Movement of Water through Soil as Influenced by Osmotic Pressure and Temperature Gradients

J. Letey
The equation used to describe steady-state water flow through a soil in response to hydraulic pressure (or suction in unsaturated soil), osmotic pressure, and temperature gradients is \( J_w = L_{vw} \text{ grad } P + L_{vD} \text{ grad } \pi - L_{vv} \text{ grad } T. \) Published research results indicate that \( L_{vv} \) is relatively independent of suction when suctions are greater than about 0.06 bar, becomes quite small when suctions are lower than 0.06 bar, and increases in a predictable manner as the average temperature increases. A value of \( 3.0 \times 10^{-3} \text{ cm}^3\text{deg}^{-1}\text{hr}^{-1} \) is suggested for \( L_{vv} \) for estimates of water flow in response to temperature gradients. \( L_{vD} \) can be considered to be zero for suctions less than about 0.25 bar except under conditions of very high clay content. The value of \( L_{vD} \) is not likely to be greater than 10 per cent of \( L_{vv} \) (3 per cent is suggested for approximate calculations) at suctions between 0.25 and 1 bar. \( L_{vD} \) would more nearly equal \( L_{vv} \) at greater suctions, but no data are available on this relationship at higher suctions. The suggested values of \( L_{vv} \) and \( L_{vD} \) are based on relatively few data and are to be considered as approximate. Additional data are required for more specific values for these coefficients.

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INTRODUCTION

Darcy’s law has been used directly or combined with the continuity equation to produce equations to describe water flow through soils. In the use of these equations, it must be assumed that osmotic pressure or temperature gradients do not exist—or if such gradients do exist, their effects on water movement are negligible. Osmotic pressure and temperature gradients under many conditions, particularly irrigated arid lands, are readily recognized. The critical question then is whether or not these gradients significantly affect the flow of water through soil.

This paper presents equations for water flow which include the osmotic pressure gradient and the temperature gradient and reviews the information available on the effect of the osmotic pressure and temperature gradients on water flow through soil.

THEORY

The equations developed will be based upon the theory of thermodynamics of irreversible processes. Katchalsky and Curran (1965) will be used extensively.

If an adiabatic system is at equilibrium, the entropy will be maximum. Alteration of the variables so that the system is not at equilibrium means that the entropy is no longer maximum. The amount of change in entropy that results from modification of a variable from equilibrium is used as the measure of the tendency of the variable to change. If \( a_i \) is the variable, \( \delta S/\delta a_i \) is considered the force or affinity causing \( a_i \) to change and will be symbolized as \( X_i \). Also \( da_i/dt \) is considered the flux or flow of component \( a_i \) and will be symbolized as \( J \). (The theory applies to systems not far from equilibrium. The extent that a system can be removed from equilibrium before the theory becomes invalid must be experimentally determined for each system.)

The rate of entropy production within the system \( (\sigma = dS/dt) \) is related, therefore, to the summation of the products of the fluxes and forces and can be mathematically stated as:

\[
\sigma = \sum_i J_i X_i .
\]

The choice of fluxes and forces is somewhat arbitrary as long as two conditions are met: (1) The product of any flow and its conjugate force must have the dimensions of entropy production. (2) For a given system, the sum of the products must remain the same for any transformation of flows and forces. The choice of fluxes and forces will be more evident as we proceed.

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Another basic equation is the relationship between the flux—which we are generally interested in—and the forces:

\[ J_i = \sum_{k=1}^{n} L_{ik} X_k \, (i = 1, 2, \cdots n). \]

Katchalsky and Curran (1965) give two basic equations for the rate of entropy production:

(1) \[ \sigma = J_q \cdot \text{grad} \, 1/T + \sum J_i \cdot \text{grad} (-\mu_i/T) + J_{ch} A/T, \]

where \( J_q \) is the heat flux, \( \mu_i \) is the chemical potential of component \( i \), \( J_{ch} \) is the chemical reaction rate, and \( A \) is the affinity of a chemical reaction. Their other equation:

(2) \[ \sigma = (J_s/T) \cdot \text{grad} \, (-T) + \sum (J_i/T) \cdot \text{grad} (-\mu_i) + J_{ch} A/T, \]

where \( J_s \) is the flux of entropy.

It is convenient here to use the dissipation function \( \Phi = T \sigma \). Assuming no chemical reaction in the system,

(3) \[ \Phi = J_s \cdot \text{grad} \, (-T) + \sum J_i \cdot \text{grad} (-\mu_i), \]

where \( \Phi \) is in ergs cm^{-3} hr^{-1}, \( J_s \) is in ergs cm^{-2} hr^{-1} deg^{-1}, \( J_i \) is in gm cm^{-2} hr^{-1}, and \( \mu_i \) is in ergs gm^{-1}.

Any one of the three equations could be chosen as starting points for developing flow equations. I will use equation (3) because it leads to the simplest and most useful equation to describe water flow through soil.

The following development, which provides a transformation of forces and fluxes, was found to be helpful:

(4) \[ \text{grad} \, (\mu_w) = \bar{V}_w \, (\text{grad} \, P' - \text{grad} \, \pi') \]

where \( \bar{V}_w \) is the partial molar volume in cm^3 gm^{-1}, \( P' \) is the pressure in dynes cm^{-2}, \( \pi' \) is osmotic pressure in dynes cm^{-2}, and subscript \( w \) denotes water. It is assumed that \( P' \) and \( \pi' \) are the only factors affecting the chemical potential of water. (Gravity is not considered as part of \( \mu_w \) and will be incorporated into the equations later.)

(5) \[ \text{grad} \, (-\mu_s) = -\bar{V}_s \, \text{grad} \, P' - \text{grad} \, \pi' / \bar{c}_s, \]

where \( \bar{c}_s \) is the average concentration and subscript \( s \) denotes solute.

Substitution of (4) and (5) into (3) leads to:

(6) \[ \Phi = -J_S \cdot \text{grad} \, T + J_w \cdot [\bar{V}_w \, \text{grad} \, P' - \text{grad} \, \pi'] \]

\[ + J_s \cdot [\bar{V}_s \, \text{grad} \, P' - \text{grad} \, \pi' / \bar{c}_s]. \]

Gathering terms leads to:

(7) \[ -\Phi = J_S \cdot \text{grad} \, T + (J_w \bar{V}_w + J_s \bar{V}_s) \cdot \text{grad} \, P' + \]

\[ (J_s / \bar{c}_s - J_w \bar{V}_w) \cdot \text{grad} \, \pi'. \]

The total volume flux \( J_v \), is equal to the sum of fluxes of water and solute:
\[ J_s = J_w \overline{V}_w + J_s \overline{V}_s , \]

(note that dimensions of \( J_s \) are cm hr\(^{-1} \)) and

\[ J_s / \overline{c}_s - J_w \overline{V}_w \cong J_s / \overline{c}_s - J_w / \overline{c}_w = v_s - v_w = J_D \]

where \( v_s - v_w \) is the difference in velocity between the solute and water and is symbolized by \( J_D \). The subscript \( D \) is chosen to denote diffusion of solutes.

The original fluxes of \( J_w \) and \( J_s \) have been transformed into new fluxes \( J_v \) and \( J_D \).

Substitution of equations (8) and (9) into (7) gives:

\[ \Phi = -\overline{J}_s \cdot \text{grad} \ T + \overline{J}_v \cdot \text{grad} \ P' + \overline{J}_D \cdot \text{grad} \ \pi' . \]

The rate of entropy production was originally postulated to equal the sum of the products of the fluxes and forces. It is recognized in equation (10) that \( \overline{J}_s, \overline{J}_v, \) and \( \overline{J}_D \) represent the fluxes, and \( \text{grad} \ T, \text{grad} \ P', \) and \( \text{grad} \ \pi' \) represent the forces.

Using the relationship between fluxes and forces

\[ \sum_{k=1}^{n} L_{ik} X_k \ (i=1,2,3, \ldots n) \],

the following flux equations result:

\[ J_v = -L_v \overline{V}_v \text{grad} \ P + L_{vD} \text{grad} \ \pi - L_{vq} \text{grad} \ T , \]

\[ J_D = L_D \overline{V}_v \text{grad} \ P - L_{DD} \text{grad} \ \pi - L_{Dq} \text{grad} \ T , \]

\[ J_s = L_q \overline{V}_v \text{grad} \ P + L_{qD} \text{grad} \ \pi - L_{qq} \text{grad} \ T . \]

The equations were developed assuming horizontal flow. For vertical flow, the gravitational component must be added to pressure in the equations. For unsaturated soil conditions, the term suction will be used, rather than pressure.

The symbols \( P \) and \( \pi \) are used instead of \( P' \) and \( \pi' \), because the units in (11), (12), and (13) for these properties will be centimeters of water rather than dynes cm\(^{-2} \). Different units are used so that units of \( L_{eq} \) can be cm hr\(^{-1} \) rather than cm\(^3\) dyne\(^{-1}\) hr\(^{-1} \). Under uniform salt and temperature conditions, (11) reduces to an equation which is identical in form to the more familiar Darcy's law. The coefficient \( L_{vq} \) is equivalent to the hydraulic conductivity. Inasmuch as the hydraulic conductivity traditionally has been reported in units of length per unit time, it is desirable to give \( L_{eq} \) the same units.

This change in units creates one hazard. The Onsager reciprocal relation states that \( L_{ik} = L_{ki} \); for example, in our equations, \( L_{Dv} = L_{vd} \), or \( L_{qv} = L_{qv} \). Since the numerical value of \( P \) and \( \pi \) is \( 10^3 \) lower than \( P' \) and \( \pi' \), the numerical value of coefficients associated with \( P \) and \( \pi \) will be \( 10^3 \) greater than for \( P' \) and \( \pi' \). Since both \( L_{vd} \) and \( L_{Dv} \) will be \( 10^3 \) greater, they will still be equal and thus consistent with the Onsager reciprocal relation. However, \( L_{eq} \neq L_{qv} \) because \( L_{qv} \) would be \( 10^3 \) greater as a result of changing the units of \( P \). From a practical point of view, this should not create any great problems.

Although \( J_v \) represents the total volume of solution flux, hereafter it will be referred to loosely as water flux.
The coefficients $L_{ik}$ are, by nature, empirical. Nothing in the theory of thermodynamics of irreversible processes indicates the magnitude of these coefficients. They must either be measured or calculated from other theory. For example, $L_{vw}$ is equivalent to the familiar hydraulic conductivity. Traditionally, the hydraulic conductivity of a soil has been measured empirically. There are, however, theories which can be used to calculate the hydraulic conductivity based upon pore-size distributions. Experience has shown that the hydraulic conductivity is greatly dependent upon pore size. It is also recognized that the hydraulic conductivity depends upon temperature and salt content of the soil. Previous research has provided an understanding of factors which will influence the hydraulic conductivity. Research data on $L_{vD}$ and $L_{vq}$ are much more limited. It is the main task of this report to investigate factors that will influence the value of the latter two coefficients.

**EFFECT OF TEMPERATURE GRADIENT**

If we assume that the pressure and osmotic pressure are uniform throughout the soil, (11) reduces to $J_v = -L_{vq} \text{grad} \, T$. To determine the effect of temperature gradients on water flow, we need to know the magnitude of $L_{vq}$. It would also be helpful if the factors which influence the magnitude of $L_{vq}$ were understood.

Cary (1965) presented the following equation for the flow of water vapor through soil as affected by temperature gradient:

$$J_v = \frac{\beta p DH}{R^2 T^3} \text{grad} \, T,$$

(14)

where $p$ is vapor pressure, $D$ is the diffusion coefficient of water vapor, $H$ is the latent heat of vaporization, $\beta$ is a unitless factor, and $R$ is the gas constant. If we assume that the water flow through a soil in response to a temperature gradient is primarily in the vapor phase, we find that $L_{vq}$ is equal to the combination of terms preceding $\text{grad} \, T$ in equation (14). Although we can measure or calculate the values for most of the terms in (14), $\beta$ must be empirically measured. Equation (14) does not, therefore, allow us to calculate the magnitude of $L_{vq}$. However, it does indicate the factors that will influence the magnitude of $L_{vq}$. $p$, $D$, and $H$ are all temperature-dependent functions. One would expect, then, that $L_{vq}$ would be dependent upon the temperature of the system. The effect of temperature can be calculated:

$$L_{vq} = 7.065 \beta p \, DH / T^3.$$

(15)

The number 7.065 is the value of $1 / R^2$ and appropriate conversion factors so that $p$ is in millibars, $D$ in cm$^2$sec$^{-1}$ and $H$ in cal gm$^{-1}$. The relationship between $D$ and $T$ at atmospheric pressure is:

$$D = D_o (T/T_o)^{1.75},$$

(16)

where $T_o = 273^\circ K$ and $D_o = .22$ cm$^2$sec$^{-1}$. Equation (15) thus becomes

$$L_{vq} = .847 \times 10^{-4} \beta p H / T^{1.25}.$$

(17)

The values of $pH / T^{1.25}$ have been plotted as a function of temperature in figure 1. This value is observed to increase as the temperature increases. One would, therefore, expect $L_{vq}$ to increase as the temperature increases. If $L_{vq}$ is empirically
measured for a system at any given temperature, it can be corrected or adjusted to a different temperature by using the data plotted on figure 1—assuming that all temperature-induced water flow is in the vapor phase.

Data by Cary (1963, 1964) can be used to evaluate qualitatively equation (17). Cary measured the movement of water in response to a temperature gradient through a vapor gap. The value of $\beta$, when no soil occurs in the system, should equal 1. $L_{eq}$ can be calculated for these systems and compared to the measured value of $L_{eq}$. The results of one report by Cary (1963) show that $L_{eq}$ does indeed increase as the temperature increases. The observed value of $L_{eq}$, however, was consistently a little higher than the calculated value for $L_{eq}$. In a later report by Cary (1964) the observed and calculated values for $L_{eq}$ agreed closely. Based upon these data, (17) can be used with considerable confidence in predicting the effect of temperature gradient on water flow through soil, if the flow is primarily through the vapor phase. The main problem, however, is to evaluate properly the value for $\beta$. At this time, it appears that empirical measurements are necessary.

Equation (11) states that for conditions of uniform pressure and osmotic pressure, the water-flow rate is linearly related to the temperature gradient, and that the curve passes through the origin. Cary and Taylor (1962a, b) presented figures in which the water-flow rate was plotted as a function of temperature gradient for soils at various water contents and at various temperatures. Their curves go through the origin, but bend slightly upward as the temperature gradient increases. Their temperature gradient was increased by holding the lower temperature constant and increasing their higher temperature. Therefore, as their temperature gradient increased, the average temperature increased, also. As has been clearly demonstrated, the value of $L_{eq}$ should increase as the temperature increases. When Cary and Taylor’s data are corrected for the increased average temperature, the curves become approximately linear, thus providing evidence for the validity of (11) and demonstrating that $L_{eq}$ depends on the average tempera-
ture but not on the gradient of temperature. Their temperature gradients were up to 0.8°C cm⁻¹, thus providing confidence in the use of (11) for temperature gradients generally occurring in soils.

The data presented in table 1 were calculated from information obtained from the Weeks et al. (1968) study of the influence of temperature gradients on water flow. Note in table 1 that both a different suction and temperature occur for each calculation of $L_{eq}$. The value of $L_{eq}$ therefore was corrected to a common temperature of 22°C, using the curve presented as figure 1. With correction, the value of $L_{eq}$ seems to be relatively constant for all values of suction and water content reported in the table. One can conclude that $L_{eq}$ is not greatly dependent upon water content, at least within the range of that study. Since the suctions reported in table 1 are in the range ordinarily encountered in irrigated soils, the use of a constant value of $L_{eq}$ appears to be feasible.

Cary has conducted several studies on the movement of water through soils in response to temperature gradients. Those data from which $L_{eq}$ can be calculated will be reviewed here.

Cary (1965) showed that the water flux in response to a temperature gradient of 0.8°C per cm was relatively constant over the range of suctions from 65 to 470 cm of water. These data indicate that $L_{eq}$ is relatively constant over a wide range of suctions, which agrees with the data of Weeks et al. (1968). In fact, Cary's (1965) suction range extends into lower values than that reported by Weeks et al. (1968)—indicating that the constancy of $L_{eq}$ goes in the higher soil-water content ranges. This is noteworthy, because at the lower suctions, some of the water which flowed in response to a temperature gradient was in the liquid rather than vapor, phase. The average value of $L_{eq}$ from Cary's data (1965) is $5.20 \times 10^{-3}$ cm² deg⁻¹ hr⁻¹. These data were taken at 18°C. The value reported by Cary (1965), therefore, is about two and one half times larger than the data presented by Weeks et al. (1968).

Table 2 summarizes the considerable data of Cary and Taylor (1962a, b) on the effects of temperature gradient on water flow, at various suctions and temperatures. The suction range is from 30 to 540 cm of water. The temperatures are 18°C, 28°C, and 38°C. For each suction, a higher $L_{eq}$ results as the temperature increases, as indicated from previous discussion. The per cent increase in $L_{eq}$ at higher temperatures when the soil suction is relatively high is approximately that expected as based on the theoretical development already presented. However, as the suction gets to relatively low values, a larger temperature coefficient appears on $L_{eq}$ than

### Table 1

<table>
<thead>
<tr>
<th>Suction (bars)</th>
<th>Water content (cm/cm²)</th>
<th>Temp. (°C)</th>
<th>Temp. gradient (°C cm⁻¹)</th>
<th>$L_{eq}$ (cm² deg⁻¹ hr⁻¹)</th>
<th>$L_{eq}*$ (cm² deg⁻¹ hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.596</td>
<td>0.133</td>
<td>24</td>
<td>1.43</td>
<td>2.11</td>
<td>1.89</td>
</tr>
<tr>
<td>0.378</td>
<td>0.155</td>
<td>23</td>
<td>2.10</td>
<td>2.22</td>
<td>2.10</td>
</tr>
<tr>
<td>0.304</td>
<td>0.167</td>
<td>22</td>
<td>2.81</td>
<td>2.16</td>
<td>2.16</td>
</tr>
<tr>
<td>0.268</td>
<td>0.174</td>
<td>21</td>
<td>3.27</td>
<td>1.88</td>
<td>1.99</td>
</tr>
<tr>
<td>0.239</td>
<td>0.181</td>
<td>20</td>
<td>3.58</td>
<td>1.76</td>
<td>1.97</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>2.02</strong></td>
<td></td>
</tr>
</tbody>
</table>

* $L_{eq}$ numbers adjusted to 22°C using data from fig. 1.
at the higher suctions. The theoretical calculation for the temperature coefficient of $L_{eq}$ is based upon all the water flow being in the vapor phase. This is probably true for the higher suctions. However, at the low suctions, considerable amount of water is probably flowing in the liquid phase. The data in table 2 would suggest that the coefficient affecting water flow due to temperature gradients in the liquid phase is more temperature-dependent than in the vapor phase.

Now, considering constant temperature and the effect of suction on the value of $L_{eq}$, we find that $L_{eq}$ increases slightly as the suction decreases from 540 to 190. As the suction is reduced below 190, the value of $L_{eq}$ decreases rather rapidly and is relatively low for 30 cm of water suction.

The average value of $L_{eq}$ at the higher suctions is somewhat higher than the value reported by Weeks et al. (1968), but it is lower than the result reported by Cary (1965) in a different study.

Hanks et al. (1967) kindly supplied some of their data on the effect of temperature on evaporation for my calculation of $L_{eq}$ (tables 3 and 4). These data are significant because the values for the water content ranged from relatively high to extremely low. The temperatures were relatively high.

Since both water content and temperatures were variable, the value of $L_{eq}$ was standardized at 22°C. This allowed $L_{eq}$ to be evaluated as a function of water content. In each case, the value of $L_{eq}$, when corrected to a value of 22°C, was relatively constant over the entire water-content range. This finding agrees with that of Weeks et al. (1968) and Cary (1965). The values of $L_{eq}$ at 22°C reported in tables 3 and 4 were somewhat lower than those reported by Weeks et al. (1968) at the same temperature. The values for Rago silt loam were also slightly lower than the values for Valentine sand.
Although the research was conducted on different soils—and different approaches were used to obtain the values of $L_{eq}$—each of the various investigators found that $L_{eq}$ was relatively constant over a wide range of suction. Only when the suction gets below about 60 mb does the value of $L_{eq}$ seem to decrease greatly. Although the various investigators report relatively constant values of $L_{eq}$ over all water-content ranges, there is a slight difference in the average values. The differences are relatively small when compared to other transmission properties of the soil, such as hydraulic conductivity.

Apparently, types of soils studied and the results obtained by the various investigators are not associated. For example, Hanks et al. (1967) obtained approximately the same results on a Valentine sand and a Rago silt loam. These results were generally lower than Cary and Taylor (1962a, b) found for loam soils. Weeks et al. (1968) used a sandy loam soil. Although Hanks et al. obtained comparatively low values for the silt loam, the value of $L_{eq}$ may be somewhat associated with sand content of a soil, since lower $L_{eq}$ values were obtained in soils of higher sand content.

Another factor, however, may cause the slight differences in $L_{eq}$ given by the different reporters. Hanks et al. (1967) and Weeks et al. (1968) used a soil column for their experiments. Cary and Taylor (1962a, b) used soil layered between two water compartments. Cary and Taylor measured the movement of water from one compartment through the soil layer into the other compartment, whereas the other investigators measured movement within the soil itself. Salt concentration gradients were reported by Weeks et al. (1968); they also occurred in the experiments of Hanks et al. (1967). It is likely that insignificant salt concentration gradients resulted from the technique used by Cary and Taylor (1962a, b). Tables 1 through
4 do not account for the effect of salt concentration gradients. If water flowed in response to a salt concentration gradient in any of the studies, the calculated values of the $L_{eq}$ would be too low. Since the higher salt concentration gradients developed in the studies of Weeks et al. (1968), and probably Hanks et al. (1967), and since these authors also reported the lower values of $L_{eq}$ perhaps the differences in the observations among the investigators are associated with the neglect of the salt concentration gradient in the analysis. A quantitative evaluation of this factor will be made after the next section.

**EFFECT OF SALT CONCENTRATION GRADIENTS**

For the case of uniform pressure and temperature, equation (11) reduces to $J_v = L_{vd} \text{ grad } \pi$. The coefficient $L_{vd}$, therefore, represents the effect of the osmotic pressure gradient on water flow. Quantitative values for $L_{vd}$ and an understanding of soil factors, which would influence the magnitude of $L_{vd}$, would help to predict the effect of a salt concentration gradient on water flow through the soil.

Much of the work and ideas concerning $L_{vd}$ comes from the research of Kemper and his colleagues. Inasmuch as many of their results are reported in terms of the osmotic efficiency coefficient, the osmotic efficiency coefficient should be related to equations which have been developed in this publication. For a system at uniform temperature, (11) may be written:

$$J_v = L_{vv} (- \text{grad } P + \sigma \text{ grad } \pi)$$

where $\sigma$ is the osmotic efficiency coefficient. (The term reflection coefficient has also been applied to $\sigma$ by some authors.) It is obvious that $\sigma$ is equal to $L_{vd}/L_{vv}$. The theoretical range of $\sigma$ is from 0 to 1. $\sigma$ will equal 0 in a case when $L_{vd} = 0$. (Salt concentration gradients cause no water flow.) $\sigma$ will equal 1 in a case when $L_{vd}$ is equal to $L_{vv}$, in which case the osmotic pressure gradient is as effective in causing water to flow as the pressure gradient. Although values of $\sigma$ can be used to infer the relative magnitude of $L_{vd}$, caution is required in a direct conversion of osmotic efficiency coefficient to $L_{vd}$, because the osmotic efficiency coefficient is also influenced by $L_{vv}$. In other words, we may find a factor which alters the magnitude of $\sigma$ but does not necessarily alter the magnitude of $L_{vd}$. The magnitude of $\sigma$ is altered because these factors could alter $L_{vv}$.

Kemper and Evans (1963) concluded that the magnitude of $\sigma$ would depend upon the differential restriction of the solute relative to solvent by a membrane. The greater the restriction of the solute relative to the solvent, the greater will be the magnitude of $\sigma$. Complete restriction of the solute by a membrane would result in $\sigma = 1$. Kemper and Evans (1963) experimentally studied rather large molecular weight organic compounds, which could be restricted partially by the membrane they used because of geometric factors. They calculated $\sigma$ based upon the relative size of the pores and molecules. Calculations using their equation would indicate that the osmotic efficiency would be negligibly small in a soil-water system, if the only factor causing differential restriction of the salt and water were the relative sizes of the ions, molecules, and pores. However, electrostatic interactions occur between ions and dominantly negative charges of clay particles. Anions are repelled by the negative charge on the clay platelets; therefore, this mechanism could restrict the movement of anions relative to the flow of water through a clay system. Kemper and Rollins (1966) measured the osmotic efficiency coefficients across compacted montmorillonite clay. They studied the effect of
average salt concentration, calcium as opposed to sodium, and chloride as opposed to sulfate on the magnitude of $\sigma$ for the system. Measurements were also made with clays containing various quantities of water. They found that $\sigma$ was increased by decreasing the average solution concentration, saturating the clay with monovalent rather than divalent cations, using divalent rather than monovalent anions, and decreasing the water content of the clay. All of these factors are in qualitative agreement with the fact that $\sigma$ will be greater under conditions in which the solute is restricted relative to the solvent.

As previously noted, the magnitude of $\sigma$ is influenced both by $L_{VD}$ and $L_{vv}$. Inasmuch as all of the above factors potentially could influence both $L_{VD}$ and $L_{vv}$, it is not immediately obvious from the data on $\sigma$ what their effect would be on $L_{VD}$. Letey and Kemper (1968) recalculated the data to determine the effect of these factors on $L_{VD}$. $L_{VD}$ was found to increase when the average solution concentration was decreased, when the clay was saturated with a monovalent rather than a divalent cation, and when a divalent rather than monovalent anion was used. These factors are the same as those found for the osmotic efficiency coefficient, although they influenced $L_{VD}$ to a relatively smaller extent than they did $\sigma$. $L_{VD}$ was found to increase as the water content of the clay increased. This result was in opposition to the result found with respect to $\sigma$. The different effects of water content on $\sigma$ and on $L_{VD}$ result from the sensitivity of $L_{vv}$ to water content. $L_{vv}$ was influenced to a much greater extent by water content than was $L_{VD}$.

Kemper and Rollins (1966) extrapolated their results theoretically to unsaturated soils; their conclusions, however, require experimental verification.

Data on water movement in response to salt concentration gradient in unsaturated soil are scarce. Abd-El-Aziz and Taylor (1965) measured movement in an unsaturated soil system and found that the osmotic pressure gradient had a very slight effect upon water movement. Letey et al. (1968) measured the value of $L_{VD}$ as a function of suction in three different soil types, using two different experimental procedures. In their “steady-state” experiments, the value of $L_{VD}$ was found to be equal to zero, until the suction was greater than about .25 bar. A maximum value of $L_{VD}$ was found at about .5 bar suction; $L_{VD}$ decreased then as the suction was raised above that value. The experimental procedure allowed a maximum suction of only .66 bar to be applied. The value of $\sigma$ increased with increasing suction up to the highest suction used in the experiments.

In experiments which Letey et al. (1968) refer to as “transient experiments,” a maximum value of $L_{VD}$ was found at about .50 bar suction—when the salt concentration range was from 0.01 to 0.04 N. These findings agree with the steady-state measurements. When the salt concentration was in the range of 0.08 to 0.11 N, a maximum value of $L_{VD}$ was measured at about 5 bar suction; and $L_{VD}$ decreased when suction went up to 15 bars for Ascalon sandy loam. The values of $L_{VD}$ for a Pine River clay were found to decrease as suction was increased from .33 to 1 bar. The transient experiment did not allow measurement of $L_{vv}$, and therefore $\sigma$ could not be calculated. A value of $L_{vv}$ was measured for one condition (.33 bar suction for Ascalon fine sandy loam), and $\sigma$ was calculated to equal .014. The value of $L_{vv}$ is well known to decrease greatly as the suction is increased. The value of $L_{VD}$ did not decrease drastically from relatively low suctions to relatively high suctions. It can be inferred from these data, therefore, that $\sigma$ will continue to increase as the suction increases and could approach relatively high values at the higher suctions. These findings would agree with those of Kemper and Rollins (1966).
Whether osmotic pressure gradients are considered to be important in causing water flow through soils depends upon whether one is interested in the absolute magnitude or the relative amount of water flow as compared with that which moves in response to a pressure gradient. Regardless of the point of view, the conclusion is the same at low suctions. That is, very little water flows in response to osmotic pressure gradient when the suction is low. Also, \( \sigma \) is very low under these conditions. At higher suctions, the amount of water moving in response to an osmotic pressure gradient is still very low; however, it becomes relatively large when compared with the amount which moves due to a pressure gradient.

The values reported for \( L_{ov} \) in unsaturated soils are quite low. These experimentally determined values of \( L_{ov} \) may be, however, even higher than values which occur in the field. Measurements were made using sodium chloride or potassium chloride, whereas the natural soil is predominantly a calcium system. Kemper and Rollins (1966) point out that one would expect the osmotic pressure gradient to be less effective in causing water flow in a calcium system than in a monovalent cation system.

It must be remembered that in analyzing for the amount of water flow, the driving force must be considered along with the coefficient. In other words, the flux of water due to an osmotic pressure gradient will equal \( L_{ov} \) \( \text{grad } \pi \). The data summarized thus far in this report have dealt with values of \( L_{ov} \). The osmotic pressure gradient must be measured for any system which is to be analyzed. Ordinarily, soil salinity is measured and reported in terms of electrical conductivity. Electrical conductivity values can be converted to osmotic pressure for known salt species. Soil solutions generally differ in electrical conductivity by 1 mmho cm\(^{-1}\) for every 360 cm of water difference in osmotic pressure. Electrical conductivity on a saturated extract must be corrected to determine the equivalent electrical conductivity for the soil solution before it was diluted to saturation.

**EFFECT OF COMBINED TEMPERATURE AND OSMOTIC PRESSURE GRADIENTS**

The values of \( L_{ov} \) which have been reported in the literature, have been calculated, for the most part, without accounting for the osmotic pressure gradient in the system. Weeks et al. (1968) had a combined suction, temperature, and osmotic pressure gradient in their system. The calculated values of \( L_{ov} \) assume that the value of \( L_{oc} \) was close enough to zero to cause negligible error in the results. As suggested earlier, this factor might account for the values of \( L_{ov} \) reported by Weeks et al. (1968) being lower than those reported by Cary (1965) and Cary and Taylor (1962a, b). The reported values of \( L_{oc} \) can now be used to estimate the error introduced by the assumption of Weeks et al. (1968) that \( L_{oc} \) was equal to zero.

I assume that a value of \( \sigma \) equal to 0.015 (Letey et al. 1968), would be appropriate for the system studied by Weeks et al. (1968). The results of these calculations are summarized in table 5. It can be noted that by having \( \sigma = 0.015 \) rather than zero, the value of \( L_{ov} \) is increased by approximately 7 per cent. This difference is not large enough to account for the difference between the values of \( L_{ov} \) reported by Weeks et al. (1968) and Cary (1965). Also presented in table 5 are values of \( \sigma \) which would be required to raise the values of \( L_{ov} \) to 5.0 cm\(^2\)deg\(^{-1}\)hr\(^{-1}\). These values of \( \sigma \) are much higher than any which have been reported for unsaturated soil and are considered therefore to be unreasonable. The difference in the value
TABLE 5

THE EFFECT OF $\sigma$ ON $L_{vq}$

<table>
<thead>
<tr>
<th>Suction (bars)</th>
<th>$L_{vq}$, assuming:</th>
<th>$\sigma$</th>
<th>$\sigma = 0$</th>
<th>$\sigma = 0.015$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$cm^2 deg^{-1} hr^{-1}$</td>
<td>$cm^2 deg^{-1} hr^{-1}$</td>
<td>$cm^2 deg^{-1} hr^{-1}$</td>
<td>$cm^2 deg^{-1} hr^{-1}$</td>
</tr>
<tr>
<td>0.596</td>
<td>1.89</td>
<td>1.97</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>0.378</td>
<td>2.10</td>
<td>2.20</td>
<td>0.410</td>
<td></td>
</tr>
<tr>
<td>0.304</td>
<td>2.16</td>
<td>2.34</td>
<td>0.241</td>
<td></td>
</tr>
<tr>
<td>0.268</td>
<td>1.99</td>
<td>2.16</td>
<td>0.274</td>
<td></td>
</tr>
<tr>
<td>0.239</td>
<td>1.97</td>
<td>2.17</td>
<td>0.228</td>
<td></td>
</tr>
</tbody>
</table>

*The value necessary to make $L_{vq} = 5.0 \times 10^{-3}$. of $L_{vq}$ reported by Weeks et al. (1968) and Cary are differences which cannot be accounted for by osmotic pressure gradients which occurred in Weeks' et al. experiment.

SUMMARY AND CONCLUSIONS

Equation (11) seems to be a reasonable equation to use for describing water flow through a soil system in which there are combined suction, osmotic pressure, and temperature gradients. It must be recognized that this is a steady-state equation. No satisfactory transient-state equation has been developed to the author’s knowledge. The transient state might be approached by assuming successively changing steady-state systems.

If the distribution of suction, osmotic pressure, and temperature is known through a soil profile, an estimate of the water flow can be made if the appropriate transmission coefficients are known. The coefficient $L_{vv}$ (hydraulic conductivity) has been the subject of many previous studies. In brief, it can be stated that $L_{vv}$ is strongly dependent upon suction. The value of $L_{vv}$ decreases quite rapidly as the suction increases. Also a function of temperature, it increases as the temperature increases. This function can be approximated by assuming that the change is associated with a change in viscosity of the solution as it is modified by temperature. $L_{vv}$ is also a dependent upon the salt concentration and ionic species present in the soil.

The coefficient $L_{vq}$ is associated with the temperature gradient. The data indicated that $L_{vq}$ is relatively independent of suction, if the suction is greater than about .06 bar. The value of $L_{vq}$ becomes quite small at lower suctions and is temperature dependent. The relationship between $L_{vq}$ and temperature is known and can be calculated using information presented in figure 1. Although all of the investigators found that $L_{vq}$ was independent of suction, the value of $L_{vq}$ reported by each investigator was somewhat different and could not be associated with any specific soil or water property. Therefore, until more information becomes available on the value of $L_{vq}$, it is suggested that the intermediate value of $3.0 \times 10^{-3} cm^2 deg^{-1} hr^{-1}$ be used for the value of $L_{vq}$ at $22^\circ C$ for making estimates on the water flow in response to a temperature gradient. This should be approximately correct for all values of suction above .06 bar.

In unsaturated soils, $L_{vd}$ will have, as a maximum, the value of $L_{vq}$ for the same conditions. $L_{vd}$ will very seldom, if ever, be as large as $L_{vp}$ in agricultural soils. The relative value of $L_{vd}$ as compared to $L_{vv}$ depends upon the restriction of the
solute movement. Soil conditions which would restrict solute movement are generally associated with very low values of \( L_{vv} \). It is apparent, therefore, \( L_{VD} \) will be relatively low in all soil systems. To approximate: If the suction is less than .25 bar, \( L_{VD} \) can be assumed to be zero, except under conditions of very high clay content. At suctions between .25 bar and 1 bar, the value of \( L_{VD} \) is not likely to become greater than 10 per cent of the value of \( L_{vv} \). (A value of 3 per cent might be used for approximate calculations.) The value of \( L_{VD} \) would become more nearly the value of \( L_{vv} \) as the soil suction increases.

No data are available on the relative value of \( L_{VD} \) and \( L_{vv} \) at higher suctions. It must be emphasized that the values suggested are approximate.

More data are needed in order to draw specific conclusions on the values of \( L_{vv} \) and \( L_{VD} \) in given soil systems.
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