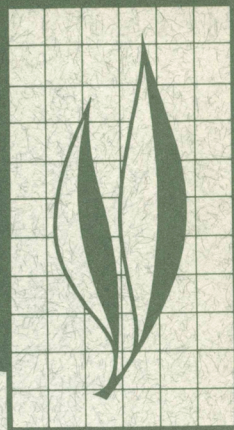


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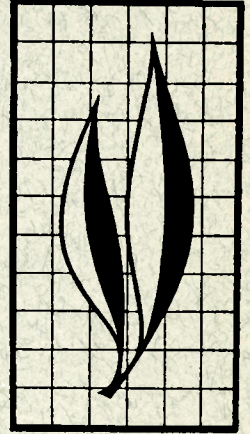


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Movement of Water through Soil as Influenced by Osmotic Pressure and Temperature Gradients

J. Letey

UNIVERSITY OF CALIFORNIA DIVISION OF AGRICULTURAL SCIENCES



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 $J_v = L_{vv} \text{ grad } P + L_{vD} \text{ grad } \pi - L_{vq} \text{ grad } T$. Published research results indicate that L_{vq} 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 $3.0 \times 10^{-3} \text{ cm}^2 \text{ deg}^{-1} \text{ hr}^{-1}$ is suggested for L_{vq} 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_{vq} 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.

THE AUTHOR:

J. Letey is Professor of Soil Physics and Soil Physicist in the Experiment Station, Riverside.

Movement of Water through Soil as Influenced by Osmotic Pressure and Temperature Gradients¹

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 α_i is the variable, $\delta S/\delta \alpha_i$ is considered the force or affinity causing α_i to change and will be symbolized as X_i . Also $d\alpha_i/dt$ is considered the flux or flow of component α_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:

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (i = 1, 2, \dots, n).$$

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

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

where J_q is the heat flux, μ_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:

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

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,

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

where Φ is in ergs $\text{cm}^{-3}\text{hr}^{-1}$, J_s is in ergs $\text{cm}^{-2}\text{hr}^{-1}\text{deg}^{-1}$, J_i is in $\text{gm cm}^{-2}\text{hr}^{-1}$, and μ_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:

$$(4) \quad \text{grad } (\mu_w) = \bar{V}_w (\text{grad } P' - \text{grad } \pi')$$

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

$$(5) \quad \text{grad } (-\mu_s) = -\bar{V}_s \text{grad } P' - \text{grad } \pi' / \bar{c}_s$$

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

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

$$(6) \quad \begin{aligned} \Phi = & -J_s \cdot \text{grad } T + J_w \cdot [-\bar{V}_w (\text{grad } P' - \text{grad } \pi')] \\ & + J_s \cdot [-\bar{V}_s \text{grad } P' - \text{grad } \pi' / \bar{c}_s]. \end{aligned}$$

Gathering terms leads to:

$$(7) \quad \begin{aligned} -\Phi = & J_s \cdot \text{grad } T + (J_w \bar{V}_w + J_s \bar{V}_s) \cdot \text{grad } P' + \\ & (J_s / \bar{c}_s - J_w \bar{V}_w) \cdot \text{grad } \pi' \end{aligned}$$

The total volume flux J_v , is equal to the sum of fluxes of water and solute:

$$(8) \quad J_v = J_w \bar{V}_w + J_s \bar{V}_s,$$

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

$$(9) \quad J_s / \bar{c}_s - J_w \bar{V}_w \cong J_s / \bar{c}_s - J_w / \bar{c}_w = v_s - v_w = J_D$$

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:

$$(10) \quad -\Phi = J_s \cdot \text{grad } T + J_v \cdot \text{grad } P' + J_D \cdot \text{grad } \pi'.$$

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 J_s , J_v , and 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

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

the following flux equations result:

$$(11) \quad J_v = -L_{vv} \text{grad } P + L_{vD} \text{grad } \pi - L_{vq} \text{grad } T,$$

$$(12) \quad J_D = L_{Dv} \text{grad } P - L_{DD} \text{grad } \pi - L_{Dq} \text{grad } T, \text{ and}$$

$$(13) \quad J_s = L_{qv} \text{grad } P + L_{qD} \text{grad } \pi - L_{qq} \text{grad } T.$$

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 π are used instead of P' and π' , 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_{vv} can be cm hr^{-1} rather than $\text{cm}^4 \text{dyne}^{-1} \text{hr}^{-1}$. 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_{vv} 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_{vv} 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 $L_{vq} = L_{qv}$. Since the numerical value of P and π is 10^3 lower than P' and π' , the numerical value of coefficients associated with P and π will be 10^3 greater than for P' and π' . Since both L_{vD} and L_{Dv} will be 10^8 greater, they will still be equal and thus consistent with the Onsager reciprocal relation. However, $L_{vq} \neq L_{qv}$ 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_{vv} 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:

$$(14) \quad J_v = \frac{\beta p D H}{R^2 T^3} \text{ grad } T ,$$

where p is vapor pressure, D is the diffusion coefficient of water vapor, H is the latent heat of vaporization, β 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), β 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:

$$(15) \quad L_{vq} = 7.065 \beta p D H / T^3 .$$

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

$$(16) \quad D = D_o (T/T_o)^{1.75} ,$$

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

$$(17) \quad L_{vq} = .847 \times 10^{-4} \beta p H / T^{1.25} .$$

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

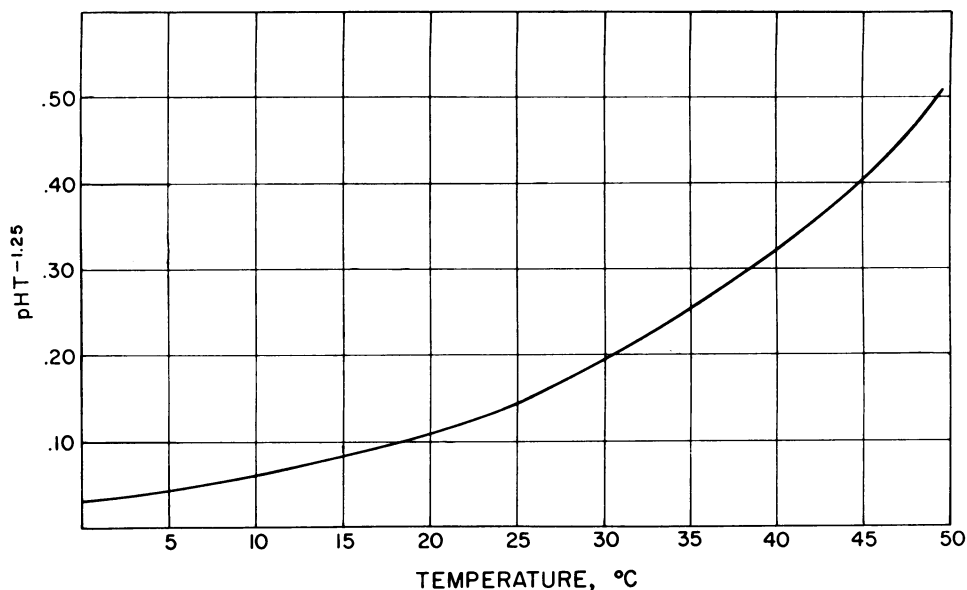


Fig. 1. The relationship between temperature and $pHT^{-1.25}$. Curve represents the effect of temperature on L_{vq} .

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 β , when no soil occurs in the system, should equal 1. L_{vq} can be calculated for these systems and compared to the measured value of L_{vq} . The results of one report by Cary (1963) show that L_{vq} does indeed increase as the temperature increases. The observed value of L_{vq} , however, was consistently a little higher than the calculated value for L_{vq} . In a later report by Cary (1964) the observed and calculated values for L_{vq} 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 β . 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_{vq} 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_{vq} depends on the average tempera-

ture but not on the gradient of temperature. Their temperature gradients were up to $0.8^{\circ}\text{C cm}^{-1}$, 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_{vq} . The value of L_{vq} therefore was corrected to a common temperature of 22°C , using the curve presented as figure 1. With correction, the value of L_{vq} seems to be relatively constant for all values of suction and water content

TABLE 1
VALUES OF L_{vq} FOR VARIOUS SOIL-WATER CONDITIONS

Suction	Water content	Temp.	Temp. gradient	L_{vq}	L_{vq}^*
bars	$\text{cm}^3\text{cm}^{-3}$	$^{\circ}\text{C}$	$^{\circ}\text{C cm}^{-1}$	$\text{cm}^2\text{deg}^{-1}\text{hr}^{-1} \times 10^3$	$\text{cm}^2\text{deg}^{-1}\text{hr}^{-1} \times 10^3$
0.596	.133	24	.143	2.11	1.89
0.378	.155	23	.210	2.22	2.10
0.304	.167	22	.281	2.16	2.16
0.268	.174	21	.327	1.88	1.99
0.239	.181	20	.358	1.76	1.97
Average					2.02

* = L_{vq} numbers adjusted to 22°C using data from fig. 1.

reported in the table. One can conclude that L_{vq} 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_{vq} 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_{vq} can be calculated will be reviewed here.

Cary (1965) showed that the water flux in response to a temperature gradient of $0.8^{\circ}\text{C per cm}$ was relatively constant over the range of suctions from 65 to 470 cm of water. These data indicate that L_{vq} 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_{vq} 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_{vq} from Cary's data (1965) is $5.20 \times 10^{-3}\text{cm}^2\text{deg}^{-1}\text{hr}^{-1}$. 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 (1962*a, 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° , 28° , and 38°C . For each suction, a higher L_{vq} results as the temperature increases, as indicated from previous discussion. The per cent increase in L_{vq} 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_{vq} than

TABLE 2
VALUES OF L_{vq} FOR VARIOUS
SOIL-WATER CONDITIONS AT
VARIOUS TEMPERATURES

Suction	Temper- ature	L_{vq}	R^*
bars	°C	$cm^2deg^{-1}hr^{-1}$ $\times 10^3$	
0.54	18	2.41	
0.54	28	4.16	>1.73
0.54	38	6.13	>1.47
0.37	18	2.85	
0.37	28	4.39	>1.54
0.37	38	5.70	>1.30
0.19	18	3.42	
0.19	28	8.66	>2.53
0.19	38	13.68	>1.58
0.11	18	1.97	
0.11	28	6.13	>3.11
0.11	38	11.4	>1.86
0.03	18	0.21	
0.03	28	1.27	>6.03
0.03	38	4.96	>3.90

* Ratio of L_{vq} for the temperatures indicated. Theoretical ratio based upon data in fig. 1 is 1.79 for 28° and 18° C, and 1.70 for 38° and 28° C.

at the higher suctions. The theoretical calculation for the temperature coefficient of L_{vq} 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_{vq} , we find that L_{vq} increases slightly as the suction decreases from 540 to 190. As the suction is reduced below 190, the value of L_{vq} decreases rather rapidly and is relatively low for 30 cm of water suction.

The average value of L_{vq} 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_{vq} (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_{vq} was standardized at 22° C. This allowed L_{vq} to be evaluated as a function of water content. In each case, the value of L_{vq} , 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_{vq} at 22° 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.

TABLE 3
VALUES OF L_{vq} FOR VARIOUS
SOIL-WATER CONTENTS IN
VALENTINE SAND

Water content	Temperature	L_{vq}	L_{vq}^*
$cm^3\ cm^{-3}$	$^{\circ}C$	$cm^2hr^{-1}deg^{-1} \times 10^3$	$cm^2hr^{-1}deg^{-1} \times 10^3$
40 days of evaporation			
.016	41.7	3.12	1.13
.021	40.6	3.50	1.56
.033	38.6	3.17	1.32
.045	35.4	2.67	1.31
.074	32.0	2.12	1.23
.118	30.3	1.67	1.08
.187	28.6	1.46	1.04
.328	26.4	1.38	1.08
5 days of evaporation			
.054	35.8	2.50	1.23
.086	35.2	2.42	1.21
.114	34.6	2.29	1.17
.134	33.2	2.00	1.09
.154	31.6	1.85	1.10
.179	30.4	1.67	1.07
.233	28.6	1.58	1.13
.346	26.3	.92	.72

* = L_{vq} numbers adjusted to 22° C using data from fig. 1.

TABLE 4
VALUES OF L_{vq} FOR VARIOUS
SOIL-WATER CONTENTS IN
RAGO SILT LOAM

Water content	Temperature	L_{vq}	L_{vq}^*
$cm^3\ cm^{-3}$	$^{\circ}C$	$cm^2hr^{-1}deg^{-1} \times 10^3$	$cm^2hr^{-1}deg^{-1} \times 10^3$
.036	41.0	2.00	0.76
.043	39.6	2.67	1.08
.071	38.0	2.50	1.08
.121	35.2	1.92	0.96
.178	33.0	1.75	0.95
.230	31.8	1.75	1.04
.236	29.7	1.67	1.10
.250	26.8	1.21	0.92

* = L_{vq} numbers adjusted to 22° C using data from fig. 1.

Although the research was conducted on different soils—and different approaches were used to obtain the values of L_{vq} —each of the various investigators found that L_{vq} was relatively constant over a wide range of suction. Only when the suction gets below about 60 mb does the value of L_{vq} seem to decrease greatly. Although the various investigators report relatively constant values of L_{vq} 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 (1962*a, 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_{vq} may be somewhat associated with sand content of a soil, since lower L_{vq} values were obtained in soils of higher sand content.

Another factor, however, may cause the slight differences in L_{vq} given by the different reporters. Hanks *et al.* (1967) and Weeks *et al.* (1968) used a soil column for their experiments. Cary and Taylor (1962*a, 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 (1962*a, 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_{vq} 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_{vq} 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 σ is the osmotic efficiency coefficient. (The term reflection coefficient has also been applied to σ by some authors.) It is obvious that σ is equal to L_{vD}/L_{vv} . The theoretical range of σ is from 0 to 1. σ will equal 0 in a case when $L_{vD} = 0$. (Salt concentration gradients cause no water flow.) σ 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 σ 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 σ but does not necessarily alter the magnitude of L_{vD} . The magnitude of σ is altered because these factors could alter L_{vv} .

Kemper and Evans (1963) concluded that the magnitude of σ 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 σ . 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 σ 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 σ for the system. Measurements were also made with clays containing various quantities of water. They found that σ 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 σ will be greater under conditions in which the solute is restricted relative to the solvent.

As previously noted, the magnitude of σ 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 σ 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 σ . 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 σ . The different effects of water content on σ 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 σ 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 σ could not be calculated. A value of L_{vv} was measured for one condition (.33 bar suction for Ascalon fine sandy loam), and σ 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 σ 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, σ 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_{vD} in unsaturated soils are quite low. These experimentally determined values of L_{vD} 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_{vD} grad π . The data summarized thus far in this report have dealt with values of L_{vD} . 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_{vq} 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_{vq} assume that the value of L_{vD} was close enough to zero to cause negligible error in the results. As suggested earlier, this factor might account for the values of L_{vq} 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_{vD} can now be used to estimate the error introduced by the assumption of Weeks *et al.* (1968) that L_{vD} was equal to zero.

I assume that a value of σ 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 $\sigma = .015$ rather than zero, the value of L_{vq} is increased by approximately 7 per cent. This difference is not large enough to account for the difference between the values of L_{vq} reported by Weeks *et al.* (1968) and Cary (1965). Also presented in table 5 are values of σ which would be required to raise the values of L_{vq} to 5.0 $\text{cm}^2\text{deg}^{-1}\text{hr}^{-1}$. These values of σ 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 σ ON L_{vq}

Suction	L_{vq} , assuming:		σ^*
	$\sigma = 0$	$\sigma = .015$	
bars	$cm^2deg^{-1}hr^{-1} \times 10^3$	$cm^2deg^{-1}hr^{-1} \times 10^3$	
0.596	1.89	1.97	.600
0.378	2.10	2.20	.410
0.304	2.16	2.34	.241
0.268	1.99	2.16	.274
0.239	1.97	2.17	.228

*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 $3.0 \times 10^{-3} cm^2deg^{-1}hr^{-1}$ be used for the value of L_{vq} at 22° 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_{vv} for the same conditions. L_{vD} will very seldom, if ever, be as large as L_{vv} 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_{vq} and L_{vD} in given soil systems.

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