of \( \tau \) in equation [3]

\[
\tau = (\frac{\partial m}{\partial \theta})\tau, n_j
\]

because \( n_j \) is not constant as moisture content changes; thus the term \( (\frac{\partial m}{\partial \theta})\tau \) with varying \( n_j \), is no longer \( \tau \) and it could be denoted by \( \tau' \) and therefore

\[
\int_0^n \tau' \, d n_w = M S'
\]

Equation [2] after rearranging then becomes

\[
V_w (P_e - P_e) = (\mu - \mu_0) - M S' - \int_{n_0}^{n_j} \tau d n_j \ldots [5]
\]

and equation [4] becomes

\[
V_w (P_h - P_e) = - M S' \quad \text{if} \quad (\mu - \mu_p) = \int_{n_0}^{n_j} \tau d n_j \ldots [6]
\]

indicating that the pressure difference across a pressure membrane does not give the matric potential but something different.

In interpreting the results of Richards' and Ogata's experiment, two cases should be considered: First, for the group of samples of low salt content, equation [3] is applied. In this equation \( V_w \) is the partial specific volume of soil water which has been shown to have a value lower than 1 (in C.G.S. system (1)). This means that in pressure membrane apparatus the pressure applied to the system cannot be considered as matric suction, but rather it should be multiplied by a factor which is less than unity. If this factor is used to correct for the \( M S \) values of Richards' and Ogata's experiment for the sample group of low salt content, the discrepancy in comparison of \( TS \) and \( (SS + hS) \) will be minimized.

Second, according to equation [4] in cases where there is considerable salt in the soil, such as those samples of medium and high salt content, matric suction can no longer be estimated by pressure differences across the membrane. The main difficulty here is due to the fact that successive increments of solution coming out of a pressure membrane have higher salt concentration due to "salt sieving" effect (2). This would make the following effects on Richards' and Ogata's experimental results:
(a) Since their SS values were evaluated for saturated extracts, it will underestimate the actual value at any given matric suction (especially at higher suctions).

(b) The MS values are affected by this change in the salt concentration according to equations \[ 4 \] and \[ 6 \].

In short, the sum of (a) and (b) effects could be concluded to have caused the discrepancies between TS and (MS + SS) values for the medium and high salt content groups.

References


Proposition #3 - Soil moisture hysteresis could be explained to be a result of irreversibilities in the adsorption-desorption processes and is directly related to the net production of entropy.

Introduction

Hysteresis has been explained on the basis of the work of expansion or swelling during the adsorption-desorption process (2). This work is calculated from the area of the hysteresis loop, and the "entropy of hysteresis" is obtained by dividing the work so obtained by the absolute temperature. The authors of this explanation give no justification for this procedure, nor did they show the significance of the term, "entropy of hysteresis." The purpose of this work is to examine the above concept and procedure as to its validity and significance.

There are reasons to believe that if the processes of adsorption and desorption are being done reversely, there wouldn't be any hysteresis. In other words, hysteresis occurs because of irreversibility in one or both paths of the hysteresis loop. Barkas (1) stated that any work loss involves irreversible changes, and the shape of the hysteresis depends on the way in which those changes are being made (including possibility of time) as well as the limits of moisture content and the vapor pressure between which the cycle is performed.

Jurinak (5), studying adsorption-desorption of water and some gases on Li-Kaolinite clay, found that in cases where adsorption and desorption took place almost reversibly, hysteresis did not show in the adsorption-desorption curve.

Theory

If all variables other than soil water content are kept constant, equation \[ \ell_7 \] would become

\[ d\mu = HTd\theta \] \[ \ell_1 \]

According to Glasstone (4), chemical potential can be expressed in terms of partial molar quantities of enthalpy and entropy as

\[ \mu = \bar{H} - TS \] \[ \ell_2 \]

where \( \bar{H} \) and \( S \) are the partial molar enthalpy and entropy of soil water, respectively. Differentiating this equation at constant \( T \) results in

\[ d\mu = d\bar{H} - TdS \] \[ \ell_3 \]

Comparison of equations \[ \ell_1 \] and \[ \ell_3 \] gives

\[ \bar{F} - TdS = \tau d\theta \] \[ \ell_4 \]
Equation \[ \int_4 \] can be integrated over two paths, one for the drying process, and one for the wetting process. Taking the limits of integration between the state of saturated moisture content, \( \theta^0 \), and some unsaturated state with moisture content \( \theta \), one gets for drying, denoted with the subscript 1,

\[
(\Delta H)_1 - T(\Delta S)_1 = -\int_{\theta^0}^{\theta} \tau_1 \, d \theta \quad \ldots \ldots \int_5
\]

and for wetting, denoted with the subscript 2,

\[
-(\Delta H)_2 + T(\Delta S)_2 = \int_{\theta^0}^{\theta} \tau_2 \, d \theta \quad \ldots \ldots \int_6
\]

where the paths of integration for the right side of equations \[ \int_5 \] and \[ \int_6 \] are shown schematically in Figure 1.1

Addition of equations \[ \int_5 \] and \[ \int_6 \] gives

\[
(\Delta H)_1 - (\Delta H)_2 - T \int (\Delta S)_1 - (\Delta S)_2 = \int_{\theta^0}^{\theta^0} (\tau_2 - \tau_1) \, d \theta \quad \int_7
\]

From Figure 1 it is obvious that the integral on the right side of equation \[ \int_7 \] must have a positive finite value, \( A(\theta) \), different from zero, which corresponds to the area enclosed by the hysteresis loop. Therefore,

\[
(\Delta H)_1 - T(\Delta S)_1 = (\Delta H)_2 - T(\Delta S)_2 + A(\theta) \quad \ldots \ldots \int_8
\]

The units of \( A(\theta) \) are specific energy and results from the amount of irreversible work performed during the wetting and drying cycles. In accordance with the definition of \( \Delta H \) and \( \Delta S \) (footnote 1), equation \[ \int_8 \] could also be written as

\[
\Sigma d H - T \Sigma d S = A(n^1) \, d n \quad \ldots \ldots \ldots \ldots \int_9
\]

where \( H \) and \( S \) are the enthalpy and entropy of the moist soil system. Integration of \[ \int_9 \] over the limits of the wetting and drying cycles at constant \( T \) and \( P \) gives

\[
\delta H - T \delta S = A(\theta) \, \Delta \theta \quad \ldots \ldots \ldots \ldots \int_{10}
\]

But

\[
A(\theta) \Delta \theta = \int_{\theta^0}^{\theta^0} (\Delta \mu_2 - \Delta \mu_1) \, d \theta \quad \ldots \ldots \ldots \ldots \int_{11}
\]

as may be seen from equations \[ \int_1 \] and \[ \int_7 \]. Therefore, the right side

---

1It should be noticed that \( H = \frac{\partial H}{\partial \theta} \) where \( H \) is the enthalpy of moist soil and \( (\Delta H)^2 = \frac{\partial (\frac{\partial H}{\partial \theta})}{\partial \theta} - \frac{\partial (\frac{\partial H}{\partial \theta})}{\partial \theta} \). The term \( \Delta S \) has, of course, a similar interpretation.
of equation (10) is the area of the hysteresis loop, denoted by A, as is shown in Figure 1, where \( \Delta \mu \) is plotted versus moisture content. Substituting equation (11) into equation (10) and dividing it by T results in

\[
\frac{\delta H}{T} - \frac{\delta S}{T} = \frac{1}{T} \int_{\alpha_{1}}^{\alpha_{2}} (\Delta \mu_{2} - \Delta \mu_{1}) \, d \alpha = \frac{A}{T}
\]

The left side of equation (12), according to Glasstone (4), is equal to \( S_{\text{net}} \), therefore

\[
S_{\text{net}} = A
\]

where \( S_{\text{net}} \) is the net production of entropy resulting from the irreversible wetting and drying cycles. It would be equal to the quantity \( \frac{A}{T} \) if either the wetting or drying cycle were carried out reversibly. Hysteresis may thus be interpreted as a natural phenomenon associated with spontaneous process.

References


Figure 17. Hypothetical hysteresis loop produced by the wetting and drying cycles where $\Delta \mu$ and $\tau$ are plotted versus moisture content.
Proposition 41: In countries where the peasants\(^1\) are poor and practically illiterate, land reform\(^2\) as a first step toward improvement is a serious mistake.

(In defending this proposition I will mostly be referring to the present conditions in Iran, which is my home country. That is, whatever statements are made here are strictly true for Iran and most probably for those countries in which the same conditions exist.)

Most of the countries that are being considered "underdeveloped" or "newly developed" are agricultural countries. That is, more than three-quarters of the population are engaged in agriculture. Also, as a general rule, most of the poverty and illiteracy existing in those countries are concentrated among this group of people. Tenancy is a feature of the land tenure system of these countries. The proportion of tenants to the total number of peasants varies widely from one country to another. Tenancy is, of course, not in itself an unsatisfactory form of tenure, where rents are not excessive and where security of tenure is safeguarded by legislation. But these conditions, generally speaking, are lacking in those poor agricultural countries where tenancy is characterized by exhorbitant rent charges and lack of security of tenure (?).

"Crop sharing" method is a prevalent form of tenancy in Iran and probably in most of the Middle Eastern countries (5, 6). Although the exact form of crop sharing varies widely from place to place, nevertheless, as a general rule, this method is based on five major elements or factors of production, including: land, water for irrigation, seed, labor (including implements), and draft animals (4). Each of these is considered to be equally as important as the others and, therefore, whoever provides one element will receive one-fifth of the crop. Usually the land owner provides land, water, seed, and occasionally draft animals; thus, he gets four-fifths of the crop; and the peasant who is only furnishing the labor would get only one-fifth. There is no security of tenure as was mentioned above. The land owner has the absolute power to hire or fire a peasant or transfer him from one farm to another.

The average annual income of a peasant is 60 dollars (8). In case of a bad year, they might practically get nothing and they would starve to death. With the exception of a few localities, civilization is practically nonexistent in the villages. Most of the peasants know nothing about outside of where they live.

The farming system is very inefficient. With the exception of a few places, land cultivation systems have not improved since 2000 years ago. Thousands of acres of land are being eroded due to being overgrazed by

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\(^1\)According to Webster's dictionary, peasant is referred to as a rustic laborer, farmer, or a countryman. In this proposition peasant is referring to those who work on the farm for the land owners, either as a tenant or worker.

\(^2\)Generally, land reform is referred to as any change in the land ownership system; either fragmentation or redistribution. In this proposition it is referred to as land distribution among peasants.
hungry goats. Water is wasted because of the poor method of irrigation and the lack of knowledge of how to conserve and use water efficiently. Most of the lands are exhausted and worn out due to the fact that there has been practically no return in the form of fertilizer to the soil. The animal manure is being used as a fuel in most villages.

Marketing systems, not only in rural communities but in the whole country, are very poor. The prices are not stable. If the year is good for the peasant and the yield is high, the prices are low; and if the year is bad with low yield, the prices are high. Therefore, the peasants suffer in any case.

Credit and agricultural indebtedness is considered as one of the most important factors for the present rural poverty. A report on land reform by the United Nations (7) states:

High rates of interest and high burdens of farm debt are characteristic features of the agrarian structure in many under-developed countries. Shortage of credit is both cause and effect of poverty. It is a cause in that lack of ready money in the hands of the farmer prevents investments in the farm. But it is also the effect or symptom of poverty in that the high interest rates and a high burden debt reflects a chronic insufficiency of the farmers’ income, and a permanent tendency for consumption to outrun production.

In Asia and the Middle East a peasant obtains credit from one of three sources: one is the village shopkeeper who gives credit on day-to-day purchases at rates of 100 to 250 percent per annum; the second is the landlord who himself borrows from other sources; the third is the middle man or money lender who usually lends money to large farm owners. As a result, the farmer is always burdened with the payment of high interest rates incurred through his poverty in the past. Thus, he cannot make the investment in the farm to increase its productivity.

Lack of a decent transportation system is another important factor that has caused, in part, the present poverty in rural communities. The only type of transportation available in most villages is animal. This, of course, has been the main reason for most of the villagers' ignorance of the outside world. Communication in many agricultural areas from large cities or the capital is ceased during rainy seasons because of bad roads.

The peasants have been told what to do and how to do it for centuries and do not possess self-dependence. This is true especially in the case of a financial point of view. If a poor peasant gets rich by earning some money from a certain source, he would not know what to do with the money; however, in many cases he would get himself an extra wife, or he may consider himself financially eligible to go to Mecca or any other religious
In this case he also borrows money from any possible source with high interest rate (3). As a result he will go broke again, and he usually ends up with a worse situation.

These above mentioned conditions, under which most of the peasants in the newly developed countries have existed for thousands of years, create many obstacles for any kind of reform in those areas.

As this proposition states, unless there is something done to raise standards of living of the rural community, any agrarian reform would not change things effectively. In the following sections, attempts are made to demonstrate some examples of land reform attempts which have taken place in different areas and have ended with unsatisfactory results due to unreadiness of the rural communities.

Iran

The government of Iran has at times attempted to transfer land ownership to the peasants by decree, but these efforts have not been successful. Here is an example reported by Franklin S. Harris (1), of a land reform attempt which took place in an area in Seistan, which is a province in the southeast part of Iran. This area was once public domain, various parts of which were rented to tribal leaders who managed the villages and permitted the peasants who actually tilled the land to retain a portion of the crops. In the early 1930's a new system supervised by the Ministry of Finance was introduced for this part of Seistan. Under this plan, most of the land was so distributed that the government dealt directly with the peasants. In this distribution each peasant was awarded as much land as approximately 10 acres. However, the new distribution system was in operation for only 4 or 5 years, but from the beginning it seemed doomed to failure. The land gradually reverted to the control of the tribal leaders and other powerful landlords (1, 2). The total production was reduced by the amount of 75 percent (2).

Harris (1) held the following reasons for the failure of the plan:

1. The peasants were not accustomed to managing their affairs; they have always depended on the landlords for direction. They failed to maintain the irrigation system, for instance, because the individual peasants had never worked out a plan of cooperation among themselves. When the land was divided, there was no one to assign tasks to the peasants, and they had no system of their own for cooperation.

2. The individual peasants lacked capital for improvements and living expenses.

3. There was no adequate system for selling the products of a single farmer.

In the Moslem religion it is necessary for a Moslem to go to Mecca once in his life as soon as he becomes financially able to do so.
4. In short, the failure may be attributed to the lack of an adequate understanding and cooperation.

**Japan (3)**

Japan was considered an underdeveloped agricultural country in the 19th century. In 1868 when Meiji became emperor, the majority of people were illiterate and sick with no communication between them. The emperor took a serious action for the welfare of his people by establishing school systems in rural areas and building roads and bridges everywhere. By 1870 compulsory education was established for all men and women. First attempts toward industrialization of the country were made. The effect of this reform was so effective that in the early twentieth century the farmers formed an agricultural organization and asked the government for more reasonable conditions of land tenure system. The activity of this organization was stopped during the Second World War, but immediately after the war, the farmers, through their organization, asked the government for land distribution. In that time 95 percent of the Japanese people were educated and Japan was considered as one of the progressing industrial countries in the world. The Ministry of Agriculture, under the supervision of SCAP prepared a land distribution plan which was passed through legislation and was under execution in October, 1946. The peasants were so rich that they could pay 75 percent of the price in cash.

**China (3)**

Ever since thousands of years ago, the Chinese emperors have ordered the distribution of land among peasants at various times. But each time after 20-30 years the land was reverted to the control of minority groups to powerful landlords. Thus the peasants stayed poor and sick. Finally, the pressure of poverty of millions of naked and hungry people could no longer be ignored, and with the help of Communist block, a bloody revolution took place in 1927 that took the Chinese people to the Communist world forever.

**Mexico (7)**

Land reform in Mexico was the outcome of the revolution of 1910. Before that revolution, the land was owned by large plantation owners, employing laborers on a semi-feudal basis. The land distribution under the reform has been granted under a special form of tenure known as "ejido", which is most likely a cooperative farm. Private ownership in neither the water nor the subsoil can be established under this type of reform; they may be help only under concession.

In evaluating the result of the reform, it seems generally agreed, as is stated by a United Nations report (7), that from the economical point of view, the results have been unsatisfactory. The yield per acre on "ejido" farms was somewhat lower than on privately owned farms of comparable size. There would appear to have been little improvement in farming methods. Shortage of credit remained one of the many obstacles to
improvement. The process of land distribution has been very slow and inefficient. According to the 1940 statistics, 42 percent of the total number of people employed in agriculture were registered as rightful claimants to pieces of land in the "ejido." However, of these, approximately 50 percent did not cultivate their share, owing to the lack of resources and equipment. So consequently, rather more than half of those who could have land were compelled to work as agricultural laborers.

**Cooperative systems do not work (3)**

Charles Howard (3), a British expert in rural cooperatives, makes the following statements as one of the nine principles of cooperatives: "The members should have a thorough knowledge of their cooperative, including its goals, principles, management, and member's duty; without it the result is a failure."

In Yugoslavia, after having experienced many difficulties in establishing cooperatives among peasants, the government decided that the management of such cooperatives is impossible unless the peasants are educated enough to understand the goals and principles of a cooperative system. And finally they shifted to the "collective farm" system in which the peasants work for the government.

In Iran almost all of the cooperatives which have been organized for the peasants' benefit have gone broke after a few years and are closed now.

From all these unsatisfactory results that have been encountered after land distribution among peasants in those countries, the following conclusions can be made:

- The three greatest reasons for the failure of land reform projects have been:
  1. The shortage of capital on the part of peasants.
  2. The lack of peasants' experience in managing their own farming enterprise.
  3. The lack of peasants' experience and ability to cooperate.

Problem number one could be solved by establishment of credit systems for the peasants by the government; the last two problems cannot be solved by money. It requires, rather, years of education before they are psychologically ready to own land and be able to manage it economically.

What do do then?

The existing poverty among peasants in these countries, as I think, is not due to the fact that they do not own land, but rather is a result of many other interrelated factors. Thus, if the main object is to raise
the standard of living of these people, not just a political propaganda, the following items should be considered for an effective reform:

1. Establishment of a good taxation policy.
2. Education, transportation, health (welfare).
3. Development of light industry.

The first step to minimize the class differences is by getting large amounts of taxes from the rich people (including large plantation owners) the same way as in America, and spending the money on the welfare of the poor people (Step 2). The importance of the second step is obvious. In the third step the government should develop light industry like food processing, textiles, fertilizers, manufacturing, etc. This would create a job-making source for the country. The land owners, then, will have to do one of these three things (1) raise the salary or share of the peasants in order to keep their work in their farms, (2) mechanize their farms and let the peasants go to work in the factories with higher salaries; and (3) sell the land to the cultivators and go into other businesses.

In any case, it would be beneficial to the peasants and to the country. It is seen here that the land reform is practically and automatically done and in case there is a further need for it, the farmers who are educated enough to realize this need would demand it and have it as in the case of Japan in 1945.

References

Proposition #5: The countries that are sending students to the United States or Europe to get higher education should prepare themselves to send more graduate students.

Foreign students in the United States

According to the latest report of 1962 (4), more than 58,000 foreign students are enrolled in 18,000 United States colleges and universities. This is a 10 percent increase over the previous year and represents 1.6 percent of the total enrollment in all colleges and universities of the United States. However, in Europe, this percentage is much higher. According to the UNESCO Report (4) in some countries in Europe this figure goes up to 32 percent of the total enrollment, the average being around 15 percent. In 1951-52, 39 percent of the foreign students in the United States were of graduate and research standing (1). According to a report of 1961 (2) only 13 percent of foreign students in the United States came from Europe; the rest, 87 percent, came largely from Asia, South America, and Africa.

Type of students going abroad

Students go abroad to college for three main reasons:

1. The capacity of colleges and universities in one country is insufficient to meet the number of high school graduates who wish to go to college. As an example, in Iran each year approximately 15,000 high school graduates register for college entrance examinations from which only 1500 are selected. Thus, 90 percent of the students who are rejected have to either go to Europe and the United States to study, or quit school. This type of student is either financed privately or by his government.

2. The facilities for graduate work and research are insufficient in all fields of study so that students should go to another country to go to graduate school for specialization. These students are mostly financed by their governments or some other foundation.

3. Exchange students. In this case students of one country go to another for a short period (1 to 2 years) to learn something about education in other countries on an exchange basis. These students are usually financed by the government.

The object of this proposition is to minimize the number of students of the first category and only encourage the students of the second and third type.

As it was mentioned before, a big majority of the foreign students in the United States and Europe come from newly developed countries. The main idea for those students is to finish school here and go back to help their country to catch up with the fast-growing modern world. Therefore,
if by any chance some students stay in this country and refuse to go back home the whole idea has failed. According to a recent report (3), 10 percent of the foreign students stay in this country and never go back.

In the following paragraphs, I am going to compare the characteristics of graduate students and high school graduates with respect to their behavior in a foreign country. The possibilities of the idea will be discussed at the end.

Maturity

Maturity, in most cases, is directly related to the age. Thus, it could be concluded that graduate students are more mature than high school graduates. To study in a foreign country, especially for students who come from a completely different culture, maturity is a very important factor. With relation to this point, Du Bois (1) in his book, Foreign Students and Higher Education in the United States, makes the following statements favoring graduate students:

Graduate students are usually more mature, and therefore, (a) they can develop a better grasp of the host country in a short time; (b) the grasp they develop is more likely to be objective; (c) they are more likely to adapt to American culture than to emulate it; (d) they are better able to give Americans an informal picture of their own country.

The main important thing here is that generally high school graduates (usually 18 to 19), have been financially and morally under the control of their parents before they came here. But, as soon as they leave their country, they are on their own. Considering the amount of freedom that a person could have in this country, there is an abrupt change in the lives of these arriving young students; consequently, many of them start to divert from their study and become involved in many things that they should not. For instance, I have seen many undergraduate students who buy a sports car one month after they arrive here; and, of course, this is the beginning of diversion.

Alienation

Du Bois (1) believes that alienation or denationalization is a function of age, length of sojourn, and the nature of the student's stake in his home land. The younger the student, the longer is his stay abroad; and the looser become his ties to his country, and the greater are the risks of alienation. It seems natural to say that graduate students are older, they stay a shorter time, and their ties to their homeland are stronger. Therefore, the risk of alienation for graduate students is much less. Another aspect of alienation is the fact that it is usually a result of mixed marriages, which chance for a graduate student is less.

Academic achievements

Here again Du Bois (1) is of the opinion that graduate students have more clearly defined career and study goals and are, therefore, more likely
to concentrate on their objectives. This is true because a graduate student as a general rule, has already chosen his field of study before he arrives here; and he, therefore, does not waste his time. His maturity, of course, is the main important factor for his concern for his study.

Usefulness for the home country

Suppose that a high school graduate comes to this country and starts to study in college with a major in entomology and pest control or agricultural economics, and he gets a B.S. or M.S. or Ph.D. degree. This student has learned about insects which are agriculturally important for the conditions of this country or he has learned about marketing systems that are in operation here. Thus, when he goes back home he is faced with the big problem of not knowing much about his own country, plus the fact that for a B.S. major a student should take humanity courses such as sociology, art, etc., which are mostly unique for this country. This problem does not exist for a graduate student, because he has been in college at home for four years and has learned enough about his own country. The graduate study abroad would be some additional information for him.

The question of engineering training

A graduate of an engineering college in the United States is considered an engineer trainee and has to have four years of training under the supervision of a senior engineer before he can work privately as an engineer. In the case of foreign students, they usually go back home and start to work as an engineer. This is because of two main reasons: (a) the home countries do not require the four years of training, and (b) there are not many engineering training jobs open to foreign students. Considering the fact that these inexperienced engineers in their home countries may bring some loss of prestige to American institutions, the importance of this training program becomes clear. And also, it is the training that is more important for an engineer, not the four years of theory. However, it is much easier for the home countries to offer the four years of theoretical training but not the practical ones.

Possibilities of the suggestion

There are two important things for the providing of sufficient college and university facilities to train undergraduate students; personal and financial. In my opinion both could be solved very easily in the case of certain countries. For example, there are 14,000 Iranian students studying in the United States and Europe. Of these, 4,000 are graduate students and 10,000 are undergraduates. Approximately 7,000 undergraduates are government-sponsored students who are getting an average of $2,000 per year. This would amount to 14 million dollars which is about three times as much as the annual budget of the University of Tehran (5 million dollars annual budget with 13,000 students). This means that they really could use the money to establish sufficient colleges at the undergraduate level. The
providing of professors is no problem in Iran because there are many Ph.D.'s from the United States and Europe who return to Iran but find no decent job, and finally they go back to the host country.

References


APPENDIX B
\[ t = 20.0^\circ C \]

### \( \theta = 34.3\% \)

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<th>Est. pressure (millibars)</th>
<th>Matric potential (joules per Kg)</th>
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<tr>
<td>948</td>
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<td>-6.64</td>
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<td>1209</td>
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\[ b = -0.059^a \]
\[ S_b = 0.0025 \]

### \( \theta = 31.2\% \)

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\[ b = -0.215 \]
\[ S_b = 0.0111 \]

### \( \theta = 22.6\% \)

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\[ b = -0.071 \]
\[ S_b = 0.0043 \]

### \( \theta = 27.1\% \)

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<th>Est. pressure (millibars)</th>
<th>Matric potential (joules/Kg)</th>
</tr>
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<tbody>
<tr>
<td>867</td>
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<tr>
<td>935</td>
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<td>1002</td>
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<tr>
<td>1138</td>
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</tbody>
</table>

\[ b = -0.217 \]
\[ S_b = 0.021 \]

\(^a\)"b" is the slope of the regression line which was statistically calculated.
\[ t = 20 \pm 0.5^\circ C \]

\[ \theta = 24.7\% \]

<table>
<thead>
<tr>
<th>Est. pressure (millibars)</th>
<th>Matric potential (joules/Kg)</th>
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<tbody>
<tr>
<td>873</td>
<td>-18.5</td>
</tr>
<tr>
<td>942</td>
<td>-20.05</td>
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<tr>
<td>1009</td>
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<td>1083</td>
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<td>1145</td>
<td>-25.40</td>
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<tr>
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</table>

\[ b = -0.240 \]
\[ S_b = 0.013 \]

\[ \theta = 16.4\% \]

<table>
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<th>Est. pressure (millibars)</th>
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<tbody>
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<tr>
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<td>-15.6</td>
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<tr>
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<td>1077</td>
<td>-20.6</td>
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<td>1138</td>
<td>-23.3</td>
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<tr>
<td>1206</td>
<td>-26.5</td>
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\[ b = -0.399 \]
\[ S_b = 0.0163 \]

\[ \theta = 16.6\% \]

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<td>-70.8</td>
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\[ b = -0.450 \]
\[ S_b = 0.013 \]

\[ \theta = 20.5\% \]

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<th>Est. pressure (millibars)</th>
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\[ b = -0.204 \]
\[ S_b = 0.0108 \]

\[ \theta = 17.6\% \]

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\[ b = -0.464 \]
\[ S_b = 0.010 \]
\[ \theta = 24.1\% \]

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<tr>
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<td>-33.23</td>
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\[ b = -0.197 \]
\[ S_b = 0.0097 \]

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\[ b = -0.119 \]
\[ S_b = 0.0077 \]

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\[ b = -0.151 \]
\[ S_b = 0.012 \]

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\[ b = -0.146 \]
\[ S_b = 0.008 \]