THERMODYNAMICS OF SOIL MOISTURE[1])

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SUMMARY
The various equations used by several authors to express the partial molar free energy of soil moisture as a function of certain parameters are compared with a "parent" equation derived in this paper. It is pointed out that aside from differences in terminology also some more basic differences of approach seem to exist, which only lead to identical results under certain limiting conditions. It is shown that from this "parent" equation some equations with practical applicability may be derived. The methods available for the experimental determination of the partial molar free energy of soil moisture are reviewed, with special reference to the assumptions underlying the application of the freezing point depression of soil moisture.

1 INTRODUCTION

Since the appearance of EDLEFSON and ANDERSON's "Thermodynamics of Soil moisture" in 1943 (6) several authors (ref. 1 through 15) have attempted to extend the treatment given by E. and A. in the light of increasing knowledge of the system soil-water. Although undoubtedly useful improvements on the original approach of EDLEFSON and ANDERSON were obtained, at the same time a diversion in the use and meaning of certain thermodynamic variables occurred which may occasionally give rise to confusion. This diversion in terminology is partly a matter of personal preference, although in certain cases differences of opinion may exist with regard to the principles governing the interaction between water and solid phase.

As progress in any field is always hindered by such a lack of unanimity in symbols and definitions, it would seem useful to reconsider the existing literature in order to establish in what respect differences are only of superficial nature or whether actually basic differences of opinion exist. This should be of special interest to those, who, although not having worked on the subject themselves, are concerned with the application of the thermodynamics of soil moisture to soil physical problems.

Naturally it is outside the scope of this paper to give complete derivations of all thermodynamic equations employed. Instead it has been attempted to give satisfactory evidence for the equations to render them plausible and allow the reader to acquire an insight in their background and limitations. For further detail the reader is referred to standard textbooks and to ref. 6.

As will be shown it seems doubtful whether one generalized equation for the system soil water will exist, which combines absolute generality with both sufficient detail and practical applicability. Depending on the specific nature of the system considered, different variables may be determinable, and accordingly different "working" equations would be preferred. Nevertheless it should be possible to relate all these equations to one "parent" equation which, although

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not suitable for practical use, should serve the purpose of providing the necessary background against which the particular equations are to be seen.

With regard to the terminology and symbolics to be employed it may prove difficult to reach unanimity of opinion, because of differences in background of the workers concerned. Even if certain differences in symbolics will persist in the literature, it should be possible to agree on the relationships between the parameters employed. With regard to this a warning may be sounded against the use of terms and symbols already in use in related fields, as e.g. chemical thermodynamics. Unless it can be shown explicitly that the use in this particular field covers completely the meaning adopted in other fields, this will undoubtedly lead to confusion.

With the above in mind it will be attempted in the following sections to compare the approaches employed by the mentioned authors. For those who where not involved in this field before, a section on basic relationships is included. No differences of opinion seem to exist with regard to the contents of this. The next section is concerned with the generalized equation for the partial molar free energy of a constituent of a system. Although presumably in essence accepted by all authors cited it may still be seen as a starting point of the diversion discovered later on. When this equation is applied to the soil moisture system, differences arise. According to the present authors these differences could be explained as a result of the difficulty to find truly independent, and at the same time practically determinable, parameters to characterize the complex system. Most differences in final equations may thus be traced back tot the method of splitting the partial molar free energy in determinable terms. It should be ascertained at the beginning that there may be several ways of splitting the partial molar free energy, which could all be essentially correct. It has occurred, however, that the effect of certain parameters was counted twice, hidden as it was in other terms. This serves to illustrate that utmost care must be used when working out a certain way of splitting terms. At the same time one should be aware that although an equation may be formally correct the practical application may lead to erroneous results if it is not checked that variables that were introduced as independent, are indeed varied independently in the process used to determine the value of certain partial derivatives (cf. section 6).

2 Basic relationships

In thermodynamics several variables of state of a system are used. Of these the "Gibbs' free energy" has been found to be most useful, because its value may be easily expressed as a function of pressure and temperature.

The Gibbs' free energy, G [2]), is defined according to:

$$G = E + PV - TS \qquad (2.1)$$

in which E = internal energy of the system, P = pressure, V = volume, T = temperature, S = entropy. With help of the first and second law of thermodynamics a criterium for equilibrium based on the value of G can be found. According to the first law:

$$dQ = dE + PdV + dW' \qquad (2.2)$$

[2]) In anglo-american literature the symbol F is used for the free energy.

in which dQ is heat added to the system, and dW' stands for work (other than the work of expansion, which is covered by PdV) done by the system on its surroundings. The condition for equilibrium of a system as formulated by the second law is:

$$dS = \frac{dQ}{T} \qquad (2.3)$$

Combining (1), (2) and (3) another condition for equilibrium is found; viz.

$$dG = VdP - SdT - dW' \qquad (2.4)$$

which implies that for reversible processes (which may be seen as a series of successive equilibrium states) G may be calculated from the changes in P, T and W'. The term dW' may be replaced by —dW, i.c. the work done by the surroundings on the system. This quantity can be written formally as:

$$dW = \Sigma \, Y \, d \, X \qquad (2.5)$$

in which the summation term on the right hand side indicates that the work term must be seen as a summation of different types of work, each type being formally equal to the product of an intensive parameter and an extensive parameter (e.g. force $\times$ distance). Substituted in (4) this gives:

$$dG = VdP - SdT + \Sigma \, Y \, d \, X \qquad (2.6)$$

This implies that for a system at equilibrium with fixed values of P, T and X the free energy G is at its minimum value, according to:

$$dG_{P,T,X} = 0 \qquad (2.7)$$

in which the subcripts indicate that P, T and X must be kept constant. The relationship (6) may also be written formally as:

$$dG = \left(\frac{\delta G}{\delta P}\right)_{T,X} dP + \left(\frac{\delta G}{\delta T}\right)_{P,X} dT + \Sigma \left(\frac{\delta G}{\delta X}\right)_{P,T} dX \qquad (2.8)$$

since according to (6) the free energy of a system is a function of P, T and X only.

The above relationship is, however, valid only for systems with a fixed composition. If in addition to the variables P, T and X also the composition is varied (by transfer of material into, or out of the system) equation (8) must be expanded to cover also the changes in composition. This is done formally by adding a set of terms according to:

$$dG_{P,T,X} = \Sigma_i \left(\frac{\delta G}{\delta n_i}\right)_{P,T,X,n_j} dn_i \qquad (2.9)$$

in which $dG_{P,T,X}$ conform the earlier adopted convention signifies the changes in G if P, T and X are kept constant, while the composition is varied, whereas n_i indicates the amount of component i present. The partial differentiations covered by the summation term must naturally be performed at constant values of P, T, X and of the amounts of all components other than the one with respect to which is differentiated. Combining (9) with (8) the final expression for dG is found as:

$$dG = (\frac{\delta G}{\delta P})_{T,X,n} dP + (\frac{\delta G}{\delta T})_{P,X,n} dT + \Sigma (\frac{\delta G}{\delta X})_{P,T,n} dX + \underset{i}{\Sigma} (\frac{\delta G}{\delta n_i})_{P,T,X,n_j} dn_i$$

$$(2.10)$$

which equation indicates that the total change of G may be expressed as the sum of the changes effected by P, T, X_A .... X_Z, n_a .... n_z .

Furthermore a comparison with (6) gives:

$$(\frac{\delta G}{\delta P})_{T,X,n} = V$$

$$(\frac{\delta G}{\delta T})_{P,X,n} = -S \qquad (2.11)$$

$$(\frac{\delta G}{\delta X})_{P,T,n} = Y$$

The last summation term may then be simplified by defining:

$$\overline{G}_i = (\frac{\delta G}{\delta n_i})_{P,T,X,n_j} \qquad (2.12)$$

The quantity G_i is called the partial molar free energy of component i.

Applying again the equilibrium condition for a system without material transfer through its boundaries (so-called closed system), i.e.

$$dG_{P,T,X} = 0$$

one finds as a new criterium for a closed system in equilibrium:

$$\underset{i}{\Sigma} \overline{G}_i dn_i = 0 \qquad (2.13)$$

Since also the total amount of each component in the system is constant (closed system) one finds

$$dn_a = 0, dn_b = 0 ..... dn_z = 0 \qquad (2.14)$$

Combination of (13) and (14) then gives the well known equilibrium condition for a closed system at fixed values of P, T and X, viz. the partial molar free energy of each component is *constant* throughout the system. Thus the original equilibrium condition, which referred to the system as a whole, has now been replaced by a much more practical criterium referring to the value of the partial molar free energy of the individual components. Thus in the soil, equilibrium implies that $\overline{G}_{H_2O}$ is constant throughout the entire soil system, including vapor phase, adsorbed layers, etc.

3 THE PARTIAL MOLAR FREE ENERGY

In order to apply the foregoing it is necessary that the value of the partial molar free energy of a component in a system is expressed as a function of measurable parameters. The more complicated a system becomes the more difficult it is to find a satisfactory set of parameters for this purpose.

Although no differences of opinion are found with respect to the basic relationships described in section 2, no such unanimity of expression is found with regard to the equations relating $\overline{G}$ to measurable parameters. Nevertheless, as will be

shown here, the lack of unanimity is probably rather superficial and refers more to the appearance of the equations used than to their contents. In order to explain these differences it is useful to consider first a completely formal approach, which may then be adapted to specific systems of increasing complexity.

The partial molar free energy of a component of a system depends on the pressure, temperature, position in force fields and the concentration (e.g. mole fraction, molarity) of all components. Thus one may put formally:

$$d\overline{G}_i = (\frac{\delta \overline{G}_i}{\delta P})_{T,X,c} \; dP + (\frac{\delta \overline{G}_i}{\delta T})_{P,X,c} \; dT + \Sigma \; (\frac{\delta \overline{G}_i}{\delta X})_{P,T,c} \; dX + \Sigma \; (\frac{\delta \overline{G}_i}{\delta c_k})_{P,T,X,c_j} \; dc_k$$

(3.1)

It should be noted that equation (3.1) has much in common with equation (2.10), P, T, X and c being the variables. Nevertheless there is a difference in the meaning of the variables P and X employed here, in comparison to those mentioned in equation (2.10). In this case the value of $\overline{G}_i$ may be considered in all parts of a system, and accordingly the local values of P and X are to be used. In equation (2.10) the system is considered as a whole, and P and X refer necessarily to the ones acting on the system.

Thus for the calculation of G of the water in a beaker one employs the external pressure (e.g. atmospheric) and the position of the beaker in the gravitation field. In calculating the value of $\overline{G}_{H_2O}$ one may choose any location to perform this calculation, and should accordingly use the (varying) hydrostatic pressure with the corresponding height in the gravitation field. Naturally this will give a constant value of $\overline{G}_{H_2O}$ in case of equilibrium, notwithstanding the pressure and position terms vary throughout the beaker.

Also the partial derivative with respect to the total number of moles in the system must in this case be replaced by a differentiation with respect to a concentration variable (e.g. mole fraction). Furthermore it is pointed out that G_i must be differentiated with respect to the concentration of all components, including c_i , as is indicated by the use of c_k , k thus varying from a .... z. During each differentiation all concentrations, other than the one with respect to which is differentiated, are kept constant, as is indicated by the subscript c_j .

Equation (3.1) may be applied to simple systems without any difficulty. For example the partial molar free energy of a solute, s, in an ideal solution is determined by the pressure, temperature and concentration c_s , of the solute. In this case P, T and c_s are constant throughout the solution. Thus one may put:

$$d\overline{G}_s = (\frac{\delta \overline{G}_s}{\delta P})_{T,c_s} \; dP + (\frac{\delta \overline{G}_s}{\delta T})_{P,c_s} \; dT + (\frac{\delta \overline{G}_s}{\delta c_s})_{P,T} \; dc_s$$

(3.2)

The first two terms may be transformed by changing the following order of differentiation, according to:

$$(\frac{\delta \overline{G}_s}{\delta P})_{T,c_s} = (\frac{\delta (\frac{\delta G}{\delta n_s})_{P,T}}{\delta P})_{T,c_s} = (\frac{\delta (\frac{\delta G}{\delta P})_{T,c_s}}{\delta n_s})_{P,T} = (\frac{\delta V}{\delta n_s})_{P,T} = \overline{V}_s$$

and similarly:

$$(\frac{\delta \overline{G}_s}{\delta T})_{P,c_s} = -\overline{S}_s$$

in which $\overline{V}_s$ and $\overline{S}_s$ are the partial molar volume and entropy, respectively. Since for ideal solutions

$$(\frac{\delta \overline{G}_s}{\delta c_s})_{P,T} \ dc_s = RT \ d \ln c_s \ ,$$

equation (3.2) becomes:

$$d\overline{G}_s = \overline{V}_s \ dP - \overline{S}_s \ dT + RT \ d \ln c_s \qquad (3.3)$$

At a given P and T this becomes:

$$d\overline{G}_{s_{P,T}} = RT \ d \ln c_s \ ,$$

or

$$\overline{G}_{s_{P,T}} = RT \ln c_s + \text{constant} \qquad (3.4)$$

If one puts now $\overline{G}_{s_{P,T}}(c_s = 1) = \overline{G}_s^{\,\circ}$

(standard value of $\overline{G}_s$ at the given P and T), then:

$$\overline{G}_s = \overline{G}_s^{\,\circ} + RT \ln c_s \ . \qquad (3.5)$$

This equation is often used in the form:

$$\mu_s = \mu_s^{\,\circ} + RT \ln c_s \qquad (3.6)$$

(with c_s in mol/liter), in which

$$\mu_s = (\frac{\delta G}{\delta n_s})_{P,T}$$

is given the name chemical potential. For non ideal systems

$$(\frac{\delta \overline{G}_s}{\delta c_s})_{P,T} \ dc_s$$

is no longer equal to RT d ln c_s , because of interaction of the solute with the solvent, and if present, with other solutes. In that case a term must be maintained to cover the effect of the concentration of all components (cf. the summation term in equation 3.1). Since $\overline{G}_s$ is in general mainly determined by c_s , and only secundarily by other concentration terms (because of interaction) it is formally possible to separate the summation term in two other terms, viz.

$$\Sigma (\frac{\delta \overline{G}_s}{\delta c_k})_{P,T,c_j} \ dc_k = (\frac{\delta \overline{G}_s}{\delta c_s})_{P,T,c_j} \ dc_s \ (\text{ideal}) + d\overline{G}_{s_{P,T}} \ (\text{inter.})$$

in which the last term signifies the effect of the interaction between solute s and other components, thus covering in effect all that is left of the summation term of equation (3.1) after

$$(\frac{\delta \overline{G}_s}{\delta c_s})_{P,T,c_j} \ dc_s$$

has been taken out. This term can then be expressed as

$$d\overline{G}_{s_{P,T}} \text{ (inter.)} = RT \, d \ln \gamma_s \, ,$$

with γ_s = activity coefficient of the solute. Defining now $a_s = \gamma_s \cdot c_s$, one finds for non-ideal solutions:

$$d\overline{G}_{s_{P,T}} = RT \, d \ln \gamma_s c_s = RT \, d \ln a_s$$

Putting now $\overline{G}_{s_{P,T}} (a_s = 1) = \overline{G}_s^{\circ}$, equation (3.5) is transformed into

$$\overline{G}_s = \overline{G}_s^{\circ} + RT \ln a_s \qquad (3.7)$$

or

$$\mu_s = \mu_s^{\circ} + RT \ln a_s \qquad (3.8)$$

According to the foregoing the chemical potential, μ_s, thus equals the partial molar free energy in systems where P, T and the concentrations (activities) are the only variables of concern. In solution chemistry this is usually the case, which accounts for the extensive use of equation (3.8). For these systems the equilibrium condition is then:

$$\mu_s = \text{constant} \qquad (3.9)$$

For all other systems (i.e. systems in which P, T, c *and* X are of concern) one should employ the original condition, i.e.

$$\overline{G}_s = \text{constant} \qquad (3.10)$$

in which $\overline{G}_s \neq \mu_s$.

One could consider extending the meaning of μ to cover all effects, although in chemical thermodynamics generally no mention is made of the X terms of equation (2.10). Thus GLASSTONE (in Thermodynamics for Chemists, p. 242), discussing the presence of surface effects, introduces

$$\mu_i = (\frac{\delta \overline{G}}{\delta n_i})_{P,T,O} \, ,$$

the subscript O signifying constant surface area. On the other hand in electrochemistry, where a term $zF\psi$ appears if $\overline{G}_i$ of charged components is considered, the chemical potential μ_i is usually replaced by

$$\overline{\mu}_i = (\frac{\delta G}{\delta n_i})_{P,T,\psi} \, ,$$

the electrochemical potential. To avoid confusion it would seem advisable to avoid the name "chemical potential" for $\overline{G}_i$ in systems where force fields are of concern, as e.g. in soil moisture. There "partial molar (or specific) free energy" should be preferred, or if this name is too long for practical use, "thermodynamic potential" (in cal or erg per mole) or "moisture potential" (in erg per gram) could be considered.

The expression for $\overline{G}_s$ as a function of P, T, c and X will then be:

$$d\overline{G}_s = \overline{V}_s \, dP - \overline{S}_s \, dT + \Sigma \, \overline{Y}_s \, dX + \sum_i (\frac{\delta \overline{G}_s}{\delta c_i})_{P,T,X,c_j} \, dc_i \qquad (3.11)$$

in which $\overline{Y}_s$ stands for $(\frac{\delta Y}{\delta n_s})_{P,T,c}$.

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Departing from equation (3.11) one may attempt to define the variables that determine $\overline{G}_{H_2O}$. Listing all factors which may be of concern as follows: temperature, pressure, concentration of solutes, moisture content, surface free energy, adsorption forces, gravity field (and in special cases centrifugal field) one should select a particular set of variables which covers the effects of all factors listed, without omissions or duplications.

In fact different possibilities exist with regard to the selection of the set of variables to be used, depending on the manner in wich the system is described (cf. Takagi in ref. 14). Thus one may choose to regard the soil-water-air system as a three phase system, of which only the phase "water" is considered.

Alternatively it is also possible to disregard the heterogeneity and treat the system as one single phase, containing at least two components, viz. water and "solid". Both the "three phase" and the "single phase" approach may then be divided into a "macro" or "micro" approach. Each of these four possibilities requires different variables to describe the partial molar free energy of water in a consistent manner. Naturally, all four methods should eventually lead to identical results if the correct expressions are used. As will be shown, none of the four methods is entirely satisfactory from a practical point of view, i.e. generally it is not possible to obtain a set of completely independent, practically determinable parameters to describe the system. Again this does not imply that the resulting equation is incorrect, but only that practical application is not always possible.

Treating the different approaches mentioned separately the following may be said.

a_1. *Macro approach, considering water as one phase of the three phase system soil-water-air.*

In this case the water phase is considered as a system by itself, being a body of water with a definite surface, which separates the phase from the other phases. The solid phase particles are not included in this phase, and consequently the liquid phase is considered to be an electrolyte solution, i.e. water with dissolved solutes. The variables determining the partial molar free energy of water in such a system are P_e (the external pressure on the system), T, the concentration of solutes, the position of the system in the gravitational field, the surface energy terms and the adsorption forces extending from the solid phase. Thus the appropriate equation for this case reads:

$$dG = \overline{V}dP_e + (\frac{\delta\overline{G}}{\delta T})_{P_e, \omega, h, \overline{O}, a} dT + d\omega + Mgdh + \sigma d\overline{O} + da \quad (4.1)$$

in which $d\omega$ signifies the osmotic effect of the solutes, $\sigma =$ surface tension of water against air, $\overline{O} =$ surface area of the air-water interface per mole of water and $a =$ energy of adsorption of the water by the solid. It should be stressed that here P_e and h refer to the system (i.e. the phase water) as a whole. The three last terms of (4.1) correspond to the $\Sigma\overline{Y}dX$ term of equation (3.11).

a_2. *Micro approach*

Since the partial molar free energy of the water is constant throughout the

water phase it is advantageous to express $\overline{G}$ at a conveniently chosen location as a function of local parameters. This allows one to obtain detailed information on the values of certain parameters at different locations. With this approach one selects a "test body" of water, if possible situated in such a manner that it lies outside the region of influence of all interfaces. The variables of concern are now T, P (the local pressure), ω and h. Although it is always possible to stay outside the interface water-air it may not always be possible to select a body completely outside the range of interaction forces of the solid phase. In that case a term $d\alpha$ must be included. The result of this approach is then:

$$d\overline{G} = \overline{V}dP - \overline{S}dT + d\omega + Mgdh + d\alpha \qquad (4.2)$$

The obvious difference between (4.1) and (4.2) is that now P contains P_e *and* the local increment of pressure, p, according to $P = P_e + p$. Thus in effect the term $d\overline{O}$ has been incorporated in $\overline{V}dP$. In this case the last two terms are regarded as $\overline{Y}dX$ terms conform equation (3.11).

b_1. *Macro approach, considering the soil-water-air system as one, homogeneous system*

Although this approach is less straightforward than a_1 it deserves attention, because it allows one to introduce the moisture content as a variable (cf. ref. 1, 2, 15). The variables to be considered are then P_e (as in a_1), T, h, solute concentration, Θ (moisture content, e.g. the weight fraction of water in the "homogeneous" system) and a geometry factor. The latter will be indicated with χ , without further specification (e.g. pore size distribution) and must be included, because at constant P_e , T, h, solute concentration and Θ the partial molar free energy is influenced by rearrangement of solids and water. (In fact this last statement is inconsistent with the very acceptance of the one-phase system). The corresponding equation would read:

$$d\overline{G} = \overline{V}dP_e + \left(\frac{\delta\overline{G}}{\delta T}\right)_{P_e,\chi,\Theta,\omega} dT + \left(\frac{\delta\overline{G}}{\delta\Theta}\right)_{P_e,T,\chi,\omega} d\Theta + \left(\frac{\delta\overline{G}}{\delta\chi}\right)_{P_e,T,\chi,\omega,\Theta} d\chi$$
$$+ d\omega + Mgdh \qquad (4.3)$$

Although superficially acceptable, closer consideration indicates that this equation is not generally applicable. Thus a change in Θ will change the concentration of solutes, comprising both the free salts and the adsorbed ions. It would seem advisable, therefore, to split the osmotic term according to:

$$d\omega = d\omega_o + d\omega_a ,$$

ω_o referring to the free salts, ω_a to the contribution of the adsorbed ions. Since the change in ω_a at constant salt concentration of a freely swelling clay paste, caused by a change in Θ , is covered fully by the effect of Θ on $\overline{G}$, one is forced to omit the $d\omega_a$ term if $\left(\frac{\delta\overline{G}}{\delta\Theta}\right) d\Theta$ is maintained, in order to avoid counting the same effect twice. Replacing (4.3) by:

$$d\overline{G} = \overline{V}dP_e + \left(\frac{\delta\overline{G}}{\delta T}\right)_{P_e,\chi,\Theta,\omega_o} dT + \left(\frac{\delta\overline{G}}{\delta\Theta}\right)_{P_e,T,\chi,\omega_o} d\Theta + \left(\frac{\delta\overline{G}}{\delta\chi}\right)_{P_e,T,\Theta,\omega_o} d\chi$$
$$+ d\omega_o + Mgdh \qquad (4.4)$$

remedies this partly. Nevertheless (4.4) is not entirely satisfactory either, because a change in the salt concentration at constant Θ will also affect $d\omega$ (cf. ref. 4) which indicates that, although $d\omega_a$ is covered in part by the Θ term, there are some additional effects on the $d\omega_a$ term which are not covered by the Θ term.

One could formally adjust $d\omega_0$ to cover both the direct osmotic effect of the added salts, and the secundary effect on $d\omega_a$ which is not taken care of by the Θ term. This would then imply that $d\omega_0 \simeq - \overline{V}d\pi + d\omega_0'$ in which $- \overline{V}d\pi$ signifies the "ordinary" salt effect, and $d\omega_0'$ is the secondary effect on $d\omega_a$. It is obvious that this makes general application of equation (4.4) impossible.

It is important to note that the temperature term of equation (4.4) is not the same as in equation (4.2), because different parameters are kept constant during the differentiation of $\overline{G}$ with respect to T. In equation (4.2) the soil water is considered to be an electrolyte solution constituting one phase of the three phase system. Accordingly the differential $(\frac{\delta \overline{G}}{\delta T})_{P_e, \omega, a, h}$ equals $-\overline{S}_{H_2O}$, i.e. the entropy of the water component in an electrolyte solution. In principle the value of $\overline{S}_{H_2O}$ may be found from standard tables, and equals $\overline{S}_{H_2O}^o$, the standard entropy of pure water with a (small) correction for the effect of the difference in pressure between soil moisture and water under atmospheric pressure, and a correction for the presence of ionic constituents.

In equation (4.4) the soil water is considered as a component in the "one phase" water-solid system. That the term $(\frac{\delta \overline{G}}{\delta T})_{P_e, \Theta, \chi, \omega_o, h}$ does not equal $-\overline{S}_{H_2O}$ as defined above is obvious, if one realizes that upon a change of T at constant Θ as least the pressure P of equation (4.2) changes. This would give in first approximation (neglecting the influence of T on ω, h, a),

$$(\frac{\delta \overline{G}}{\delta T})_{P_e, \Theta, \chi, \omega_o, h} = (\frac{\delta \overline{G}}{\delta T})_{P, \omega, a, h,} + \overline{V}(\frac{\delta P}{\delta T})_{P_e, \Theta, \chi, \omega_o, h} \qquad (4.5)$$

indicating that $(\frac{\delta \overline{G}}{\delta T})$ of equation (4.4) contains at least a term $\overline{V}(\frac{\delta P}{\delta T})$ in addition to $-\overline{S}_{H_2O}$ as employed in equation (4.2). One could, of course, consider defining a variable $\overline{S}'_{H_2O}$ equal to $(\frac{\delta \overline{G}}{\delta T})_{P_e, \Theta, \chi, \omega_o, h}$ but it seems doubtful whether this "entropy" of soil moisture considered as a component of the hypothetical one phase system has any physical meaning. It would seem more straight-forward to maintain $(\frac{\delta \overline{G}}{\delta T})_{P_e, \Theta, \chi, \omega_o, h}$ as such, indicating that the value of this parameter may be obtained by adding at least a $\overline{V}(\frac{\delta P}{\delta T})_{P_e, \Theta, \chi, \omega_o, h}$ term to the entropy of soil water.
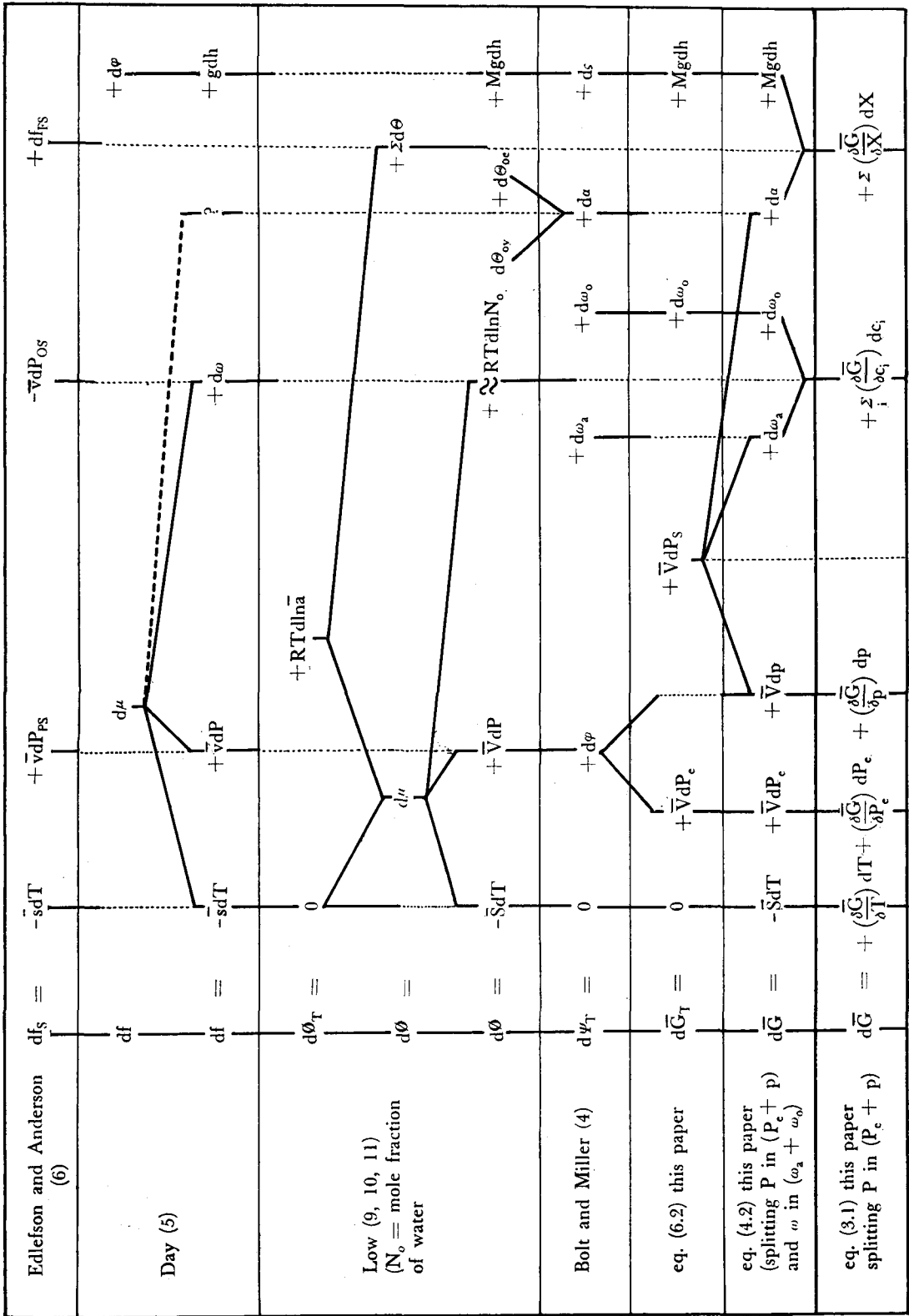
b_2. *Micro approach*

Consistent with a_2 it may be attempted to limit oneself to the consideration of micro-regions, introducing the local values of the parameters in stead of the values pertaining to the entire soil-water system. P_e would then signify

the local value of the external pressure; otherwise the equation is identical with (4.4). The ambiguity of the approach b is now clearly demonstrated. Considering a soil column with a fixed water table, the equilibrium condition implies that the variation of the Mgdh term in the capillary zone must be balanced by a change in the sum of all other terms listed in equation (4.4). In the unsaturated portion of the capillary zone this variation is obviously taken care of by the $(\frac{\delta \overline{G}}{\delta \Theta})d\Theta$ term if the soil is incompressible (i.e. has a constant pore size distribution) and by the sum of $(\frac{\delta \overline{G}}{\delta \Theta})d\Theta$ and $(\frac{\delta \overline{G}}{\delta \chi})d\chi$ if the soil is compressible (i.e. has a pore size distribution which varies with depth). Obviously the dP_e term must be taken equal to zero in this case, indicating that P_e is considered to be constant throughout the unsaturated capillary zone. If also a saturated region exists in the capillary zone ,this procedure does not work. Then $d\Theta$ equals zero, and if the soil is incompressible $d\chi$ is also zero. Thus Mgdh may not be balanced by the Θ and χ terms, and one is forced to introduce a variation in P_e to obtain a constant value of $\overline{G}$ in the soil column. Such a change of P_e could be interpreted as the result of the increasing value of the "reaction" pressure of the capillary walls on the water present in the capillaries. Of course this gives the correct result, because this "reaction" pressure necessarily equals the pressure in the water (as employed in the approach a_2), and accordingly $\overline{V}dP$ of equation (4.2). The inconsistency is, however, that also in the unsaturated portion of the capillary zone such a "reaction" pressure of the capillary wall is present (again equal to the "water" pressure P of equation (4.2), but there one is forced to put $dP_e = 0$, because of the variation of the Θ and χ terms. Thus the extension of the approach b into saturated soils makes it necessary to define P_e in a manner which differs from the definition employed in the unsaturated portion. The reason for this ambiguity is obvious: the energy level of soil moisture is a direct function of the local pressure in the water, whereas the moisture content is a derived quantity. For a given pore size distribution (i.e. constant value of χ) and constant salt concentration, Θ is a single valued function of p, or $P - P_e$ (the "pF-moisture content" curve) and the energy level may be expressed satisfactorily as a function of Θ, provided the slope of the curve relating p and Θ is finite. In the saturated region of the capillary zone this slope is infinite (below the air-entry value the moisture content is constant). Thus the use of Θ (and χ) as variables is limited to unsaturated regions. In the saturated region one is thus forced to invent another variable, which then must be P_e . The ensuing identification of P_e with P (= p + P_e) of approach a_2 remains inconsistent with the procedure employed for the unsaturated soil. Obviously extreme care must be used in employing the approach b.

5 COMPARISON WITH EXISTING LITERATURE

In table 1 the equations employed by different authors (1, 4, 5, 6, 9, 10, 11, 15) are listed in a comparative manner. In the center of the table the "parent" equation (3.1) is given, and next to it on both sides are the equations (4.2) (approach a_2) and (4.4) (approach b_1 and b_2). Obviously the approach a has been used by most authors, although the equations differ in notation.

Apparently some confusion has arisen between a_1 and a_2. Thus W. GARDNER et al. (7),

Comparison of thermodynamic expressions (rotated table/diagram):

Edlefson and Anderson (6):
$$df_S = -\bar{s}\,dT + \bar{v}\,dP_{PS} - \bar{v}\,dP_{OS} + df_{FS} + d\varphi$$

Day (5):
$$df = -\bar{s}\,dT + \bar{v}\,dP + d\mu + gdh$$
$$df = \cdots$$

Low (9, 10, 11) (N_o = mole fraction of water):
$$d\phi_T = 0 + RT\,d\ln\bar{a} + \Sigma\,d\theta$$
$$d\phi = -\bar{S}\,dT + d\mu + \bar{V}\,dP + \gtrsim RT\,d\ln N_o$$
$$d\phi = 0 + \bar{V}\,dP + d\varphi$$

Bolt and Miller (4):
$$d\psi_T = 0 + \bar{V}\,dP_e + \bar{V}\,dP_S + d\varphi + d\omega_a + d\omega_o + d\alpha \quad (d\theta_{ov},\ d\theta_{oe}) + d\varsigma$$

eq. (6.2) this paper:
$$d\bar{G}_T = -\bar{S}\,dT + \bar{V}\,dP_e + \bar{V}\,dp + d\omega_o + d\alpha + Mgdh$$

eq. (4.2) this paper (splitting P in $(P_e + p)$ and ω in $(\omega_a + \omega_o)$):
$$d\bar{G} = -\bar{S}\,dT + \bar{V}\,dP_e + \bar{V}\,dp + d\omega_a + d\omega_o + d\alpha + Mgdh$$

eq. (3.1) this paper splitting P in $(P_e + p)$:
$$d\bar{G} = +\left(\frac{\delta\bar{G}}{\delta T}\right)dT + \left(\frac{\delta\bar{G}}{\delta P_e}\right)dP_e + \left(\frac{\delta\bar{G}}{\delta p}\right)dp + \sum_i\left(\frac{\delta\bar{G}}{\delta c_i}\right)dc_i + \sum\left(\frac{\delta\bar{G}}{\delta X}\right)dX$$

Table 1

eq. (3.1) this paper splitting P in $(P_e + p)$

$$d\bar{G} = +\left(\frac{\delta\bar{G}}{\delta T}\right)dT + \left(\frac{\bar{G}}{\delta P_e}\right)dP_e + \left(\frac{\delta\bar{G}}{\delta p}\right)dp + \left(\frac{\delta\bar{G}}{\delta\Theta}\right)d\Theta + \left(\frac{\delta\bar{G}}{\delta x}\right)dx + \Sigma_i\left(\frac{\delta\bar{G}}{\delta c_i}\right)dc_i + \Sigma\left(\frac{\delta\bar{G}}{\delta X}\right)dX + Mgdh$$

eq. (4.4) this paper

$$d\bar{G} = +\left(\frac{\delta\bar{G}}{\delta T}\right)dT + \bar{V}dP_e + \left(\frac{\delta\bar{G}}{\delta\Theta}\right)d\Theta + d\omega_o + Mgdh$$

Babcock and Overstreet (1)

$$d\bar{F} = -\bar{S}dT + \bar{V}dP_e + \left(\frac{\delta\bar{F}}{\delta\Theta}\right)d\Theta + \quad d\mu \quad + d\omega_o + d\emptyset$$

Taylor (15)

$$d\mu_\omega = +\left(\frac{\delta\mu_\omega}{\delta T}\right)dT + \left(\frac{\delta\mu_\omega}{\delta P_e}\right)dP_e + \left(\frac{\delta\mu_\omega}{\delta\Theta}\right)d\Theta + \ ? \ + 0 + (+Mgdh?)$$

$$d\mu_{\omega T} = +RTdlna_\omega \qquad 0 \qquad +0$$

A comparison of the equations used by various authors to express the partial molar free energy of soil water as a function of system parameters.

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discussing $\overline{G}_{H_2O}$ in spherical raindrops suggest that a dilemma exists with regard to the necessity of counting a $\sigma d\overline{O}$ or a $\overline{V}dP$ term, or even both. Obviously these authors have used parameters belonging to two different types of approach, and when suggesting to combine the two are counting double. Naturally the change of dP in the drop is caused by the effect of surface tension, and either $\sigma d\overline{O}$ or $\overline{V}dP$ should be counted.

On the other hand BABCOCK and OVERSTREET (1, 2) and TAYLOR (15) apparently used an approach comparable to b, although not explicitly mentioned. The reason forwarded by B. and O. for using P_e and Θ as variables is that in thermodynamics only external, independent variables should be used. This is acceptable, although the author's inference that the equations of type a used by other authors are less complete than their own can be turned around to the effect that B. and O.'s equation in fact covers less than the other equations. This follows from section 4 where it was pointed out that the geometry of the system (χ term) should be maintained as a variable once Θ is adopted.

This change in pore size distribution is presumably the effect hinted at by SCHOFIELD, as quoted by B. and O. (3), when stating that the "pressure" in a soil column may vary from the top on down, invalidating Buckingham's equation. Such a change in intergranular pressure of the solid phase will affect the pore size distribution, leading occasionally to a decrease in moisture content with increase in depth (as is found in the engineering literature).

According to the foregoing discussion in b_1, B. and O.'s term equivalent to to $(\dfrac{\delta G}{\delta T})_{P_e, \Theta, \omega_o}$ does not equal $-\overline{S}_{H_2O}$. Although it is not clear from B. and O.'s equation whether $d\omega_a$ was meant to be included in the Θ term or in their "osmotic" term, it was shown above that neither choice is entirely satisfactory. The ambiguity of P_e, elaborated upon before, was apparently felt by B. and O. when discussing the water in a saturated zone (3). They then introduce P_e as a varying external pressure, not mentioning that this is inconsistent with the adoption of a constant value in the unsaturated region. Actually they suggest then that P_e may also vary in the unsaturated zone, without specifying how it would change.

If they had in mind to vary it in a manner consistent with the suggested variation below the water table, they would overlap their own Θ term, and thus count the same effect twice. Obviously the introduction of a χ term in the unsaturated zone would solve their difficulties, although the result would remain inconsistent with the procedure employed in the saturated zone.

The supposedly novel consequence of their theory for the capillary ascent of soil moisture is clearly non-existent, and is the result of the ambiguity of their choice of parameters.

The approach used initially by Low (9, 10, 11) seems consistent with equation (4.2). In a subsequent paper (12) Low apparently switches over to approach b without warning. Developing a method to determine the "entropy of soil moisture" (which in accordance with his previous papers should have been $(\dfrac{\delta \overline{G}}{\delta T})_{P, \omega, a, h}$). Low suggests that the change in swelling pressure with temperature be measured at constant value of Θ and P_e. The swelling pressure being a direct measure of $\overline{G} - \overline{G}^\circ$ (at least in salt free systems) this amounts to the determination of $(\dfrac{\delta \overline{G}}{\delta T})_{P_e, \Theta, \chi, \omega_o, h}$. In other words the "entropy"

determined by Low is the $\overline{S}'_{H_2O}$ discussed above, and not $\overline{S}_{H_2O}$ of his preceding papers.

The determination of $\overline{S}_{H_2O}$ from equation (4.2) does not involve any measurements. Considering for simplicity reasons a system in which the ω and a terms may be neglected, one finds :

$$\overline{G}_{T_1} = \overline{G}^o_{T_1} + \int_{P_e}^{P_e + p} \overline{V}_{T_1} \, dP \simeq \overline{G}^o_{T_1} + \overline{V}_{T_1} \, p$$

in which $\overline{G}^o_{T_1}$ is the molar free energy op pure water at pressure P_e (presumably atmospheric pressure), and p is now the "capillary" pressure (equivalent to the negative value of Low's "osmotic" pressure, π).

At a temperature T_2 one finds :

$$\overline{G}_{T_2} = \overline{G}^o_{T_2} + \overline{V}_{T_2} \, p.$$

Thus :

$$\frac{(\overline{G}_{T_2} - \overline{G}_{T_1})}{(T_2 - T_1)} = \frac{(\overline{G}^o_{T_2} - \overline{G}^o_{T_1})}{(T_2 - T_1)} + p \frac{(\overline{V}_{T_2} - \overline{V}_{T_1})}{(T_2 - T_1)}$$

or :

$$-\overline{S}_{H_2O} = -\overline{S}^o_{H_2O} + p \left(\frac{\delta \overline{V}}{\delta T}\right)$$

and :

$$(\overline{S}_{H_2O} - \overline{S}^o_{H_2O}) = - p \left(\frac{\delta \overline{V}}{\delta T}\right) \tag{5.1}$$

According to equation (5.1) $\overline{S}_{H_2O}$ at given value of P is determined by the product of p and the temperature expansion coefficient. It is interesting to note that Low's equation is consistent with these considerations. According to equation (4.5) :

$$(\overline{S}'_{H_2O} - \overline{S}^o_{H_2O}) = \overline{S}_{H_2O} - \overline{V} \left(\frac{\delta P}{\delta T}\right)_{P_e, \Theta, \chi, \omega_o, h} - \overline{S}^o_{H_2O}$$

(cf. equation 4.5)

$$= - p \left(\frac{\delta \overline{V}}{\delta T}\right) - \overline{V} \left(\frac{\delta p}{\delta T}\right)_{P_e, \Theta, \chi, \omega_o, h} \tag{5.2}$$

(cf. equation 5.1). This is identical with Low's equation (10) in which p has been replaced by $-\pi$. In other words Low's procedure does not lead to the determination of the entropy of soil water as it is usually defined, but is a direct measure of the effect of T on the P term of equation (4.2), which effect must be added to the known entropy of soil water in order to obtain the change of $\overline{G}$ with T at constant moisture content. As will be pointed out in section 7 these arguments have a significant bearing on the treatment of the freezing point depression of soil moisture.

A further subdivision of the adsorption term, da, as introduced by Low, BOLT and MILLER, or of the Θ term (BABCOCK and OVERSTREETJ is mainly of academic interest. The equations proposed (so-called extra-thermodynamic equations) serve to provide a better understanding of the forces that influence the adsorption of water by soil. On the other hand the constants involved in a van der Waals adsorption equation, and apparently the equation describing the effect of H-bonds and even the equation for the adsorption of water in an electric field (cf. 2, 4 and 9), are not known with sufficient certainty to

allow a calculation of the α term for practical systems. On the other hand, as will be shown in section 6 the approach a_2 makes it possible to avoid the α term entirely (i.e. by selecting a micro region outside its range of influence) at least in fairly moist soils.

The suggestion forwarded by Low (9) to combine all terms of equation (4.2) and to express the sum total by means of its antilog does not offer any new perspectives. Naturally the constancy of $\overline{G}$ (or its antilog) is used as equilibrium condition, but in order to establish whether equilibrium exists, $\overline{G}$ has to be broken down in measurable parts. The use of the antilog, then called (total) activity according to:

$$d\overline{G}_T = RT\ d \ln \overline{a}$$

or

$$(\overline{G}_T - \overline{G}_T^{\,o}) = RT \ln \overline{a}$$

in fact is rather impractical, because the variation of $\overline{a}$ in the range of interest in soil moisture studies is limited from 1.000 at $\overline{G} = \overline{G}^o$ to 0.9993 at $\dfrac{\overline{G} - \overline{G}^o}{\overline{V}}$ $= -1$ atm. and 0.993 at $\dfrac{\overline{G} - \overline{G}^o}{\overline{V}} = -10$ atm. Thus $\overline{a}$ is clearly no improvement

in comparison to the use of $\overline{G}$. Moreover the word "activity" has acquired a definite meaning in solution chemistry (covering only the effect of concentration and ionic (molecular) interaction in homogeneous systems) and the extension to the soil moisture system would undoubtedly lead to confusion.

TAYLOR (15) proposed a similar introduction of the activity of soil water (presumably not including the gravity effect) and then went even further by defining the activity coefficient of soil water. This activity coefficient equals a/Θ, in wich a = activity and Θ = moisture content. This is clearly an undesirable over-extension of the meaning of the activity coefficient as used in solution chemistry. The activity coefficient of soil water according to this definition would be *increasing* upon a decrease in moisture content, because Θ decreases much faster than $\overline{a}$ upon drying-out of the soil.

The water in a "normal" field soil would thus have an activity coefficient of about 3 at saturation (containing 30—40 % moisture). At a pF of 4 the activity coefficient would be 10, respectively 20 (assuming 10 %, respectively 5 % moisture at pF 4).

The equation used by DAY is presumably correct although force fields other than the gravitational field are not explicitly mentioned. Edlefson and Anderson's equations are consistent with approach a_2. On the other hand their treatment of the adsorption force is outdated, inasfar as the osmotic effect of the adsorbed ions, $d\omega_a$, is not mentioned.

Summarizing the situation with regard to the equations available it seems that most equations are formally correct, or could at least be interpreted in a correct manner. The equations based on approach b are missing the χ term, which in compressible soils should be present. On the other hand the approach b entails so many difficulties that it seems doubtful whether anything is gained by this approach. Nevertheless, also the equations based on approach a still contain parameters which are not independent under most experimental

conditions, thus rendering the application difficult in practice. As will be shown in section 6 some more practical equations may be obtained by suitable combinations of terms. The usefulness of such combinations is usually limited to certain specific systems, and accordingly the practical equations are not always generally applicable.

6 PRACTICAL APPLICATIONS

Since thermodynamic equilibrium implies thermal equilibrium, it is for most purposes satisfactory to consider the variation of $\overline{G}$ at constant temperature. For this case (approach a_2):

$$d\overline{G}_T = \overline{V}dP_e + \overline{V}dp + d\alpha + d\omega_a + d\omega_o + Mgdh \qquad (6.1)$$

Of this equation the first and last term are external to the system, and are usually accessible for direct measurement. The term $d\omega_o$ refers to the free salts in the system; a fair estimate of this term may be obtained from conductivity measurements in the soil solution (equilibrium dialyzate, or pressure filtrate). The remaining three terms, i.e. $\overline{V}dp$, $d\alpha$ and $d\omega_a$, together describe the influence of the solid phase on the partial molar free energy of soil water. These three cannot be measured separately, although the sum of all three is found from pressure membrane and/or tensiometer data.

At equilibrium $\overline{G}_T$ is the same in the soil water and in the water present in tensiometer or pressure membrane apparatus. Furthermore the gravity term and salt concentration are supposed to be equal in both systems (osmotic equilibrium should be established!). In the tensiometer the external pressures are also identical, and thus the sum of the three terms described is found as the gauge pressure in the tensiometerpot. In the pressure membrane apparatus the sum of the three terms plus $\overline{V}dP_e$ equals the pressure on the liquid phase collected, i.e. the barometric pressure. The sum of the three terms discussed is thus found from the difference between the applied gas pressure P_e (inside the apparatus) and the barometric pressure, i.e. $-\overline{V}(dP_e - dP_e^o)$.

Both practical and formal motives would thus favor the combination of the three terms into one. For historical (and perhaps practical) reasons this is usually done in the form of a "hypothetical" pressure, according to:

$$\overline{V}dp + d\alpha + d\omega_a = \overline{V}dP_S$$

in which P_S is thus the pressure equivalent of the three energy terms, the subscript s indicating that it is the effect of the solid phase on the water. The negative value of P_S equals the so called "Soil moisture tension".

Recently [3] a new term "Matric suction" has been proposed to cover $-P_S$.

It may be pointed out that "matrix" refers to the geometrical arrangement of the solid phase, whereas the term $d\omega_a$ is determined mainly by the structure of the ionic atmosphere on the soil particles, and only secondarily by the geometric arrangement. Strictly speaking solid (phase) suction should perhaps be preferred.

Introducing P_S in equation (6.1) one finds:

$$d\overline{G}_T = \overline{V}dP_e + \overline{V}dP_S + d\omega_o + Mgdh \qquad (6.2)$$

---

[3] T. J. MARSHALL proposed this in the interim report to the International Committee for Horticultural Congresses, March 1958.

This equation is very attractive, although much less detailed than (6.1). The four parameters are now reasonably independent. Thus one may change P_S, leaving P_c, h and ω_o constant. On the other hand it is practically impossible to change ω_o without changing P_S, at least when $d\omega_a$ is a sizable part of dP_S.

In the special case where the geometric arrangement of the solid phase is fixed (i.e. $(\frac{\delta \bar{G}}{\delta \chi})\,d\chi = 0$), and where the salt concentration is kept constant (or, alternatively, $d\omega_a$ does not contribute significantly to dP_S) one may assume that for a given temperature in unsaturated soils P_S is a single valued function of Θ (neglecting hysteresis phenomena). Now a_2 leads to approach b, with:

$$(\frac{\delta \bar{G}}{\delta P_s})\,dP_S = (\frac{\delta \bar{G}}{\delta \Theta})\,d\Theta$$

and thus:

$$d\bar{G}_{T,\omega_o,\Theta} = \bar{V}dP_c + (\frac{\delta \bar{G}}{\delta \Theta})\,d\Theta + Mgdh \qquad (6.3)$$

This is the equation proposed by BABCOCK and OVERSTREET, which may thus be classified as a practical equation valid only if T and χ are constant, if the soil is unsaturated, and if ω_o is constant or $d\omega_a$ is negligible. The factor $\frac{\delta \bar{G}}{\delta \Theta}$ then equals $\bar{V} (\frac{\delta P_s}{\delta \Theta}) = \mathrm{tg}\beta$ (the slope of the "Tension"-moisture content curve), such that:

$$d\bar{G}_{T,\omega_o,\chi} = \bar{V}dP_c + \mathrm{tg}\beta.d\Theta + Mgdh \qquad (6.4)$$

For soil systems which are not defined in detail with regard to the properties of the solid phase, equation (6.2) is the best choice. P_S must be determined experimentally, and a further division of this term, as used in equation (6.1) is mainly of academic interest. It serves to give a better understanding of the factors which make up P_S, and allows one to predict at least the direction of the effects introduced by the variation of the parameters employed, if these are not truly independent.

There are, however, some special systems, for which a further splitting of terms seems warranted. In the first place this concerns systems in which the solid phase consists of a fairly homogeneous, coarse grained material. Because of the small value of the specific surface area of such a material the terms da and $d\omega_a$ may be neglected, at least at moderately high moisture content. Thus $\bar{V}dP_S$ contains only the term $\bar{V}dp$, in which p is the pressure deficit caused by curved liquid menisci. For a fairly homogeneous material one may attempt to calculate the curvature of the menisci as a function of the moisture content, and one would find:

$$d\bar{G}_{T,P_c} = \bar{V}d\,\frac{2\sigma}{r}\cos\varphi + d\omega_o + Mgdh \qquad (6.5)$$

in which σ = surface tension, φ = wetting angle and r = mean radius of curvature of the menisci ($= f(\Theta)$). Thus $\bar{G}$ could be calculated as a function of Θ, or, conversely, the calculation could be checked against experimental data.

The second system of interest is a paste of peptized clay particles. If the intergranular pressure in the paste is zero (particles do not touch each other) negatively curved menisci cannot exist.

Aside from thermal equilibrium, thermodynamic equilibrium also implies mechanical equilibrium. Thus a negative value of p caused by curved menisci must be balanced by a "reaction" pressure of the walls of the capillary. If these are not rigid, as is the case in a fully swelling and shrinking clay paste, the capillary walls (i.c. the particles) will approach each other upon a decrease in moisture content. Thus dp (due to curved menisci) equals zero.

Although p varies inside the ionic atmosphere, this variation is locally balanced by increased concentrations of the adsorbed ions. As was pointed out before one may select any location in the system to determine $\overline{G}$. Selecting the air-water interface (or the symmetry plane between charged particles) one can easily prove that at that location dp depends solely on the curvature of the meniscus, and thus equals zero (4). Furthermore one can prove that, except at very low moisture content (when the water layer is only a few molecular layers thick), also dα equals zero at the chosen location. The problem is thus shifted towards finding the ionic concentration at this location. The latter may be calculated from the double layer theory as a function of the moisture content of the system, provided the specific surface area of the solid phase is known (4). One then finds for these systems:

$$d\overline{G}_{P_e,T} = (d\omega_a)_c + d\omega_o + Mgdh \qquad (6.6)$$

in which

$$(d\omega_a)_c + d\omega_o = (d\omega)_c = - \overline{V}d\pi_c.$$

The osmotic pressure at the chosen symmetry plane or interface, π_c, may then be expressed as a function of Θ, S (specific surface) and Σc_o (the concentration of solutes in the equilibrium dialyzate).

7 DETERMINATION OF THE PARTIAL MOLAR FREE ENERGY OF SOIL WATER

As was already described in section 6, $\overline{G}_T$ may be expressed by means of the working equation (6.2). Evaluation of the variables P_e, P_S (by means of tensiometer, pressure membrane and possibly calibrated Bouyoucos blocs), ω_o and h will thus give $\overline{G}$ at the temperature employed. The calculation of $\overline{G}$ at any other temperature formally involves only the addition of a term $\int_{T_o}^{T} -\overline{S}dT$. This is in practice of little help, because the actual change of $\overline{G}$ with temperature depends on the choice made with regard to the constancy of the parameters used. Since the only practical approach is to consider the change of G with temperature at constant values of P_e, Θ and ω_o, one must conclude that $(\frac{\delta\overline{G}}{\delta T})$ for such a situation usually does not equal $-\overline{S}_{H_2O}$.

A second extremely useful means of determining G is to measure the pressure of the water vapor. By the definition of equilibrium $\overline{G}$(vapor) = $\overline{G}$(liquid), and $\overline{G}$(vapor) is a rather simple function of the relative vapor pressure.

If the water vapor is regarded as an ideal gas one finds

$$d\overline{G}_T \text{ (vapor)} = \overline{v}dp_v = RT \; d \ln p_v \qquad (7.1)$$

in which $\overline{v} =$ molar volume of water vapor, $p_v =$ vapor pressure. By integration :

$$\overline{G}_T \text{ (vapor)} = \overline{G}_T^o \text{ (vapor)} + RT \ln p_v / p_v^o \qquad (7.2)$$

in which $\overline{G}_T^o$ is the partial molar free energy of free water at temperature T, and p_v^o is the saturated vapor pressure. If expressed in pF units equation (7.2) yields the well known SCHOFIELD equation, viz.

$$pF = 6.5 + \log (2 - \log p_r) \qquad (7.3)$$

in which $p_r = 100 \; p_v / p_v^o =$ relative vapor pressure in percent. If necessary the ideal gas equation may be replaced by a more accurate equation of state of water vapor.

The only reservation with regard to the use of the vapor pressure method is the extreme accuracy required to measure $\overline{G}$ in the range of 0 to -18.10^6 erg/mole (corresponding to P_S values from 0 to $- 1$ atm.)

A third method described in the literature to determine $\overline{G}$ is the measurement of the freezing point depression of soil moisture. The principle involved is the fact that $\overline{G}$ (liquid water) equals $\overline{G}$ (ice) at the freezing point. Obviously the first requirement is now to prove that $\overline{G}$ (ice) is easily found from experimental data. Although one may assume (at least for a moderate F.P.D.) that pure water freezes out, it is much harder to prove that the ice freezes out against atmospheric pressure. Assuming nevertheless that this is the case, $\overline{G}$ (ice) at the freezing point is found as:

$$\overline{G}_{T_f} \text{ (ice)} = \overline{G}_{T_o} \text{ (ice)} - \overline{S}\text{(ice)} (T_f - T_o) \qquad (7.4)$$

in which T_f indicates the temperature at the freezing point, and T_o is the temperature at the ice point (freezing at atmospheric pressure, i.e. 0 °C) and in which it is assumed that $\overline{S}$ (ice) is constant over the temperature range concerned. Now $\overline{G}_{T_f}$ (ice) $= \overline{G}_{T_f}$ (liquid water) and thus $\overline{G}$ of the soil moisture at the freezing point is found.

Next $\overline{G}$ (liquid water) at the ice point is calculated according to:

$$\overline{G}_{T_o} \text{ (liquid water)} = \overline{G}_{T_f} - \overline{S}\text{(liq.)} (T_o - T_f) \qquad (7.5)$$

Combination of (7.4) and (7.5) then gives:

$$\overline{G}_{T_o} \text{ (liquid water)} = \overline{G}_{T_o} \text{ (ice)} - \left\{ \overline{S}\text{(liq.)} - \overline{S}\text{(ice)} \right\} (T_o - T_f). \qquad (7.6)$$

Now $\overline{G}_{T_o}$ (ice) is the partial molar free energy of ice at 0 °C, which must equal the partial molar free energy of liquid water that just freezes at 0 °C, or in other words, the molar free energy of "free" water at 0 °C. Defining now $\triangle G_{T_o}$ (liquid water), that is the free energy depression of the soil moisture at 0 °C as:

$$\triangle \overline{G}_{T_o} \text{ (liq.)} = \overline{G}_{T_o} \text{ (liq.)} - \overline{G}_{T_o}^o = \overline{G}_{T_o} \text{ (liq.)} - \overline{G}_{T_o} \text{ (ice)}$$

in which $\overline{G}^{o}$ indicates the molar free energy of "free" water, one finds:

$$\triangle \overline{G}_{T_o} \text{ (liq.)} = - \left\{ \overline{S}\text{(liq.)} - \overline{S}\text{(ice)} \right\} \text{ (F.P.D.)} \qquad (7.7)$$

According to this relation the free energy depression of the soil moisture (at 0 °C) may be expressed as a function of the F.P.D.

The above considerations were extended by TAKAGI (14) who introduced actual equations of state to improve the accuracy of equation (7.7). The present authors have some severe objections to such an extension, because it suggests the possibility of obtaining high accuracy, whereas the assumptions underlying this treatment seem very week indeed.

Thus TAKAGI assumes:

a. That the ice freezes out as pure ice under atmospheric pressure, and consequently the corresponding value of the entropy of pure ice may be used.

b. That the change in $\overline{G}$ of the liquid phase with a change in temperature equals $\int \overline{S}^{o} \, dT$. As was pointed out before, there are no reasons to believe that the change of $\overline{G}$ (soil moisture) with T (at presumably constant values of P_e, Θ, ω_o) is covered by an $\overline{S}^{o} \, dT$ term, since $d\omega_a$ and dp would also change.

Finally a last complication arises because the value of $\overline{G}$ (soil moisture) at "field" temperature is sought. Only if $\overline{S}$ (soil moisture) equals $\overline{S}^{o}$ (entropy of free water) and if also the effect of temperature on $\overline{G}$ (soil moisture) is adequatly described by a term SdT, may one put:

$$\triangle \overline{G}_T = \overline{G}_T - \overline{G}_T^o \ (= \triangle \overline{G}_{T_o}^o \ - \int_{T_o}^{T} (\overline{S} - \overline{S}^o) \ dT) = \triangle \overline{G}_{T_o}$$

This leads to a third assumption hidden in Takagi's treatment, viz.

c. That even over the entire temperature range from 0 °C to field temperature, the change of $\overline{G}$ (soil moisture) with temperature at constant moisture content is covered adequatly by a term $\int \overline{S}^{o} \, dT$.

Only if the above three conditions are satisfied is an improvement of the existing equation (7.7) by means of equations of state, warranted. Till now little evidence is available to support such a treatment of F.P.D. data. On the contrary Low's procedure for determining $(\frac{\delta \overline{G}}{\delta T})_{P_e, \Theta, \chi, \omega_o, h}$ as commented on in sections 5 and 6 suggests that this differential is generally *not* equal to $\overline{S}_{H_2O}^o$.

According to the present authors it would be safest to dismiss the determination of the F.P.D. as a measure of the partial molar free energy of soil moisture until the effect of a temperature change on $\overline{G}$ (soil moisture) has been evaluated. For this purpose the simultaneous determination of the freezing point depression and the vapor pressure at several temperature values should be considered.

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