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ON THE ENTHALPY AND ENTROPY OF SOIL WATER

by

Robert A. Kohl

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DEFINITION OF SYMBOLS

Major letters and symbols	Definition
A	surface area
C_c	specific heat of container
C_s	specific heat of soil
E	total energy
E	energy per mole or per gram
$\overline{E}$	partial molar or partial specific energy
F	free energy
H	total enthalpy
H	enthalpy per mole or per gram
$\overline{H}$	partial molar or partial specific enthalpy
h_o	heat of immersion of clean adsorbent
h	heat of immersion with preadsorbed adsorbate on adsorbent
ℓn	natural logarithm
M_c	mass of container for soil sample
M_s	mass of moist soil
M_w	mass of water adsorbed
n	number of moles
P	total pressure
p_o	saturation pressure of adsorbate
p	pressure of adsorbate
Q_i	integral heat of adsorption
q_i	integral heat of adsorption per mole or per gram
q_d	differential heat of adsorption

q_{φ}	thermodynamic integral heat of adsorption per mole or per gram
q_{st}	isosteric heat of adsorption
R	universal gas constant
S	entropy
s	entropy per mole or per gram
$\bar{s}$	partial molar or partial specific entropy
T	absolute temperature
t	time
V	volume
v	volume per mole
Γ	surface excess or surface concentration
Δ	difference
Λ	rate of heat loss
Ω	number of quantum states
φ	two dimensional, spreading pressure
μ	chemical potential

Subscripts

g	gas phase
l	liquid phase
s	sorbed phase

INTRODUCTION

Just twenty years have passed since the first papers were published on the application of chemical thermodynamics to the soil-water system (11, 14). Since then, soil physicists have used thermodynamics in an attempt to characterize and learn more about this intricate system.

Because of the complicated nature of a natural system such as the soil-water system, it invariably becomes necessary to study small parts of the system separately until the whole can be studied as a sum of parts or as an integrated unit. It was with this in mind that attention was focused on the enthalpy and entropy of soil water and their related heat effects.

The approach decided upon was a calorimetric one with the possibility of comparison with isosteric values. It was not until near the conclusion of this research project that it was realized that existing interpretations of the differential and isosteric heats of adsorption of water on soil materials were in error. Therefore, an attempt to collect integral thermodynamic data was made.

REVIEW OF LITERATURE

Thermodynamic Development of Adsorption Equations

Confusion exists in the soils literature concerning the thermodynamics of adsorption. Therefore, the derivation of the basic thermodynamic adsorption equation will be reviewed here. Emphasis will be placed on the assumptions and properties inherent in the resulting thermodynamic quantities.

Integral heat of adsorption

In order to treat adsorption with reasonable simplicity, the following initial assumptions are made:

1. only one gas is present,
2. the adsorbent is completely inert; i.e., all its thermodynamic properties are the same in the presence as in the absence of adsorbed molecules; [Certain adsorbate molecules will perturb surface adsorbent molecules, but this perturbation is probably a strictly second-order effect in the case of physical adsorption on solids, especially solids with relatively strong intermolecular or interionic forces (19).],
3. adsorbents which swell are excluded; [Millville loam does swell and, therefore, does not lend itself to as rigorous a thermodynamic application as nonswelling adsorbents. However, Hill (19) mentions that he has developed the thermodynamic quantities to treat swelling but did not present them in that paper.],

4. the surface area and structure of the adsorbent are independent of temperature and pressure over the ranges of interest.

These assumptions allow us to discuss the thermodynamic functions of the adsorbate molecules alone.

Consider the process of n moles of species X passing from the gas phase to an adsorbed phase

$$n X(gas, P, T) \rightarrow n_s X(adsorbed, \Gamma (or\ \varphi), T) \qquad (1)$$

where P and T are the pressure and temperature respectively, Γ is the surface excess in moles per unit area, and φ is the spreading or two dimensional pressure of the adsorbed phase. The integral heat of adsorption, Q_i, is then given by

$$Q_i = E_g - E_s \qquad (2)$$

or, on a per mole basis

$$q_i = E_g - E_s \qquad (3)$$

where $q = Q_i/n$ and $E = E/n$. E_g and E_s are the energies of the gaseous and sorbed phases respectively. The quantity Q_i or q_i corresponds to a calorimetric heat measured in such a way that no PV work is done, as, for example, if the adsorption is allowed to occur by opening a stopcock between the adsorbent and the gas phases, where both vessels are immersed in the same calorimeter.

Other quantities are also needed to describe the thermodynamic properties of the adsorbed phase. Development of the equations which define these quantities begins with the condition for equilibrium between X in the gas phase at (P, T) and on the adsorbent at (φ, T) which is

$$\mu_g(P,T) = \mu_s(\varphi,T) \tag{4}$$

where μ_g and μ_s are the chemical potentials in the gas and sorbed phases respectively. The chemical potential is the partial molar free energy of a particular component in a multicomponent system. However, when a single component system is considered, the chemical potential is identical with the molar free energy. For a small variation in conditions

$$\left(\frac{\partial \mu_g}{\partial P}\right)_T dP + \left(\frac{\partial \mu_g}{\partial T}\right)_P dT = \left(\frac{\partial \mu_s}{\partial \varphi}\right)_T d\varphi + \left(\frac{\partial \mu_s}{\partial T}\right)_\varphi dT \tag{5}$$

For the case of φ held constant, eq. (5) may be rearranged to yield

$$\left(\frac{\partial P}{\partial T}\right)_\varphi = \frac{\left(\frac{\partial \mu_s}{\partial T}\right)_\varphi - \left(\frac{\partial \mu_g}{\partial T}\right)_P}{\left(\frac{\partial \mu_g}{\partial P}\right)_T} \tag{6}$$

For the gas phase

$$T\left(\frac{\partial \mu_g}{\partial T}\right)_P = \mu_g - H_g = -TS_g \tag{7}$$

and

$$\left(\frac{\partial \mu_g}{\partial P}\right)_T = V_g \tag{8}$$

An appropriate equation must be developed for the adsorbed phase. Equation (26.18) of Glasstone (16) written for a one component gas phase becomes

$$dE_g = T\,dS_g - P_g\,dV_g + \mu_g\,dn_g \qquad (9)$$

The analogous equation for the adsorbed phase takes the form

$$dE_s = T\,dS_s - \varphi\,dA + \mu_s\,dn_s \qquad (10)$$

where a two dimensional pressure term replaces pressure and area replaces volume. The integrated form of eq. (10) is

$$E_s = T S_s - \varphi A + \mu_s n_s \qquad (11)$$

or, on a per mole basis,

$$E_s = T s_s - \frac{\varphi}{\Gamma} + \mu_s \qquad (12)$$

On differentiating eq. (12) and comparing it with eq. (10), one obtains

$$0 = s_s\,dT - \frac{d\varphi}{\Gamma} + d\mu_s \qquad (13)$$

or

$$\left(\frac{\partial \mu_s}{\partial T}\right)_\varphi = -S_s = \frac{\mu_s - E_s - \varphi/\Gamma}{T} \qquad (14)$$

On inserting eqs. (7), (8), and (14), into eq. (6), one obtains

$$\left(\frac{\partial P}{\partial T}\right)_{\varphi} = \frac{\mu_s - E_s - \varphi/\Gamma - \mu_g + H_g}{T\,V_g} \qquad (15)$$

Assuming the gas obeys the ideal gas law, $V_g = RT/P_g$, and that the system is at equilibrium, $\mu_s = \mu_g$, one may simplify eq. (15) to

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\varphi} = \frac{H_g - E_s - \varphi/\Gamma}{RT^2} \qquad (16)$$

The same ideal gas assumption applied to eq. (3) leads to

$$q_i = E_g - E_s = H_g - RT - E_s \qquad (17)$$

or

$$H_g - E_s = q_i + RT \qquad (18)$$

Inserting eq. (18) into eq. (16) yields

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\varphi} = \frac{q_i + RT - \varphi/\Gamma}{RT^2} \qquad (19)$$

Thus far in the development, total or integral thermodynamic quantities have been used. As a result, these equations can be used to calculate the difference between two integral quantities, as, for example, the difference between the energy of free water vapor and adsorbed water.

Eq. (19) allows the calculation of the integral heat of adsorption from two relatively close isotherms. However, φ must be evaluated first; and this requires the appropriate form of the "Gibbs equation" (19). Eq. (13) can be rearranged to give

$$\frac{d\varphi}{\Gamma} = S_s dT + d\mu_s \qquad (20)$$

At constant temperature eq. (20) becomes

$$d\varphi = \Gamma d\mu_s \qquad (21)$$

Since $d\mu_s = d\mu_g$ at equilibrium and $d\mu_g = RTd\ln p$, eq. (21) yields

$$d\varphi = RT\Gamma d\ln p \qquad (22)$$

which is the "Gibbs equation" needed to evaluate eq. (19). Upon integration of eq. (22), one obtains

$$\varphi = RT\int_0^p \Gamma d\ln p \qquad (23)$$

This equation has been verified by the use of statistical mechanics (7). The evaluation of eq. (23) requires accurate low pressure measurements, as an error in this region is carried through all values of φ.

Very severe degassing techniques may remove more water vapor from an adsorbent than less severe methods. Therefore, the adsorption isotherm for the more severely degassed sample is likely to lie above that of the other sample. The two isotherms would yield somewhat different values for $\varphi = f(p)$. Even though all adsorbed water should be removed to yield more accurate values of φ , caution must be exercised, as very severe degassing may lead to crystal perturbations or modifications which could result in a mixture of physical and chemical adsorption along the isotherm.

Since theoretically φ represents two dimensional spreading pressure, some question has arisen as to its usefulness when localized adsorption is involved (15). However, there is no question that eq. (22) can be evaluated, as the evaluation is made on the chemical potential of the gas phase which is in equilibrium with the adsorbed phase. Though its physical interpretation may be questioned, the value of φ lies in its usefulness in the calculation of integral thermodynamic quantities, particularly integral entropy values (21).

The equation for the gas phase equivalent to eq. (12) is

$$E_g = TS_g - P_g V_g + \mu_g \qquad (24)$$

At equilibrium, $\mu_g = \mu_s$; and the combination of eqs. (12) and (24) yields

$$E_s - TS_s + \varphi/\Gamma = E_g - TS_g + P_g V_g \qquad (25)$$

or

$$E_s - TS_s + \varphi/\Gamma = H_g - TS_g \qquad (26)$$

which leads to

$$H_g - E_s - \varphi/\Gamma = T(S_g - S_s) \tag{27}$$

Combining eqs. (18) and (27) produces

$$q_i + RT - \varphi/\Gamma = T(S_g - S_s) = q_\varphi \tag{28}$$

The use of eqs. (19), (23), and (28) on two accurate isotherms allows the calculation of the difference between two integral entropies. Hill <u>(19, 20)</u> prefers to call q_φ the integral heat of adsorption on thermodynamic grounds because at equilibrium

$$q_\varphi = (H_g - H_s) = T(S_g - S_s) \tag{29}$$

This is not a true calorimetric heat of adsorption but is related to it through eq. (28). The term q_φ has also been called the equilibrium heat of sorption. The choice of q_i or q_φ is left up to the individual as it suits his procedures. However, the reader should be careful so as not to confuse the two quantities.

It must be strongly emphasized that the usual entropy discussed qualitatively or quantitatively (statistical mechanics) in terms of order-disorder, randomness of motion, etc., of the adsorbed molecules is the integral entropy, S_s.

$$S_s = R \ln \Omega \tag{30}$$

where Ω is the number of quantum states of the sorbed component

(21, 22). A return to this clarification will be made later.

Differential heat of adsorption

Under special circumstances differential heats of adsorption are also of interest. They may be calculated from two adjacent isotherms. Differential heats of adsorption are ordinarily used in multicomponent systems where the use of partial molar quantities is in order.

We shall begin our development by taking the differential of eq. (2)

$$q_d = \left(\frac{\partial Q}{\partial n_s}\right)_{A,T} = \left(\frac{\partial E_g}{\partial n_s}\right)_T - \left(\frac{\partial E_g}{\partial n_s}\right)_{A,T} = \bar{E}_g - \bar{E}_s \quad (31)$$

where q_d is the differential heat of adsorption. A bar over a quantity indicates that it is a partial molar quantity. If one assumes ideal gas behavior for the adsorbate, eq. (31) may be written as

$$q_d = E_g - \bar{E}_s \quad (32)$$

which becomes

$$q_d = H_g - RT - \bar{E}_s \quad (33)$$

Next of interest is the development of the isosteric heat of adsorption, q_{st}, from a Clausius-Clapeyron type equation. The condition for equilibrium between X in the gas phase at (P,T) and on the adsorbent at (Γ, T) is

$$\mu_g(P,T) = \mu_s(\Gamma,T) \tag{34}$$

Notice that μ_s is now written as a function of Γ in contrast to eq. (4) where it is written as a function of φ . The choice is arbitrary, as either combined with temperature will define the adsorbed phase. However, the choice does determine the heat of adsorption which is finally obtained.

For any small variation in conditions

$$\left(\frac{\partial \mu_g}{\partial P}\right)_T dP + \left(\frac{\partial \mu_g}{\partial T}\right)_P dT = \left(\frac{\partial \mu_s}{\partial \Gamma}\right)_T d\Gamma + \left(\frac{\partial \mu_s}{\partial T}\right)_\Gamma dT \tag{35}$$

For the case of Γ held constant, eq. (35) may be rearranged to read

$$\left(\frac{\partial P}{\partial T}\right)_\Gamma = \frac{\left(\frac{\partial \mu_s}{\partial T}\right)_\Gamma - \left(\frac{\partial \mu_g}{\partial T}\right)_P}{\left(\frac{\partial \mu_g}{\partial P}\right)_T} \tag{36}$$

If one uses $\bar{E}_S$ as defined by eq. (31), the partial molar form of eq. (10) becomes,

$$\bar{E}_s = T\bar{S}_s + \mu_s \tag{37}$$

which leads to

$$\left(\frac{\partial \mu_s}{\partial T}\right)_\Gamma = -\bar{S}_s = \frac{\mu_s - \bar{E}_s}{T} \tag{38}$$

On substituting eqs. (7), (8), and (38) into eq. (36), one obtains

$$\left(\frac{\partial P}{\partial T}\right)_{\Gamma} = \frac{\mu_s - \bar{E}_s - \mu_g + H_g}{T\,v_g} \qquad (39)$$

Considering the equilibrium condition, $\mu_s = \mu_g$, and making the usual approximation that $v_g = RT/P$, one obtains

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\Gamma} = \frac{H_g - \bar{E}_s}{RT^2} = \frac{q_{st}}{RT^2} \qquad (40)$$

Notice that when $\left(\partial \ln P/\partial T\right)$ is evaluated at constant φ, an integral heat of adsorption is obtained; and when it is evaluated at constant Γ, a differential heat of adsorption is obtained. Also note that it is Γ and not n_s that is held constant; the difference involves the change in total surface area with temperature and usually is neglected. Combining eqs. (33) and (40), one obtains the relation

$$q_d = H_g - \bar{E}_s - RT = q_{st} - RT \qquad (41)$$

The differential calorimetric heat of adsorption should be equal to the isosteric heat of adsorption within an uncertainty of RT calories per mole, since usually there is some exchange of work between portions of the gas and not all of the gas lies within the calorimeter. The difference, RT, is frequently neglected, as it amounts to about 5-10% of the total differential heat of adsorption which is often less than the total experimental error (6).

From eq. (41) we can see that

$$q_{st} = q_d + RT = H_g - \bar{E}_s = T(S_g - \bar{S}_s) \quad (42)$$

Note that q_{st} leads to a partial molar entropy for the adsorbed gas. Therefore, the quantity referred to as "ΔS" obtained from the use of the Clausius-Clapeyron equation is actually $(S_g - \bar{S}_s)$ or $(\bar{S}_g - \bar{S}_s)$, the difference between two partial molar quantities and not two integral quantities. Therefore, the values of $(S_g - \bar{S}_s)$ should not be interpreted by the use of eq. (30) and its accompanying discussion. This mistake has been made in the soils literature and is one of the main reasons for including the thermodynamic development in the detail presented.

Heat of immersion

The relationships between the thermodynamic quantities thus far developed and those obtained from heat of immersion data will now be discussed. The ideal gas law is reasonably valid at the low pressures encountered in adsorption and immersion work. The ideal gas law allows us to write

$$\Delta F = \Delta H - T\Delta S = RT \ln \frac{p}{p_o} \quad (43)$$

Written for the process of one mole of species X passing from the liquid phase to the adsorbed phase, eq. (43) becomes

$$T(S_s - S_L) = (H_s - H_L) - RT \ln \frac{p}{p_o} \quad (44)$$

or

$$T(S_S - S_L) = (E_S - E_L) + \varphi/\Gamma - PV_L - RT\ln\frac{p}{p_o} \quad (45)$$

where the terms S_L, H_L, etc. refer to the liquid phase.

Meaningful heat of immersion data must be taken from the use of clean adsorbents, that is, adsorbents which have been degassed or degassed and a known amount of immersion liquid added. When samples are dried in desiccators, gasses present in air are adsorbed on the surface; and energy is required to remove them. In this case the thermodynamic equations developed here would not apply. For further discussion on this problem, see proposition 1 in the appendix.

Let h_o be the heat of immersion (in the liquid adsorbate, X) of the clean solid adsorbent, and let h be the heat of immersion of the solid with n_S moles of X adsorbed on it. Similar to eqs. (2) and (3), we may write

$$\frac{(h - h_o)}{n_S} = (E_S - E_L) \quad (46)$$

Upon inserting eq. (46) into eq. (45) and omitting the negligible volume term, one obtains

$$T(S_S - S_L) = \frac{(h - h_o)}{n_S} + \frac{\varphi}{\Gamma} - RT\ln\frac{p}{p_o} \quad (47)$$

which is the same as eq. (2) of Jura and Hill (23).

Eq. (19) requires the use of φ twice, once to determine the values of pressure and temperature at constant φ, and once in the

φ / Γ term in order to obtain the integral heat of adsorption from which the other integral thermodynamic functions are calculated. In some cases very serious errors in φ may arise, owing to an uncertain extrapolation of the adsorption isotherm to $p = 0$. An alternative and, in general, more precise method of obtaining S_S and E_S is to combine a computation of φ from a single adsorption isotherm with heats of immersion or ordinary integral calorimetric heats of adsorption, measured at the same temperature (23).

Chessick and Zettlemoyer (9) showed the relationship between the heat of immersion and the isosteric heat of adsorption as

$$\frac{(h - h_0)}{n_s} = \int_0^{\Gamma} q_{st} \, d \ln \Gamma - \Delta H_L \qquad (48)$$

where ΔH_L is the molar heat of liquefaction. This equation demonstrates once again that the isosteric heat of adsorption is a differential quantity and must be integrated in order to obtain integral thermodynamic quantities.

This development is an amalgamation and modification of those developments found in the chemical literature (1, 15, 19, 20, 23). It is suggested that anyone contemplating research in the field of adsorption of water on soil materials thoroughly read and understand the material presented in these papers.

In the interest of clarity and conciseness, certain quantities which are usually negligible were omitted from this development. For a more complete development, see Hill (19, 20).

The Application of Thermodynamics to Soils

The initial application of thermodynamics to soil moisture attempted to define capillary potential in thermodynamic notation (14, 11). These equations had the advantage of expressing soil moisture potential, a chemical potential term (11), in terms of measurable, macroscopic variables.

Heat of immersion

One of the first papers in the soils literature which dealt with the calculation of the enthalpy and entropy of soil water was that of a heat of immersion study by Robins (33). He determined the integral heat of immersion on three soils equilibrated in desiccators over sulfuric acid solutions of various relative humidities. The integral values showed the characteristic rapid decrease in the heat of immersion with increasing amounts of preadsorbed water. He then determined the differential heat of immersion and called it the specific heat content. In so doing, he neglected the PV work term and changed to partial specific quantities (per gram basis). He determined the specific free energy by the relation $\Delta F = RT \ln P/P_o$. He then calculated the partial specific entropy from the interfunctional relationship, $\Delta \bar{S} = \Delta \bar{H} - \Delta \bar{F}$. His values of $\Delta \bar{F}$, $\Delta \bar{H}$, and $\Delta \bar{S}$ were negative and became more so as the moisture content decreased. However, following the mistake of Stamm (35) and Katz (26), Robins used the integral interpretation for the partial specific entropy. As explained in the preceding section, the slope (partial specific quantity) of a line at a point gives no indication of the distance the line (integral quantity) is above or below the axis. As will be noted later, this mistake has carried through all of the pertinent soils literature known to me except for one paper (29).

Since Jura and Hill (23) pointed out the advantages of combining heat of immersion and adsorption data to calculate integral thermodynamic quantities, several workers have employed this method. Zettlemoyer et al. (38) calculated the integral entropy of water adsorbed on asbestos fibers from two isotherms and from one isotherm and heat of immersion data. Values determined by the two methods were in good agreement; but the adsorption values had a greater estimated maximum error, especially below one layer of adsorbed molecules. The entropy of the adsorbed water was considerably greater than free water when few molecules were adsorbed. At a half layer $S_S = S_L$, and S_S reached a minimum value of 4 e.u. below S_L at about one layer coverage. Beyond one layer the entropy of the adsorbed film increased to approach that of free water. The heat of immersion curve suggests that asbestos presents a very homogenous surface to adsorbing molecules.

Walen (37) conducted a similar experiment with ground quartz. His values for the entropy of the adsorbed phase were very low with less than a half layer adsorbed but only slightly below the entropy of free liquid water beyond a half layer. However, Whalen did not place much emphasis on his values, as he suggests that the ground quartz may not have been at equilibrium yet.

Morrison and Dzieciuch (30) reported small negative values for $(S_S - S_L)$ which became slightly more negative as the vapor pressure increased for water on cellulose. These authors also believe that their adsorbent was disturbed by the water.

One lone entropy value for water adsorbed on kaolinite at a monolayer coverage is reported (10). The value of S_S was -2 e.u. which the authors interpreted as reflecting a strong interaction between the water vapor and the hydrogen kaolinite with the implication that the surface was strongly perturbed. Possibly the hydration of surface ions was responsible for this abnormal result.

Differential heat of adsorption

Because of the erroneous idea that a partial molar quantity could be interpreted as that portion of the integral quantity due to a particular component (in this case soil water), partial molar enthalpies and entropies have been used extensively. This interpretative error persisted in the chemical literature until the papers of Hill et al. (19, 20, 21, 22) appeared. This error appears with decreasing frequency since Hill's papers.

Several researchers (17, 18, 24, 25, 33, 36), interested in the thermodynamics of soil water, calculated partial specific enthalpies and entropies and gave them integral interpretations, even though a few of these workers (18, 25) refer to papers (22, 29) in which the integral and partial molar interpretations are explained.

Differential heat of adsorption values for silica and kaolinite ranged from 720 cal/g at one layer to 800 cal/g at a half layer (37, 24).

The differential heat of adsorption curve for water adsorbed on montmorillonite had both a minimum and a maximum with values ranging from near zero to 560 cal/g H_2O between 0.05 and 0.37 g H_2O/g clay (3, 4). A natural soil showed negative values of $(\bar{H}_S - H_L)$ in the tensiometer range (36). Also Li-kaolinite showed a minimum in its curve of $(\bar{H}_S - \bar{H}_v)$ versus coverage at about one-third of a layer (24).

Integral heat of adsorption

It is regrettable that only one paper has appeared in the soils literature concerning the integral entropy of soil water. Martin (29) calculated integral entropy values at constant surface pressure with the help of the Gibbs equation. He also calculated differential entropy values. These later data agreed roughly with those of Goates and Bennett (17) and Jurninak and Volman (24). However, the integral entropy of water adsorbed on kaolinite was greater than that of free water over the range below 50% relative humidity, and became larger as zero coverage was approached. This means that the water adsorbed on kaolinite possesses greater freedom of movement than free water and is contrary to the many erroneous interpretations of differential entropy values. However, the integral entropy values are opposite to the one integral value reported by Chessick and Zettlemoyer (10).

A recent development in the field of surface chemistry has been the determination of site energy distributions of adsorbents. Several workers (2, 8, 9, 12, 34) have attempted such calculations using adsorption isotherms with a couple of promising methods immerging.

The few papers studied indicate that this area should prove very rewarding to the soil physicist or chemist interested in cation exchange as well as gaseous adsorption.

THEORY

In a preliminary experiment water vapor was brought into contact with a degassed soil sample. The temperature of the sample rose very rapidly and then dropped. When this occurrence was compared with the experiment of water vapor adsorption on wool fibers by King and Cassie (27), the following conclusions were drawn: 1) water vapor adsorption occurs very rapidly and is probably limited by the temperature of the soil sample, and 2) since the amount of heat produced was appreciable, the heat rise of the sample could be used to determine differential calorimetric heats of adsorption.

An equation suitable for the determination of the differential calorimetric heat of adsorption was logically developed by considering the production and loss of heat and the resulting temperature rise of the soil sample. With the use of consistent units of grams, calories and degrees centigrade, the temperature rise of the sample is equal to the heat produced minus the heat lost and divided by the product of the mass heated and its specific heat. Thus,

$$\Delta T = \frac{q_d M_w - \int_0^t \Lambda \, dt}{C_s M_s + C_c M_c} \tag{49}$$

where

ΔT = temperature rise of sample, °C

q_d = differential calorimetric heat of adsorption, cal/g

M_w = mass of water adsorbed at time t, g

M_s = mass of moist soil, g

M_c = mass of container for soil sample, g

C_s = specific heat of soil, cal/g °C

C_c = specific heat of container, cal/g °C

t = time, sec

and Λ = rate of heat loss, cal/sec.

Values of ΔT, M_w, M_s, and M_c were obtained by direct measurement. The value of 0.214 cal/g °C for C_c was taken from handbook data for aluminum. The value of C_s was determined by the use of a calorimeter specifically designed for specific heat determinations. A value for Λ was determined by calibrating the adsorption apparatus.

Other thermodynamic quantities were also of interest and were calculated by use of established equations. The isosteric heat of adsorption was calculated by using eq. (40) developed in the preceding chapter. The assumption was made that the total surface area of the soil sample did not change with temperature between 15 and 35 C.

The difference between the enthalpy of soil water and free, liquid water was calculated from the relationship

$$(H_s - H_l) = \frac{(h - h_o)}{n_s} + \frac{\varphi}{\Gamma} \qquad (50)$$

which is easily obtained by comparing eqs. (44) and (47).

The difference between the entropy of soil water and free water was obtained by the use of eqs. (47) and (23).

EXPERIMENTAL METHODS AND PROCEDURES

Adsorption Apparatus

An apparatus was designed to provide the data from which the differential calorimetric heat of adsorption could be obtained. This apparatus is shown in figure 1. The apparatus was constructed of 20 mm O. D. glass tubing and large bore vacuum stopcocks. The large mechanical vacuum pump reduced the pressure in the system to approximately 0.2 of Hg. The oil diffusion pump reduced the pressure further to approximately 1×10^{-5} mm of Hg. The vapor trap preceding the diffusion pump was surrounded by a Dewar flask containing dry ice and acetone at -78 C. The McLoed gage was used to measure the pressure in the system accurately to 1×10^{-4} mm of Hg and approximately to 1×10^{-5} mm of Hg during evacuation procedures. The oil manometer, which contained a vacuum pump oil with a vapor pressure less than 1×10^{-6} mm of Hg at 25 C, was used in the measurement of the water vapor pressure in the system. A cathetometer was used to read this manometer. The small spherical flask contained distilled water which had been boiled under vacuum to remove dissolved gases. The large five liter spherical flask in the constant temperature bath was used to supply the soil with water vapor of bath temperature.

Two adsorption tubes were used. One, fitted with a sensitive copper beryllium spring, was used to determine the amount of water vapor adsorbed on the soil sample suspended from the spring. The extension of the spring was read to the nearest 0.01 mm with an

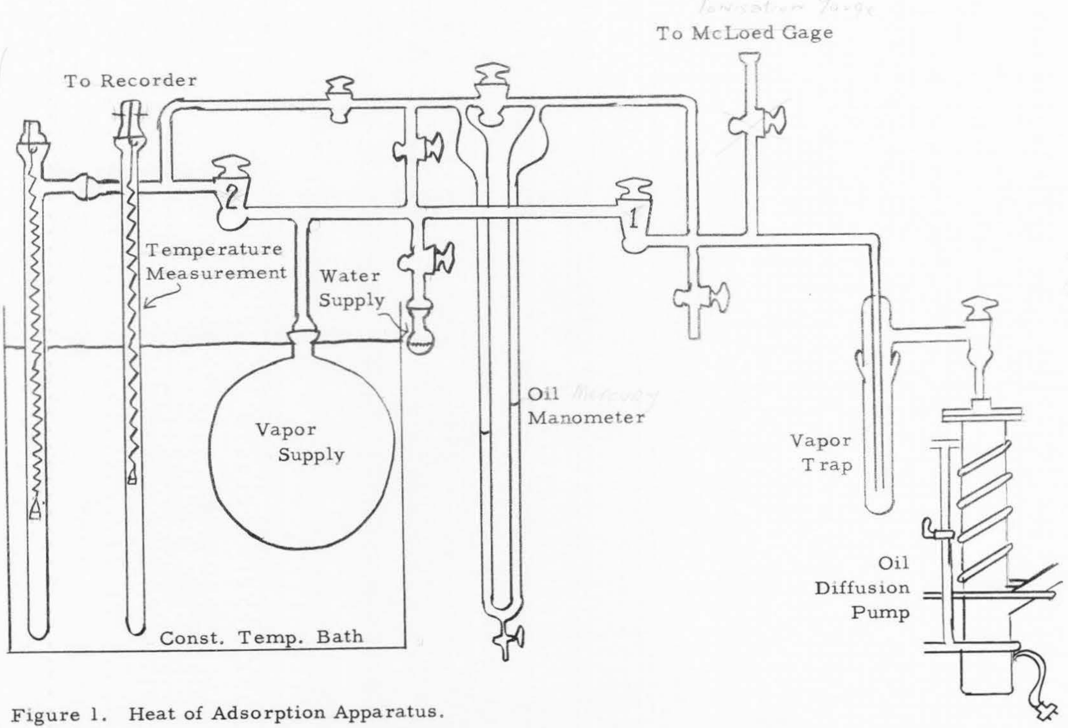

Figure 1. Heat of Adsorption Apparatus.

accurate cathetometer. The other tube contained an identical soil sample and spring plus a small thermistor with fine wire leads through the cap of the tube. The temperature of this sample was recorded on a Bristol recorder to 0.01° C. Two more leads through the cap of this tube were used to heat the soil sample for the heat loss calibration.

Calibration curves for rate of heat loss from the soil sample were obtained in the following manner. The temperature of the sample was determined by employment of a calibrated rapid response thermistor. The thermistor had a diameter of 0.007 inch. The thermistor was connected in series with a 15,000 ohm resistor to a 1.34 volt mercury cell. A Bristol recorder wired to register the potential drop across the thermistor indicated the temperature of the thermistor to 0.01 C.

A small heating disk constructed from carbon motor-brush filings mixed with glue was placed in the soil sample, as shown in figure 2.

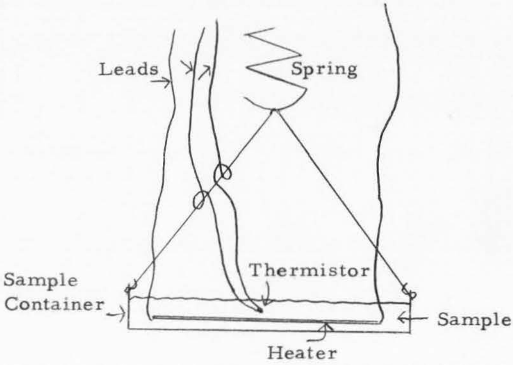

Figure 2. Temperature measuring sample and container.

Water vapor was admitted to the adsorption tubes to raise the pressure to a prescribed value. A small current was applied to the heater and the system allowed to come to equilibrium. At equilibrium the temperature of the sample was elevated enough beyond that of the bath that the heat input from the heater balanced the heat loss to the surrounding portions of the system. At this time the voltage drop across the heater and the resistance of the heater were accurately measured. From these measurements the heat production was calculated. The vapor pressure was also accurately read. Thus, at a specific bath temperature, vapor pressure, and sample temperature elevation above that of the bath, the rate of heat loss from the sample was calculated.

The voltage in the heater circuit was then increased and the process repeated for the same bath temperature and vapor pressure. Readings gathered in this manner were taken until a curve was established relating rate of heat loss to temperature elevation above bath temperature for a specific bath temperature and vapor pressure.

This entire process was then repeated for various vapor pressures until the range from zero to saturation vapor pressure was covered. This produced one set of calibration curves for the soil sample at one bath temperature. The process was repeated for the other bath temperatures. A sample set of curves is shown in figure 3. Intermediate curves were also determined and used in the calculations but were omitted from figure 3 for reasons of clarity or presentation.

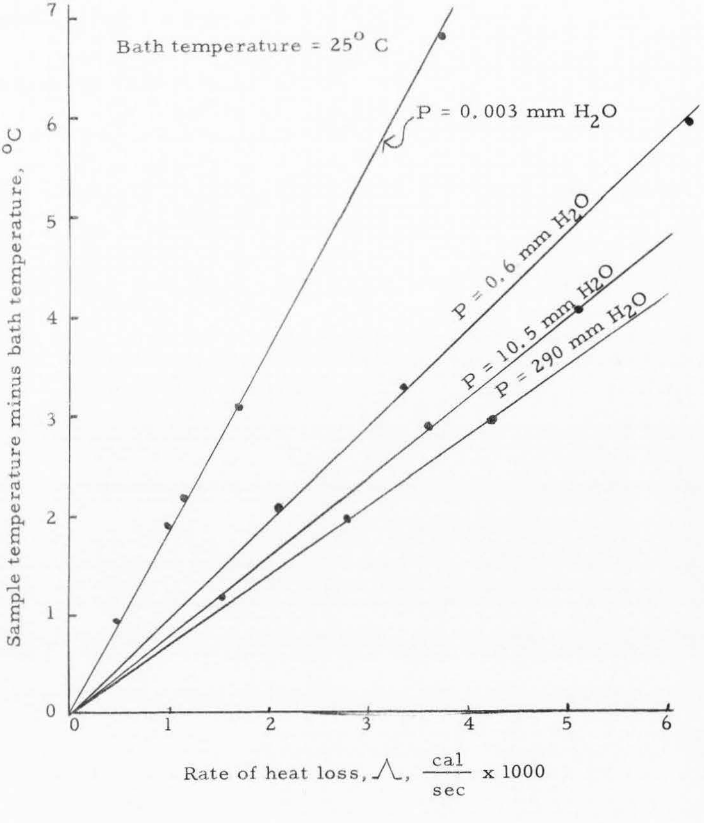

Figure 3. Rate of heat loss from sample as a function of sample temperature elevation above bath temperature for Millville loam.

The pattern of the curves for the three temperatures was similar but with the slope of a curve for a given vapor pressure decreasing slightly with increasing bath temperature.

After calibration the small heater was removed from the temperature measuring container. The actual data were collected as follows. The sample was evacuated for 48 hours at 10^{-5}/mm of Hg. The length of the spring in the adsorption tube was noted. A small amount of water vapor was added to the center manifold of the adsorption apparatus. The recorder was started, valve number 2 was opened, and a stop watch was started. A strict time schedule of spring extension and oil manometer readings was observed.

The readings of major interest were those which occurred just after the sample reached its maximum temperature. A representative temperature curve is shown in figure 4. At the inflection of the curve, the sample and thermistor should be as near equilibrium as possible on the high part of this curve. Therefore, this inflection point was chosen as the time measurement.

Equation (49) was used to analyze the data. The integral representing heat loss was graphically integrated from time zero to the inflection time. The spring extension gave the mass of water adsorbed at this time, and the manometer reading gave the vapor pressure at which the measurement occurred.

Supplementary Equipment and Procedures

The remaining unknown in eq. (49), the specific heat of the soil, was measured in a calorimeter especially designed for specific heat

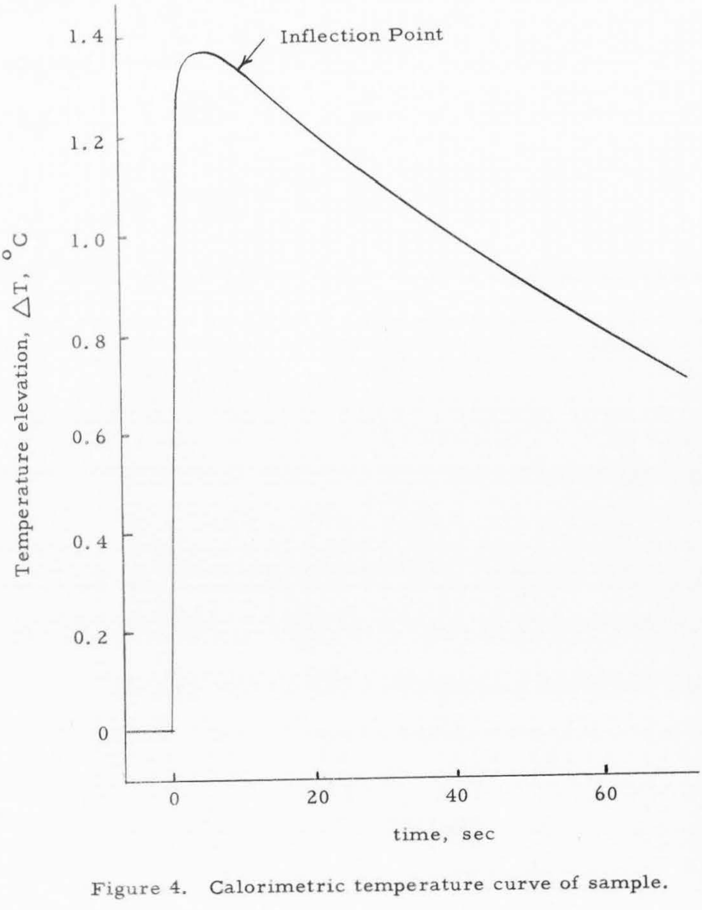

Figure 4. Calorimetric temperature curve of sample.

determination. The calorimeter and procedure are described by Rice (32). Regrettably, this calorimeter which had a reported accuracy of three places only yielded two place accuracy. The mean value for the specific heat of Millville loam was slightly less than 0.22 cal/g °C.

The data for the adsorption isotherms were obtained by allowing the soil sample to come to complete equilibrium after each temperature measurement run. At low surface coverages equilibrium was obtained very rapidly. At high vapor pressures several hours were required. The spring extension and manometer readings provided the basic data from which the isosteric heat of adsorption was calculated.

A precision calorimeter for heat of immersion measurements was constructed after the one described by Pierce et al. (31). Two modifications were made. First, the temperature in the air bath surrounding the Dewar flask was controlled by circulating water through extensive copper tubing networks in the air bath and in a separate constant temperature water bath. Second, the temperature in the calorimeter was measured by employing two high resistance thermistors in opposite arms of a wheatstone bridge circuit, the unit being calibrated as a whole.

The surface area of the soil was determined by the modified Dyal and Hendrichs (13) ethylene glycol retention method described by Bower and Gschwend (5). Millville loam yielded a total area of 79 m^2/g and an external area of 38 m^2/g. Kaolinite yielded an area of 22 m^2/g.

EXPERIMENTAL DATA AND ANALYSIS

Differential Calorimetric Heat of Adsorption

The differential calorimetric heats of adsorption for Millville loam, as calculated from eq. (49), are shown in figure 5. At low relative pressures values of q_d are from one to two hundred calories per gram higher than the heat of vaporization. This indicates that water adsorbed on the soil is in a lower energy state than free water and would require from one to two hundred calories more to evaporate one gram of soil water than free water.

Beyond thirty percent relative humidity an interesting condition exists. The values of the differential calorimetric heat of adsorption suggests that less energy is required to evaporate one gram of soil water than one gram of free water. Practically, this is not the case. In analyzing the temperature curves represented by figure 4 for relative humidities above fifteen percent, it was noted that the temperature of the soil sample dropped faster than would have been inferred by the heat loss curves. This suggests that part of the heat energy of the sample was being used for an endothermic reaction within the sample.

The reaction suggested by this phenomenon is expanding of the lattice of the montmorillonite type clays present in Millville loam. Barshad (3) concludes from his data that water molecules adsorb on the external surface of expanding lattice clays and then drive the platelets apart and move in between them. This sequent of events

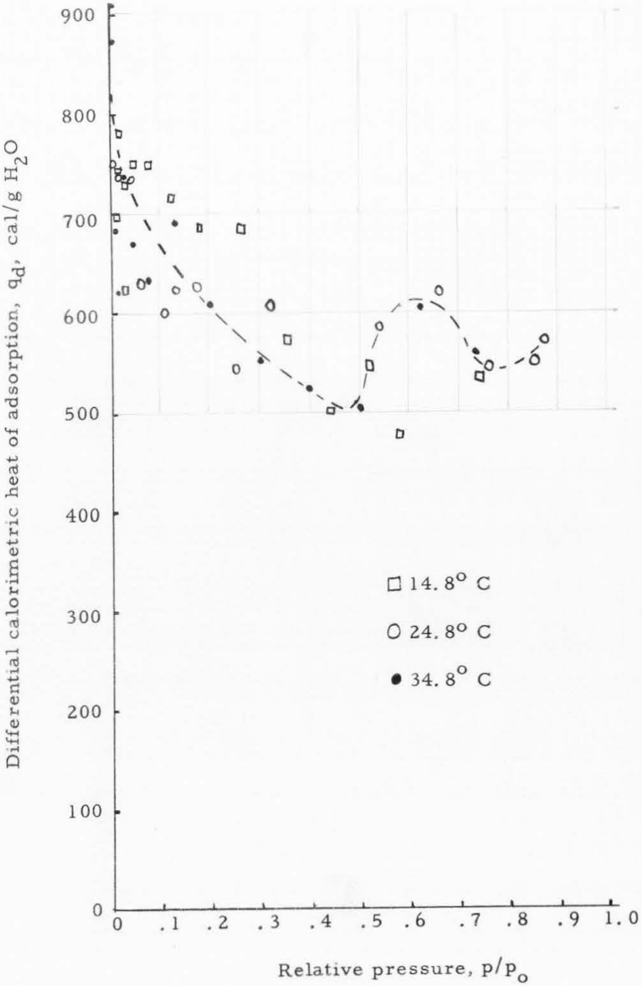

Figure 5. The differential calorimetric heat of adsorption for Millville loam.

could readily explain the data in figure 5. At low relative pressures the expanding lattice clays present in Millville loam remain in fixed positions with regard to expansion. As more water vapor is added, the clay systems reach the threshold of expansion. An added increment of water vapor at this point would result in the expanding of the clay platelet systems. Since the free energy of soil water becomes less as temperature increases, the temperature rise at this point of expansion due to water vapor adsorption accelerates the expansion process. This means that the heat energy of the sample is being used as the heat is being produced, resulting in a smaller temperature rise than would have been the case without lattice expansion. The net result is a lower differential calorimetric heat of adsorption than would have been the case without lattice expansion.

The above conclusion and data should not be interpreted to mean that less heat energy is required to evaporate one gram of soil water adsorbed between clay platelets than one gram of free water. The endothermic, lattice expansion process utilizes the heat energy which is produced by the water molecules passing to a lower energy state. Thus, it is likely that more energy would be required to remove the inter-lattice water molecules than to evaporate free water molecules or even externally adsorbed water molecules. It should be emphasized that the data were taken on a dynamic system and not on one at equilibrium.

The major factor which limited the accuracy of the data collected in this experiment was the measurement of the amount of added water.

The amount normally added resulted in a spring extension of from 0.10 to 0.15 mm. This introduced an eight to twelve percent error.

Because of the small amount of water adsorbed on kaolinite at a given vapor pressure, the additional amount adsorbed during a differential calorimetric heat of adsorption run was so small as to render this approach highly inaccurate. Therefore, data for kaolinite are not presented.

Isosteric Heat of Adsorption

The basic data from which the isosteric heat of adsorption was calculated were adsorption isotherms. Examples of the isotherms for Millville loam and lithium kaolinite are shown in figures 6 and 7 respectively. The basic data from which the isotherms were drawn are given in the appendix. The isotherms show the characteristic sigmoid shape which results from a rapid filling of the more active adsorption sites at low coverages followed by a period of steady increase in adsorption and concluded by a region of greatly increased adsorption due to capillary condensation.

The isosteric heat of adsorption for Millville loam is shown in figure 8. Different curves resulted when different isotherms were used in the calculations. Theoretically, if the isosteric heat of adsorption is independent of temperature, the two curves would fall on top of one another. However, swelling adsorbents were excluded in the derivation of the equation used to calculate the isosteric heat of adsorption. Both swelling and the failure of the isosteric heat

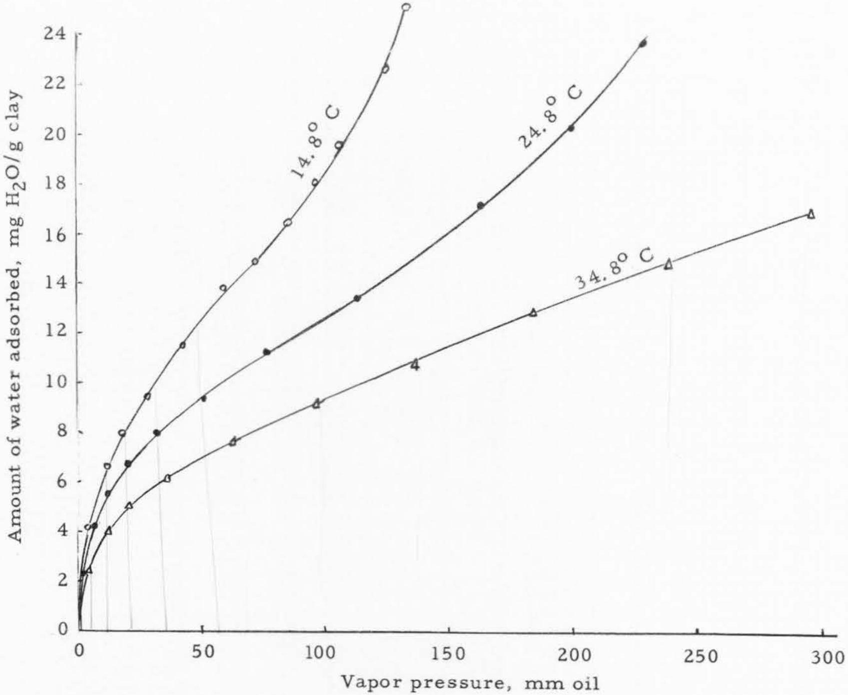

Figure 6. Adsorption isotherms for Millville loam. Specific gravity of oil = 1.0600.

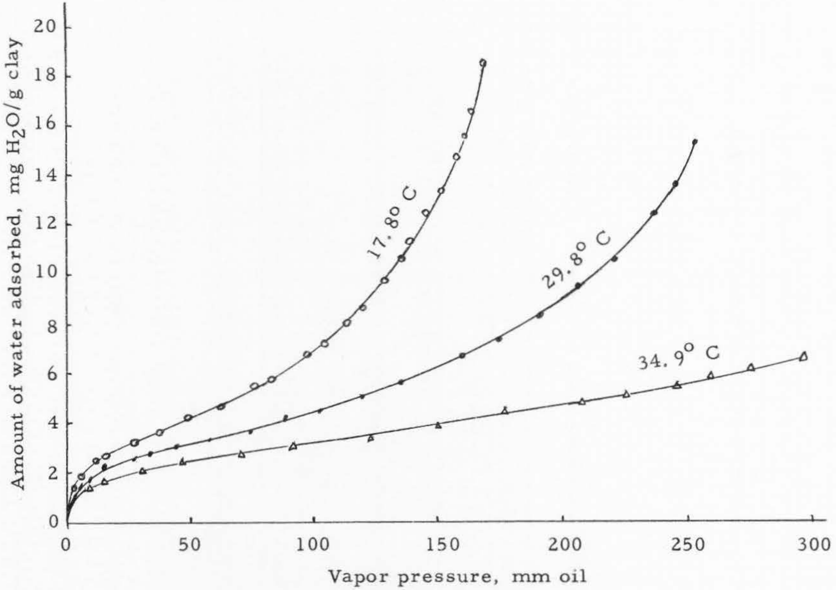

Figure 7. Sample adsorption isotherms for lithium kaolinite. Specific gravity of oil = 1.0600.

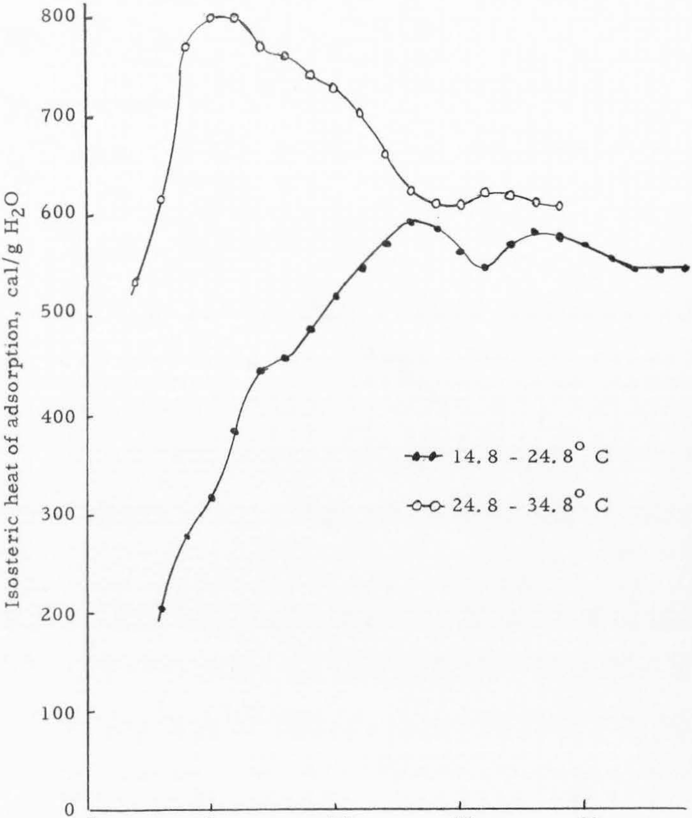

Figure 8. The isosteric heat of adsorption of Millville loam.

of adsorption to remain constant with temperature changes could have caused the phenomenon shown in figure 8. It is also likely that swelling is temperature dependent, which would also cause the isosteric heat of adsorption curves to diverge. An encouraging fact of figure 8 is that the isosteric heat of adsorption tends to approach the latent heat of vaporization of free water as more water covers the clay platelets.

The isosteric heat of adsorption and the differential calorimetric heat of adsorption should agree within the error of RT. However, this is not the case with the data represented in figures 5 and 8. Swelling is at work in both experiments. The effect of swelling on q_d has been discussed, and its effect of q_{st} can be seen from eq. (40). The value of the isosteric heat of adsorption depends on the shape of the adsorption isotherms. The shape of the isotherms depends on the amount of water moving in between the clay platelets. This may render the values of the isosteric heat of adsorption useless unless interpreted in the light of swelling effects. Therefore, little importance is placed on these values at this time. As saturation is approached, swelling becomes complete; and more importance can be placed on the isosteric heats of adsorption.

The isosteric heat of adsorption of water vapor on lithium kaolinite is shown in figure 9. These curves should also coincide. Although the curves do not coincide, they do have similar shapes and would be very similar if displaced slightly so that the maxima would coincide. The isosteric heat of adsorption should carry the

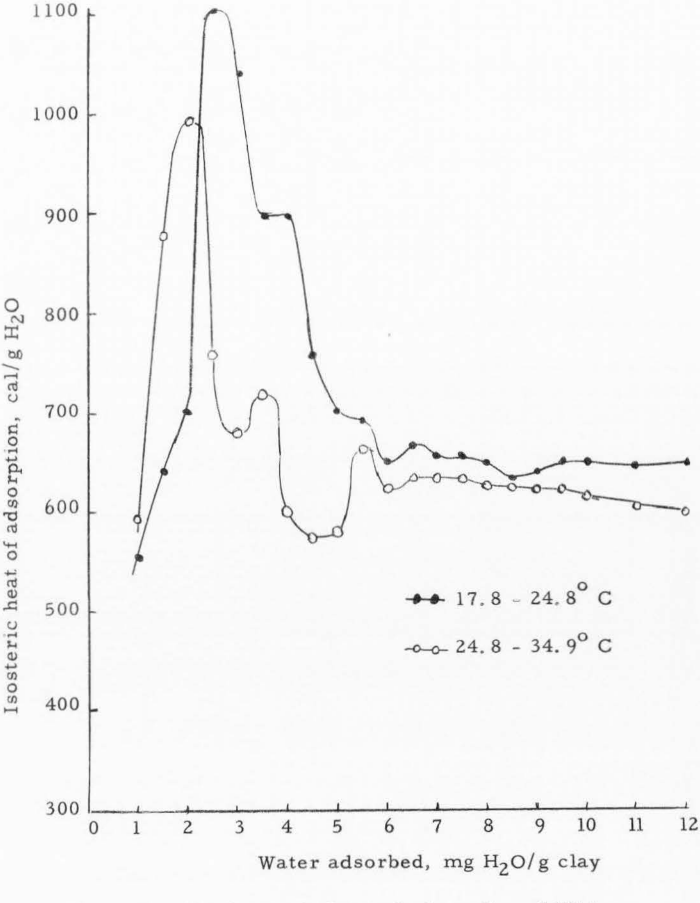

Figure 9. The isosteric heat of adsorption of lithium kaolinite.

physical significance that it represents the amount of heat input required to evaporate one gram of water from a large body of soil at a particular temperature and moisture content. Figure 9 shows that this amount of heat input increases from a moderate value to a sharp maximum and then decreases to approach the latent heat of vaporization of free water. The maximum could be caused by the movement of the lithium ions out of the surface cavities in the kaolinite to new locations where they could react with the adsorbing water molecules. This movement of the lithium ions is undoubtedly temperature dependent and could cause the displacement seen in the isosteric heat of adsorption curves. However, caution should be exercised in interpreting isosteric heats of adsorption in regard to physical mechanisms as the isosteric heat of adsorption represents the difference between partial molar quantities and not integral quantities.

Heat of Immersion

The data representing the heats of immersion are shown in figure 10. The heat of immersion curve decreases monotonically as expected, except for the region between 0.2 and 0.3 relative pressures. The displacement in this curve is real and similar to the one obtained by Whalen (37) for quartz.

It is interesting to note that the maximum in the isosteric heat of adsorption curve occurs near the point at which the heat of immersion curve passes through a minimum. This suggests that the same mechanism is operating in both cases. The movement of the

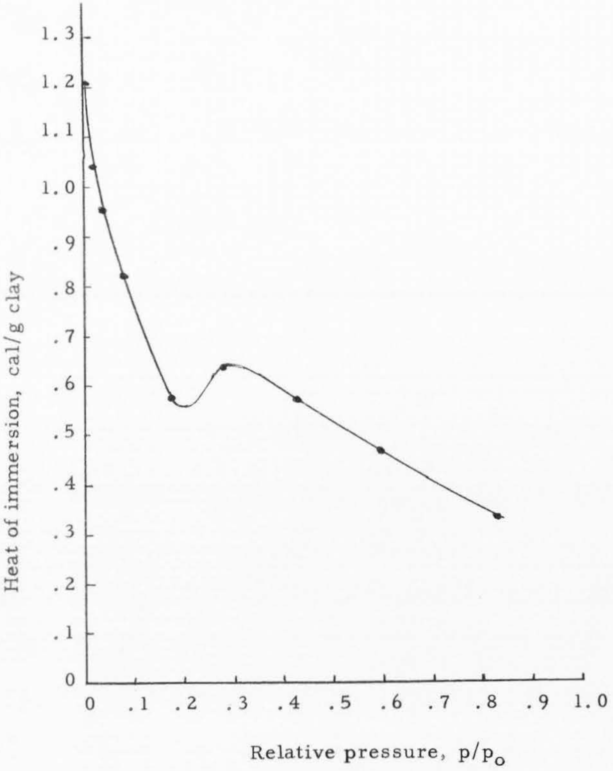

Figure 10. The heat of immersion of degassed lithium kaolinite samples as a function of relative pressure.

lithium ions out of the surface cavities could easily cause the displacement in the heat of immersion curve.

The heat of immersion value of 1.21 cal/g for degassed lithium kaolinite is close to the values for kaolinite reported in Grimm's book on clay mineralogy. However, no heat of immersion data for kaolinite with various amounts of preadsorbed water were found in the literature.

Figure 11 shows the heat of immersion for lithium kaolinite left for two months in desiccators over salt solutions of various relative humidities. Each point is the average of two replications. The samples were considered to have come to equilibrium with the relative humidity in the desiccators by the end of this time. The heat of immersion for the sample stored over P_2O_5 is slightly below that of the degassed sample shown in figure 10. The phenomenon could be easily accounted for by the energy required to remove adsorbed gases as discussed in proposition 1 in the appendix.

The curves in figures 10 and 11 tend toward the value of 0.3 cal/g if extrapolated to saturation vapor pressure. This is close to the value calculated for the destruction of about 20 square meters of air-water interface.

Enthalpy and Entropy of Soil Water

Using the heat of immersion data of figure 10 and the adsorption isotherm for 24.8 C shown in figure 7, the difference between the enthalpy and entropy of adsorbed water and free, liquid water was

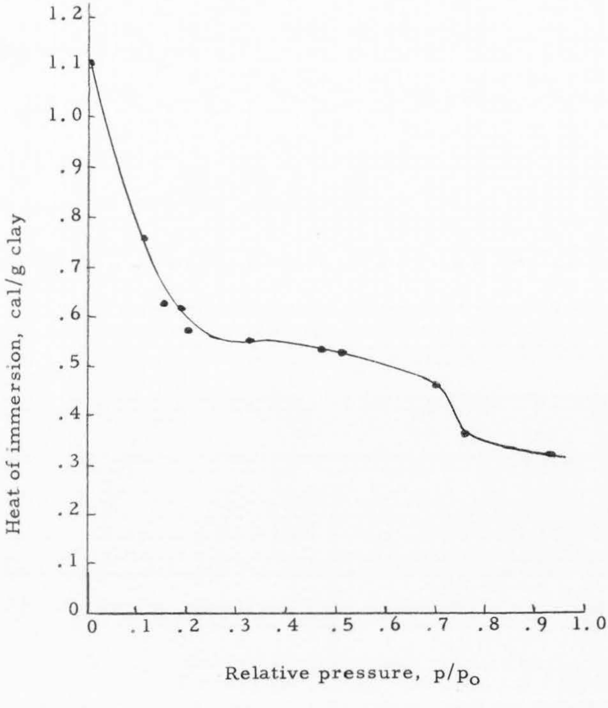

Figure 11. The heat of immersion of lithium kaolinite samples equilibrated in desiccators as a function of relative pressure.

calculated according to eqs. (47) and (50). The results are shown in figures 12 and 13.

Both the enthalpy and entropy of soil water show a minimum near a relative pressure of 0.17. A minimum in this curve is expected in the region of a monolayer coverage as shown by Hill et al. (22). This loose monolayer corresponds to an area of about 20 $Å^2$ per molecule. This value is high when the size of the molecule is considered. However, water molecules are strongly dipolar and, when orientated in the first layer, would repel each other. It is similar to bringing two small bar magnets together with like poles orientated in the same direction. Thus, the molecules would be expected to occupy a larger area than their physical size would indicate.

The entropy of soil water shows large positive values as zero relative pressure is approached. This is expected since the last term on the right in eq. (47) approaches infinity as the relative pressure approaches zero. The positive values for the difference between the entropy of soil water and free water support Martin's theory (29) that the clay particles have a structure breaking effect on the water network. When the first layer is filled, the entropy of soil water and that of free water is the same. This does not necessarily mean that the adsorbed water molecules are held in the same configurational pattern as liquid water molecules. It indicates that their freedom of movement is similar. Beyond a relative pressure of 0.2, the entropy curve rises.

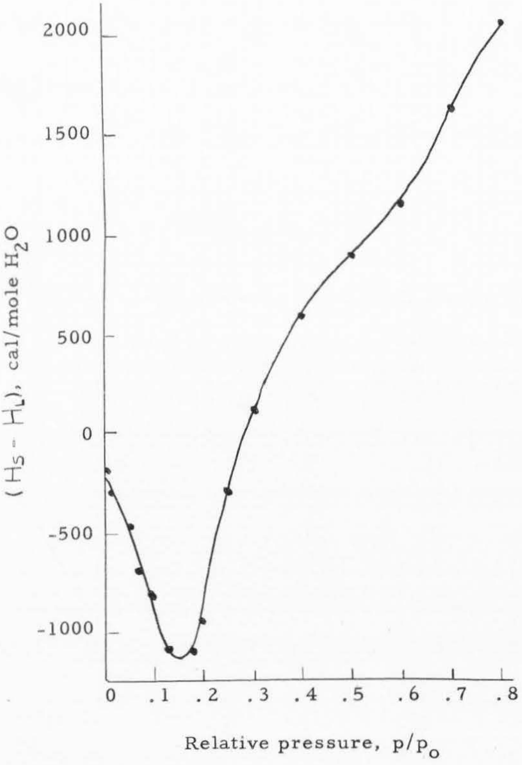

Figure 12. The difference between the enthalpy of soil water and that of free water as a function of relative pressure.

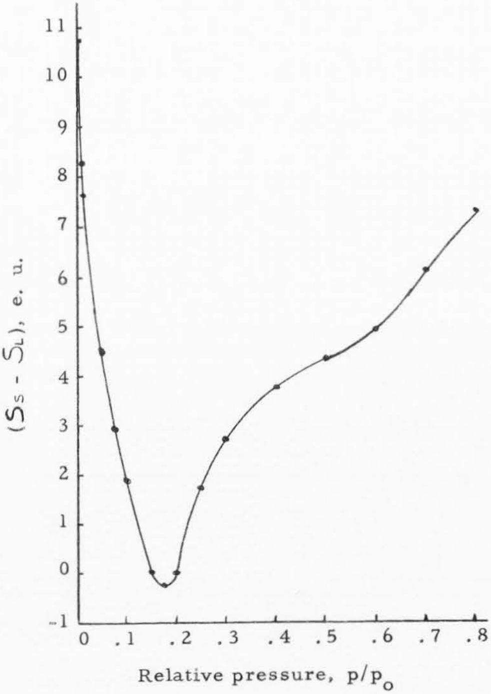

Figure 13. The difference between the entropy of soil water and that of free water as a function of relative pressure.

The enthalpy of the soil water is less than that of free water at low relative pressures. This is logically expected from a physical consideration of soil water. However, (H_S - H_L) becomes more positive as more water adsorbs on the kaolinite sample. This does not follow the theoretical argument that (H_S - H_L) should approach zero as saturation vapor pressure is approached. The same mechanism is operative in causing the enthalpy and entropy curves to deviate from zero at relative pressures beyond 0.2 as was operative in the isosteric heat of adsorption curves and heat of immersion curve. The movement of lithium ions into the sorbed water would strongly affect the thermodynamic properties of the system. Thus, eq. (47) is not applicable beyond a relative pressure of 0.2, since the adsorbent does not conform to the assumption that its thermodynamic properties are the same in the presence as in the absence of adsorbed molecules.

CONCLUSIONS

The calorimetric approach to the measurement of differential heats of adsorption is feasible though severely limited when used with swelling adsorbents. However, if the sensitivity of the gravimetric measurement of the amount of water adsorbed could be increased ten-fold, this method would be very useful on non-swelling adsorbents such as kaolinite. The differential calorimetric heat of adsorption measurements did confirm the hypothesis that about 750 calories are required to evaporate one gram of soil water at low relative pressures.

The isosteric heat of adsorption curves for Millville loam emphasizes the large effect that swelling has on the adsorption isotherms. The calorimetric and isosteric approaches to the heat of adsorption of water on Millville loam imply that a new approach must be found to treat swelling adsorbents.

The isosteric heat of adsorption of water on kaolinite shows that large amounts of heat energy are required to evaporate a gram of water from a large kaolinite system in equilibrium with twenty percent relative humidity. The amount required is almost twice that for an equivalent amount of free water.

The isosteric heat of adsorption of water on kaolinite suggests a major change in the slope of the integral heat of immersion at about twenty percent relative humidity but not a change to a negative slope as would be indicated by figure 10 for this region. However, it is suggested that these irregularities are caused by the lithium ions which have moved out of the surface cavities in the kaolinite and into the adsorbed water.

The heat of immersion of kaolinite approaches a value at saturation which is comparable to the destruction of twenty square meters of air-water interface. The lower heat of immersion value for the dry desiccator sample supports the arguments put forth in proposition 1 in the appendix.

The integral entropy of soil water is greater than that of free water at very low relative pressures and reaches a minimum at what could be considered a monolayer coverage. The entropy of soil water then increases as expected. However, it continues to increase as saturation vapor pressure is approached. Lithium ions which have moved out of surface cavities in the kaolinite and into the adsorbed film could cause this behavior. The conclusion is reached that eq. (47) is not applicable beyond a relative pressure of 0.2, since the adsorbent does not conform to the assumption that its thermodynamic properties are the same in the presence as in the absence of adsorbed molecules.

Because of the important data which the integral thermodynamic approach offers in the understanding of soil water properties, this approach should be refined and applied to other soil materials.

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APPENDIX

Proposition 1. The development of the wetting front could be explained on the basis that desorption of the adsorbed gases must occur before water can adsorb.[1]

Why are soil samples left in desiccators over constant relative humidity solutions for several weeks or months rather than only for a few hours? In order to reach equilibrium is the stock answer. Yet clay in an adsorption apparatus reaches equilibrium in an hour or so although the clay is sometimes left for a day just to be very sure that it has reached equilibrium. Why the difference? Perhaps we can get an idea from the pretreatment given the samples in each case.

Samples to be equilibrated at specific relative humidities are either dried or wetted to near saturation before being placed in desiccators so that they approach equilibrium along one side or the other of the hystersis loop. However, adsorption samples are placed in the apparatus and evacuated to 10^{-5} mm Hg for a day or two. The object--to remove all adsorbed gases so that the gas or vapor which is to adsorb on the sample will encounter a clean surface.

If a day or two of severe evacuation is required to remove the adsorbed gases, how much time would be needed for water molecules to replace adsorbed gas molecules (N_2, O_2, and CO_2 primarily) which are present? Evidently several weeks or months depending on the porous nature of the adsorbent would be the answer. However, it has been stated that this period of time can be reduced by partial evacuation of the desiccator.

Pidgeon and Van Winsen (6) determined the water vapor adsorption isotherm on asbestos fibers with and without air present. For the range of data reported (no values below 24% R.H. in the presence of air) both adsorption curves were the same. However, using the authors' own words "...the time required for the establishment of equilibrium is enormously reduced by the removal of air."

Stepping aside for a moment, the question might be asked--how should water enter or move through soil if only pore size and shape and viscosity and molecular speed of water are considered? My guess is the following curve:

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[1] The spark which developed into this proposition was gleaned from a conversation with Dr. John Cary in which he mentioned Dr. W. D. Kemper's concern for the effect of adsorbed gases on the angle of contact of a liquid on a solid.

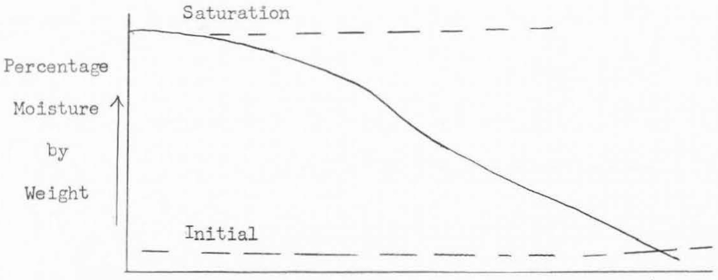

Figure 1. Distance from source

Why? ---because vapor would diffuse ahead of the water films and adsorb on the soil upon contact, the water films would race ahead of the liquid water due to the energy gradient, and liquid water would finally fill up the remaining voids.

But what does an actual moisture content distribution look like?

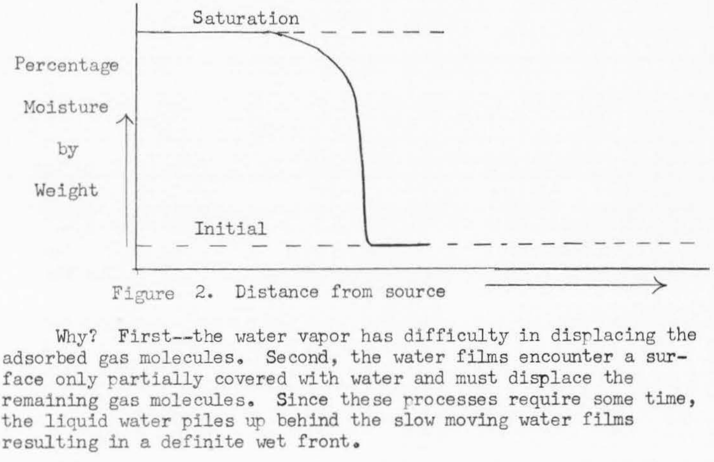

Figure 2. Distance from source

Why? First--the water vapor has difficulty in displacing the adsorbed gas molecules. Second, the water films encounter a surface only partially covered with water and must displace the remaining gas molecules. Since these processes require some time, the liquid water piles up behind the slow moving water films resulting in a definite wet front.

Colman and Bodman's (2) paper supports this idea by showing that a wet front moves faster in a slightly wet soil than in an air dry one. In this case the water film over the soil particles keeps the gas molecules at the film surface instead of on the soil. The moistening water films are able to quickly displace the gas molecules adsorbed on the adsorbed water due to the strong dipole interaction between the moistening film and the adsorbed water molecules. This allows the water film to move rapidly. The moisture content distribution across a wetting front in a soil at various initial moisture contents is shown in figure 3 taken from Gardner and Mayhugh (4):

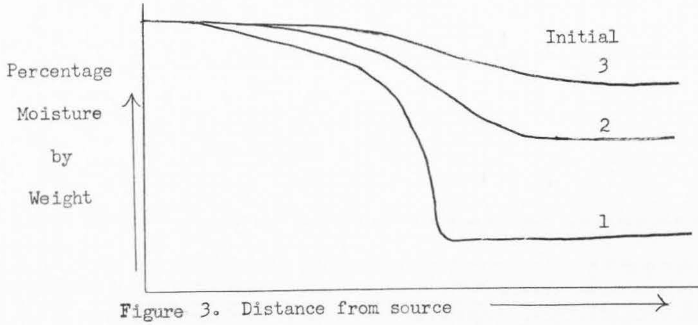

Figure 3.

James Biggar (1) reported activation energies ranging from 2.3×10^9 to 4.4×10^9 ergs per gram from measurements of the pressure potential difference across the wet front plane. He also states, "...as the system becomes drier, this phenomenon of energy barriers becomes more pronounced". In all probability, much of this energy is needed to displace the adsorbed gas molecules.

This proposition suggests two studies:

(1) The rate of water vapor adsorption on soil (or clay) from a gaseous mixture saturated with water vapor and containing various partial pressures of N_2 and/or O_2

An adsorption balance as described in the recent book edited by Katz (5) would be used to suspend a black bucket containing a thin layer of soil down into a black tube. This design would allow for a fairly rapid temperature equilibration during adsorption. The sample would first be equilibrated at a specific partial pressure of N_2 or O_2. Then a gas mixture would be introduced which would maintain the same partial pressure of N_2 or O_2, but would contain saturation vapor pressure of water. The rate of adsorption of water vapor would be determined under these conditions to study the effects of the adsorbed gas on this rate.

(2) Moisture content distribution across the wetting front as influenced by N_2 and O_2 Pressure.

This experiment would be set up similar to a diffusivity study using a gamma radiation device like the one described by Davidson, Nielsen, and Biggar (3) to measure moisture content as a function of distance. This would allow the soil column to remain attached to a vacuum and gas control apparatus. After equilibrating the soil with a specific gas partial pressure as before, liquid water would be allowed to enter one end of the column to form the wetting front. This study could take a number of different courses, but it should establish the effect of the adsorbed gases on the rate and type of water movement in soil.

An additional note

An explanation of the hydrophobic nature of paraffin can be made along similar lines. London dispersion forces could be stronger between the paraffin and the air molecules of N_2 and O_2 than between paraffin and water. As a result, paraffin would maintain a surface layer of air to the exclusion of water. An easy test of this idea would be to place a piece of paraffin in a small bell jar with a separatory funnel inserted in the top. After evacuating the sample to 10^{-5} mm Hg, water vapor would saturate the space in the jar. A drop of water from the funnel should spread out on the surface if surface forces are strong enough to overcome the surface tension of the water.

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Proposition 2. When replacing shifting agriculture in expensive fertilizer areas of the tropics with permanent agriculture, the permanent agriculture should center around fruit production and plant-animal cycles.

In many tropical countries (Ghana, Nigeria, Uganda, Liberia, Viet Nam, Burma, Laos, etc.) a form of shifting agriculture is practiced. The farmers cut the forest or shrub cover, burn it and plant their crops among the stumps for two or three years. At the end of this time their yields have fallen off somewhat, so they move on to a new plot, leaving the old field to revert to natural vegetation. If sufficient time is allowed, which varies from several years on the areas bordering on savannah to 20 or 30 years in the rain forests, the fertility of the soil seems to be improved to the point where the cycle can be repeated.

Since the land area available for this form of agriculture is constant and the population of most of the countries is increasing rapidly, the cropping and fallow cycle is becoming shorter. The fertility of the soil is declining and production per acre dropping, while the number of mouths to feed is increasing. Thus, agronomists must aid in the development of a more permanent and productive agriculture in these areas.

Climate, plants, and soils. I will limit my proposition to that major portion of the area where shifting agriculture is practiced, which lies between the dense rain forest and the savannah. The area is typified by a mean annual rainfall of 50 to 70 inches and may endure a slight to semi-deciduous forest. The undistrubed forest usually consists of three stories: 1) the emergents, 150 to 200 ft. high, 2) the upper storey of from 60 to 130 ft. with a closed canopy, and 3) the lower storey with a closed canopy at about 50 ft. Regrowth areas consist of a scattered upper storey and dense lower storey after 20 to 30 years.

The zonal soils in this area are latosols with reddish yellow latosols predominating in the area where data have been taken. These soils have characteristics associated with a balance between a moderate degree of leaching, the growth of vegetation, and the decay and destruction by worms, termites, ants, etc., of leaves, woods, and roots on and in the soil. There is usually an increase in acidity with depth. The topsoil is neutral to weakly acid because the recycled bases become available from the decomposed organic matter to saturate the base-exchange complex of the soil and organic colloid (2). Some leached bases affect the pH to a depth of several feet.

The nutrient status of these soils is roughly outlined in Table I.

Table 1. Nutrient content of soil in lb. per surface acre feet

Site	N	Av. P	Exchangeable K	Ref. No.
Kade	4100	11	580	2
Kumasi	6000	13	220	5
Belgian Congo	2500	17	300	1
Liberia	3900	30	450	7
Nutrients in trash, lianes, and litter	600	35	240	2
Ave. Nutrient removal per yr.	48	9	50	2

It will be noted that phosphorus is likely to be the first nutrient to become limiting. Even though the available P was usually determined by the Troug method, it does give an indication of the relative amounts that are present.

Some nutrients would be added when the vegetation was burned. These figures are roughly given near the bottom of the table. The last line gives an estimate of the average annual nutrient removal for a maize-maize-cassava rotation assuming yields of 37 bu. of maize and 15,000 lbs. of cassava tubers per acre per crop.

After abandonment, probably resulting from a lack of available phosphorus, the natural vegetation re-covers the area. After the establishment of deep-rooted species, plant nutrients are again brought to the surface. As small amounts of phosphorus become available from the more insoluble forms, it is also absorbed by the plant. If given sufficient time, the nutrient status of the top soil may be primarily restored.

Possibilities of a more permanent agriculture. Let us now turn to a few papers on cocoa research in Nigeria to develop a possible pattern and then branch out to other crops. Kowal (3) studied the effects of spacing on the environment and performance of cacao under Nigerian conditions. Cacao trees require fairly moist conditions and a moderate amount of shade. Therefore, a scattered upper storey of shade trees is maintained. Kowal found that stand density was positively correlated with ease of management, early yields, health, and performance. His closest spacings of 5 x 5 ft. and 5 x 6 ft. gave the best results.

In a succeeding paper Kowal (4) reported the effects of spacing on ecological factors (soil moisture, soil nitrates, shade, and microclimatic conditions). A high positive correlation was found between stand density and soil moisture, soil nitrates, organic litter, soil nutrient status, and the yield of cocoa. The closer spacings produced a closed lower canopy.

Centrosema pubescens is often used as a ground cover plant on tropical plantations because of the hearty growth this legume makes in dense shade. With good drainage Centrosema will produce about 36,000 lbs. of organic material per acre in 10 months or a nitrogen equivalent of 180 lbs. of ammonium sulfate and available phosphoric acid equivalent to 45 lbs. of trebel superphosphate (6). Its vigorous growth tends to smother weeds. It gives root competition to young seedlings, but it has a beneficial effect in mature stands.

Wilson and Lansbury (8) reported a study on the managed grazing of Centrosema pudescens grown in cleared rain forest in Ghana. West African Dwarf Forest sheep were used in the grazing and digestion trials. The pastures were stocked with an average of 5.5 head per acre and were grazed from 8 to 11 a.m. and again from 3 to 6 p.m. to avoid the dew laden (and therefore helminth-dangerous) early hours and the midday heat.

Over 11 months two flocks of wethers gained an average of 14.7 lbs. increasing from 25.9 to 40.6 lbs. from unassisted Centrosema grazing. The digestion trials yielded digestion coefficients of .54 for total dry matter and .62 for crude protein. On this basis Centrosema yielded about 1200 lbs. of starch equivalent and 400 lbs. of digestible crude protein per acre. Since the nutrient ratio of only 1:3 supplies an excess of protein, the addition of some starchy supplement as raw cassava root should produce beneficial results.

The general pattern of agriculture suggested by these studies is to maintain a closed canopy of productive trees and to grow a tolerant or shade-requiring cover crop that may be grazed.

One need not be limited greatly on the species of trees, animals, or cover crops. The mangosteen requires heavy shade, while durian, jackfruit, champedak, and breadfruit require moderate shade. These fruit trees allow the maintenance of deep-rooted upper storey trees which recycle more salts to the surface. A closed lower storey of fruit trees should aid in soil moisture and plant nutrient maintenance, while the cover crop would help to deter erosion, hold nutrients against leaching, and provide forage. Citrus require less shade but may show similar relationships between plant nutrients, soil moisture, production, and a closed canopy.

Goats are popular in Central Africa. Perhaps they would do better than sheep under forest conditions.

Other cover crops are also very promising and may have certain advantages under specific soil and rainfall patterns. These include:

Calopogonium mucunoides

Justicia flava

Digitaria velutians

Melanthera scandens, etc.

To satisfy the need to grow small crops in sunlight, narrow strips (perhaps 100 meters wide) could be cut through the forest in an East-West direction. The fields would receive some leaf fall from the adjacent upper storey shade trees and should receive all the manure from the animal pens. This process might help to maintain yields over a much longer period than now.

It is my belief that this whole field of interrelationships between trees, livestock, and forage crops offers an important key to solving the problem of developing permanent agriculture in places of the present shifting agriculture.

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Proposition 3. The search for a good "when-to-irrigate-meter" should be focused on the plant rather than the soil.

Present methods of determining when to irrigate. At present many farmers determine the time of irrigation by feeling the condition of the soil with their hands (2), observing the plants for signs of wilting, applying water on a schedule according to phenological stages of the plant, or at intervals depending upon rainfall. These methods are rough estimates, at best, and are not adequate to meet the demands of greater irrigation efficiencies. For farmers possessing the necessary laboratory facilities and technical skills, more scientifically sound soil moisture determinations may be made using electrical resistance blocks or tensiometers. With these two methods an attempt is made to measure the soil moisture stress. However, as will be discussed later, soil moisture stress is not the property which we should measure.

Factors affecting plant moisture stress. The external factors which affect plant moisture stress are associated with the rate of water loss to the atmosphere and the rate of water absorption from the soil. The rate of water loss is dependent upon atmospheric temperature, wind velocity, light intensity, and the relative humidity near the plant. The rate of water absorption is dependent upon the soil moisture stress near the plant roots, the rate of soil moisture movement, and the distance over which it has to move. Thus, rate of water adsorption is also affected by root density and root growth (6).

Internal factors affecting plant moisture stress are associated with imbibition pressures of the plant cells and tissues and with the amount of bound water in the plant tissue.

In general these are most of the factors which determine how well the plant is getting along in its environment with respect to water. Except for observing wilting signs in the plant, the methods of determining when to irrigate only consider one or two of the numerous factors which affect plant moisture stress. The plant integrates all of these factors into plant growth and production. Since we irrigate to satisfy plant needs, we should look to the plant to determine when to irrigate.

Physiological changes in plants due to water deficits. If we are to look to the plant to tell us when to irrigate, we must find some indicator process which we can measure. As water becomes limiting, the cell sap becomes more concentrated, the cell wall pressure decreases, the rate of conversion of starch to sugars is accelerated, the destruction of protein is accelerated, and the plant tissue undergoes dehydration (8). However, secondary effects may become more important. Diffusion pressure deficit (DPD) is the common scale referred to in the literature (7). If it could be accurately measured, we might find it the best index to plant moisture stress.

Present research developments. In 1958 Box and Lemon (1) published a paper describing an attempt to measure plant changes. Their method was based on measuring the electrical resistance of a segment of the plant stem by inserting two electrodes 2 1/2 cm apart. They found a fairly good correlation between electrical resistance and mean soil moisture tension with cotton plants. However, their method did not produce satisfactory results with sorghum. Box and Lemon attributed the change in resistance to a change in tissue hydration.

Slatyer (5) showed that the ratio of evapotranspiration to (free water evaporation)$^{0.75}$ for cotton plants was linearly correlated with available soil moisture content. Sorghum produced a curve highly convex to the soil moisture axis. This suggests that either the available soil moisture determinations were in error due to poor sampling or sorghum has a more extensive root system per unit evaporating surface or a more efficient water absorption mechanism. This points out the danger of trying to correlate a plant moisture indicator against soil moisture content. Perhaps the method of Box and Lemon (1) is also valid for sorghum, as their plants may never have suffered from a lack of available moisture. However, compensating processes affecting electrical resistance occur in a plant undergoing moisture stress so that electrical resistance may not be a good indicator for most mesophytes.

Farkas and Pratt (3) reported the use of a refractometer to predict when-to-irrigate. Their method consisted of correlating cell sap concentration (CSC) as measured by its index of refraction using a hand refractometer with plant need for water. The greatest problem encountered with this method is the large variation of CSC from top to bottom of the plant, between different plants, and between different stages of growth for the same plant.

A method of greater promise is the use of hydrocarbons on leaves to determine stomatal opening by rate of hydrocarbon infiltration into the leaves. It has been used by various workers on different plants. A recent successful application of the method was made by Halery (4).

A more recent attempt was designed to measure DPD using the Peltier cooling effect (9). The method is rather sensitive to temperature equilibrium and thermocouple measurements. Success has not been achieved by this method as yet.

Summary and directions for future research. Since the plant integrates all the factors which affect plant water stress, we should look to it for an indication of when to irrigate. Plant physiologists feel that DPD is the best overall measure of plant moisture stress. However, as yet they have not devised a good method of measuring it. The ideal would be a simple method that the farmer could use in the field. A good method is also needed by agronomists for use in research. With a little concentrated effort and with the aid of a good electrical engineer, a satisfactory method could be devised using electrical measurements.

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Proposition 4. Scientific journals should add two new sections or encourage two new types of papers:

(a) A section where workers could write the research ideas that they don't have the time or equipment to work out themselves, and

(b) A section for research that was conducted and failed along with the author's theories on why it failed.

Part (a)

Thinking men have good ideas, many of them about their specialized work or general field of interest. In fact, they will probably get many more ideas than they will ever be able to work on or have the equipment to do. Many of the ideas would probably make great contributions to the field if research were done on them. However, their originator is likely to use only those ideas for which he can get the funds to explore or in which he is so interested that he finds some way to acquire the equipment and the time to develop. The remaining ideas are tossed aside and usually forgotten.

If these ideas were put down in writing (maybe only a paragraph or two is needed) in the journal for his field, two important uses could be made of them. First, they could be used as guide posts by graduate students. Reading these ideas would be no substitute for reading and studying the important literature in the student's general field of interest, but they could be used to guide him to the frontier of knowledge and direct his reading. The "ideas" column could also be used by graduated research workers if they are not among those who receive an over abundance of ideas.

Second, and perhaps most important, this column would be a source of mental stimulation to other idea producers. In this case the column might become the anvil upon which basic theories of science could be hammered out.

Many researchers realize the value of talking over their ideas with their colleagues. From what little I have seen, Jim Biggar and Don Nielsen seem to be very productive; part of their abundant productivity probably could be attributed to their free exchange of ideas. Many workers, however, are not so fortunate. They are isolated from their fellow workers by states and sometimes by countries and oceans. Annual meetings help to spread ideas to a certain extent, but not all those interested in a particular problem in one's field are in attendance. Even if all should be in attendance, chances are that they would not think of all of their important ideas when there was an opportunity to discuss them. A column in "their" journal could bring together these ideas to be read and pondered.

We read of the European scientists of a century or two ago writing "letters", scholarly expressions of their ideas and theories, to some society or one another. Today we publish research that has been conducted or possibly a theory of particular merit, but generally do not publish our ideas. The "idea" column could produce the spark which could light some still dark corners of our science. It might also be looked upon as the bulletin board upon which professional workers could post and discuss their propositions.

Part (b)

With the broad educational base which is being developed today, a multitude of research workers are entering all fields of science. These workers are scattered around the world and do not have personal contact with one another. As a result, some worker may conduct research that has already been tried a number of times and failed.

In a recent conversation, Professor Ashcroft mentioned a discussion at the Western Meetings, which pointed out that several workers had tried or knew of others who had tried to determine the moisture content distribution by electrical conductance across the wet front in a soil column. These workers did not meet with much success because of the salts which were carried along with the moving water. Nevertheless, they had not mentioned their failures in the literature. With the lack of personal contact between researchers, these projects that fail usually do not become known. As a result, much time, money, and effort is wasted in the repetition of "poor" experiments.

If the research that failed was briefly written down stressing the author's thoughts on reasons for failure, suggested modification of design for improvement, and directions new research should take, the researcher could help his scientific field by his failure. Admittedly, the greatest problem will be to overcome our pride and accept a failure. However, the strong, progressive man builds on his failures as well as his successes to reach new heights of scientific endeavor.

Table 2. Data for isotherms for Millville loam

14.8 C		24.8 C		34.8 C	
X, $\frac{\text{Mg H}_2\text{O}}{\text{g clay}}$	P, mm oil[2]	X, $\frac{\text{Mg H}_2\text{O}}{\text{g clay}}$	P, mm oil	X, $\frac{\text{Mg H}_2\text{O}}{\text{g clay}}$	P, mm oil
	P_0 = 163.09 mm oil		P_0 = 300.64 mm oil		P_0 = 534.73 mm oil
0.34	0.2	1.07	0.2	0.34	0.1
1.24	0.8	2.65	2.4	1.30	0.6
2.07	1.2	4.26	6.5	1.99	1.9
2.68	2.2	5.64	12.2	2.60	3.9
3.37	3.3	6.82	20.5	3.37	7.3
4.05	4.5	7.12	32.1	4.06	12.7
5.29	7.6	8.47	31.2	5.15	21.0
6.67	12.4	9.36	52.2	6.25	37.3
8.03	19.7	11.29	76.8	7.83	63.4
9.55	29.6	13.50	113.7	9.28	96.4
11.54	42.9	17.34	162.9	10.86	137.4
13.88	59.0	20.22	199.2	12.99	184.0
14.98	72.5	23.75	228.5	14.85	238.8
16.43	84.4	29.43	256.3	16.97	295.9
18.13	95.3	31.70	262.8	19.24	346.0
19.65	105.4				
21.16	115.4				
22.74	124.2				
25.14	132.8				
28.58	141.2				

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[2] Specific gravity of oil = 1.0600.

Table 3. Data for isotherms for lithium kaolinite[3]

17.8 C		24.8 C		34.9 C	
X, $\frac{\text{Mg H}_2\text{O}}{\text{g clay}}$	P, mm oil	X, $\frac{\text{Mg H}_2\text{O}}{\text{g clay}}$	P, mm oil	X, $\frac{\text{Mg H}_2\text{O}}{\text{g clay}}$	P, mm oil
0.25	.05	0.54	.4	0.37	0.3
0.67	0.4	1.08	1.5	0.68	1.3
0.94	0.8	1.33	3.3	0.91	2.3
1.48	2.5	1.45	4.5	1.16	4.1
1.89	4.9	1.78	7.8	1.29	6.7
2.20	7.4	2.57	26.4	1.37	8.5
2.56	10.9	2.78	32.9	1.54	13.1
2.69	15.2	3.03	43.2	1.66	14.9
3.10	22.2	3.36	58.0	1.88	23.7
3.24	27.0	3.61	74.5	2.12	30.0
3.41	29.6	4.03	88.2	2.32	38.6
3.68	36.8	4.53	102.3	2.51	47.5
3.87	39.8	5.15	119.1	2.61	55.3
4.18	49.3	5.60	134.4	2.74	70.3
4.40	56.5	6.68	159.7	2.86	79.5
4.67	61.8	7.35	174.6	3.11	92.4
5.16	68.6	8.26	190.6	3.24	102.1
5.48	75.2	9.50	206.5	3.40	123.1
5.79	82.8	10.58	220.9	3.74	138.4
6.24	89.4	12.41	237.2	3.94	150.3
6.78	97.6	13.65	246.0	4.15	164.9
7.23	104.2			4.52	177.4
7.99	113.1			4.59	190.3
8.58	119.8			4.94	208.7
9.65	128.5			5.19	225.9
10.51	135.4			5.56	245.7
11.31	139.2			5.98	260.0
12.21	146.0			6.27	276.4
13.20	152.2			6.68	293.3
14.64	158.4			7.06	312.7
15.49	161.2			7.59	330.5
16.52	164.2			8.09	343.9
18.41	169.5			8.80	353.9
				9.05	369.0
				10.38	397.4
				11.12	412.2
				12.16	427.1
				12.82	437.5
				13.53	445.8
				14.53	453.3
				15.52	462.2
				17.02	471.9
				18.26	478.4

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[3] These data represent single isotherms from duplicates.

Table 4. Approximation equations for φ calculations from the 24.8 C isotherm

Pressure, mm oil	W, $\frac{g\ H_2O}{g\ clay}$
0 - 4	$W = .000744\ p^{0.5}$
4 - 15	$W = 10^{-4}\ (33\ p + 70)^{0.5}$
15 - 100	$W = .00195 + 0.000024\ p$
100 - 190	$W = 0.000043\ p$
190 - 240	$W = -\ 0.00805 + .000086\ p$
240 - 255	$W = -\ 0.03475 + .000197\ p$

Table 5. Heat of immersion data

Relative Pressure p/p_o	Heat of Immersion h, cal/g clay
0	1.205
0.013	1.004
0.033	0.960
0.078	0.820
0.169	0.572
0.282	0.637
0.462	0.574
0.593	0.462
0.828	0.334

Table 6. Directly determined ΔH_a values as a function of relative pressure

35 C		25 C		15 C	
P/P_o	ΔH_a cal/g	P/P_o	ΔH_a cal/g	P/P_o	ΔH_a cal/g
.0006	910	.0007	752	.005	744
.004	873	.008	750	.007	696
.008	683	.022	739	.013	786
.015	622	.040	735	.020	726
.027	739	.068	630	.027	625
.044	670	.11	600	.046	750
.079	633	.13	623	.076	750
.13	691	.17	628	.12	718
.20	609	.25	543	.18	687
.29	551	.32	605	.26	684
.39	522	.54	584	.35	572
.50	503	.66	620	.44	500
.62	603	.76	545	.52	545
.73	558	.85	550	.58	475
		.87	573	.64	635