BNWL-1429
UC-51

AN IRREVERSIBLE THERMODYNAMIC
APPROACH TO SIMULTANEOUS MOVEMENT
OF WATER, HEAT, AND SALT
THROUGH UNSATURATED SOILS

C. G. Enfield

August 1970

AEC RESEARCH &
DEVELOPMENT REPORT

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for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

3 3679 00061 7136

BNWL-1429

UC-51, Geology
and Minerology

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Water and Land Resources Department
Environmental and Life Sciences Division

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ABSTRACT

Literature was reviewed to obtain the basis for the simultaneous flow of water, heat, and salt through unsaturated soils. Flow theories were developed from the general theory of water flow in saturated soil under isothermal conditions to the analysis of simultaneous solution flow caused by two driving forces, such as water and heat, using Irreversible Thermodynamics.

Based on this review, conclusions were made that the theory of Irreversible Thermodynamics is the most applicable approach for modeling when both liquid and vapor transport are to be considered.

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INTRODUCTION

Radionuclide terrestrial transport studies require the capability to accurately evaluate water movement through heterogeneous saturated and unsaturated soil systems. To gain this capability, computational programs must be available (or developed) for analyzing the soilwater flow systems by simulation techniques, and good input data must be obtained to describe the physical flow parameters characteristic of the particular system under study. Developed to a high degree of sophistication, recent computational or simulation programs are universal in that their use is not limited by or dependent on the particular study area. However, the problem of acquiring input data descriptive of the soil systems of interest limits the actual application of these programs. Because such systems are heterogeneous in nature, these data may vary considerably even between closely adjacent sites. Also, soil-water parameter measurements for unsaturated flow analysis are difficult and time-consuming to make, particularly at low moisture contents.

This report outlines a research program to acquire the necessary input information on the soils beneath the 200 Areas of the Hanford project for an analysis of actual field operations related to the ground disposal of wastes and infiltration of precipitation. In addition, these data would apply to assessments of other routine and nonroutine events related to the entry of water or wastes into the 200 Areas soil systems. Although most of the work would consist of applying the selected techniques to obtain actual measurement

results, some of the effort, because of the peculiarities of local conditions, would be directed toward determining the most applicable measurement methods.

CONCLUSIONS

An irreversible thermodynamic approach of mathematically modeling the simultaneous movement of water, heat, and solute allows most soil parameters to be measured directly or indirectly. The theory of irreversible thermodynamics assumes that a linear equation will describe the flow as a summation of the individual driving forces. This resolves the difficulty of interrelationships by assuming that the driving forces are independent and linearly related to the flux.

A comprehensive program (about 3 to 5 years) to correlate the interrelationships of the different driving forces would be needed to determine the effect of driving forces and under what environmental conditions each driving force predominates or plays a significant role in the overall movement of soil solution. Such a program, in which field samples would be analyzed, would simulate actual conditions as closely as is economically practical. The osmotic efficiency, discussed in the literature review, is not equal to 1 and the solute concentration in the soil water would significantly affect the total potential observed by the psychrometer. Thus, an adjustment must be applied to the psychrometer output to obtain a reasonably accurate value for the driving force on the soil solution. Figure 1 shows the studies as an analysis sequence. The primary work load in this type of program involves many repetitive measurements; thus, for the most part it is time-consuming rather than technically complex by nature. The major phases of work likely to be involved are described below.

OSMOTIC PRESSURE IN HANFORD SOILS

To determine osmotic pressure gradients, disturbed samples of soil must be used to measure the electrical conductivity of extracts from the soil (which has been saturated with distilled water). Relating this value to the electrical

FIGURE 1. Analysis Sequence for Evaluating the Driving Forces on Soil Solution

conductivity at the moisture content observed in the soil by way of a moisture release curve would give the electrical conductivity of the soil solution, assuming no precipitation. This electrical conductivity can be directly related to the osmotic pressure. An analysis of the soil water extract would be necessary to artificially construct a "typical" solution. This artificial soil solution would help to determine the coefficient relating the water flux to osmotic pressure gradients (L_{WD}). Use of this type of artificial solution would reduce the effects caused by changing the naturally existing relationship between the soil matrix and the exchangeable cations.

DETERMINATION OF HYDRAULIC CONDUCTIVITY (L_{WW}), THE COEFFICIENT RELATING WATER FLUX TO OSMOTIC PRESSURE GRADIENTS (L_{WD}), AND THE OSMOTIC EFFICIENCY (σ)

A procedure developed by Letey, Kemper, and Noonan (1969) can be used to evaluate Hanford soils to determine the hydraulic conductivity (L_{WW}) and the coefficient relating water flux to osmotic pressure gradient (L_{WD}). If the psychrometer alone is not adequate for modeling the flow conditions in Hanford soils, the osmotic component of the water potential can be subtracted from the total potential and the matric component alone may give satisfactory results. Removal of the osmotic component would make it necessary to develop a transducer which will measure in-place the electrical conductivity of the soil water. Enfield and Evans (1969) presented a method of measuring electrical conductivity using a porous glass plate having two electrodes, and then encapsulating the electrode in such a manner as to have no external paths. However, this transducer has problems with surface conduction along the internal pores of the glass. If the problem can be overcome, then this type of transducer would

effectively measure the electrical conductivity of soil water in relatively dry soils (0 to 15 bars of matric suction).

DETERMINATION OF HYDRAULIC CONDUCTIVITY (L_{ww}) AND THE
COEFFICIENT RELATING THE WATER FLUX TO THERMAL GRADIENTS (L_{wQ})
AND THE APPARENT HEAT OF TRANSFER (β)

In relatively dry soils, the movement of water in the vapor phase tends to become more prominent. Thus, it is in these soils that a thermal gradient may play an important part in the total transport of soil solution. Experiments following the theory developed by Taylor and Cary (1964) would determine when it is necessary to consider the effects of a thermal gradient as a driving force in transport phenomena.

LITERATURE REVIEWBASIS FOR WATER FLOW UNDER ISOTHERMAL AND NONISOTHERMAL CONDITIONS

The rate of water movement in soil is of considerable importance in the study of radionuclide transport. Physical properties of the soils influence water movement in two important ways: the size and structural arrangement of the soil particles determine the space configuration through which water moves; and the interaction between the soil and soil water gives rise to the water moving forces. In soils where the pores are completely filled with water, the fluid is a single phase and forces originating from gravity, including the pressure gradient, determine the flow. The saturated flow process for the simplest case, is described mathematically by Darcy's equation and Laplace's equation.

It is most often the case, in semiarid and arid soils, that the pores are not completely saturated (filled with water) and the energy potential of water depends not only upon its position in the gravitational field, but also upon sorptive forces associated with interfacial boundaries. That is, when the interconnected free pore space of a porous medium is no longer completely filled with a given homogeneous liquid, the porous medium is considered to be unsaturated with respect to that liquid. The character of the unsaturation is, however, dependent upon the nature of the second fluid which occupies the partial pore space vacated by the homogeneous liquid. If the second fluid is another liquid and if the two liquids are mixed or immiscible, the resulting overall liquid saturation is heterogeneous. If the second fluid is a gas, or a mixture of gases such as air, then the resulting composite system of solid, liquid and gaseous phases becomes the one frequently referred to as unsaturated flow. This has been particularly

so when the ultimate concern is the hydrologic one related to the soil water, especially when the soil region involved is far above the water table. The process of water flow in such an unsaturated system could also be analyzed as a two-fluid problem in immiscible displacement, where water and air are the fluids.

Even if the second fluid is air, a further distinction can be made between an entrapped gas phase and an interconnected gas phase. In the entrapped phase, isolated bubbles or groups of bubbles exist throughout the system composed otherwise of water and porous medium. As the degree of unsaturation increases, that is, water saturation decreases, the various bubbles coalesce with each other until a reasonably continuous interconnected region of uniform gas pressure exists throughout the system, more or less intimately distributed with the water-solid phase. Although a sharp delineation between the two types may not always be possible, it is this latter type of unsaturation which forms the primary concern of this report.

General Theory

The flow of water through a porous medium or through a soil may be described by a general equation.

$$v = \sum_{i=1}^n L_i X_i \quad (1)$$

where
 v = flow rate or water flux
 n = number of driving forces acting
 L = transmission coefficient
 X = driving force.

Upon choosing the proper transmission coefficients and driving force this equation may be used to describe liquid, vapor, or absorbed phase water flow. The soil system is a highly complex and variable entity and a large volume of work has been done towards finding and describing the driving forces and fluxes.

Each driving force has an associated transmission coefficient for expressing the water flow rates through the system in response to a unit driving force. Thus, in a system where water is the only flowing component, the total driving force is an expression of the potential energy gradient and the transmission coefficient is expressed as a single term. Although the nature of the flow path, density, and viscosity are included in the transmission coefficient, under unsaturated flow conditions the flow path changes and thus the transmission coefficient is not a constant. In diffusion theory terms, the transmission coefficient is expressed as a concentration dependent diffusivity.

Isothermal Flow

Saturated Conditions

In the case of saturated conditions where the pores of the soil system are completely filled with water and the system remains constant, the transmission coefficient depends principally on the viscosity and density of the water and the nature of the porous media.

The rate of water flow through soil or other porous material is usually given by Darcy's equation as:

$$v = - L \frac{\Delta P}{\Delta x} \quad (2)$$

where

v = water flux

L = hydraulic conductivity

P = pressure

x = length.

Except for the saturated condition at constant temperatures, Darcy's equation as originally postulated does not apply precisely to water flow through soil. Darcy's equation for describing flow through porous materials has been used since 1856 with little reservation until recently.

Unsaturated Flow

When soils contain both a liquid and a gaseous phase, the most frequently used modification of Darcy's equation involves substituting the gradient of the capillary potential for the hydraulic pressure gradient as the driving force. Under these conditions, the transmission coefficient is no longer a constant but is a function of capillary potential as well as temperature, which gives an equation

$$v = - L(\psi_m, T) \frac{d\psi}{dx} \quad (3)$$

where

v = flow rate or water flux

L = transmission coefficient (unsaturated hydraulic conductivity)

ψ_m = capillary potential (matric potential)

x = length

T = temperature.

The capillary potential gradient, $\frac{d\psi}{dx}$ is the driving force and for isothermal conditions the temperature dependence is eliminated.

A more generalized form of Equation (3) is written as

$$v = - L \nabla \Phi \quad (4)$$

where

v = flow rate or water flux

L = transmission coefficient

Φ = total potential of soil water = $\psi + Z$.

The potential of soil water (Φ) is the amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water at a specified elevation at atmospheric pressure to the soil water (at the point under consideration).

In an unsaturated soil, the assumption of uniform water content may no longer be adequate. This necessitates finding an appropriate relationship between the water content and the water potential. Introduction of the expression for the conservation of mass, called the equation of continuity, will account for the change in water content at any point in the system.

Klute (1951) derived the equation of flow through a porous media by using the equation of continuity and Darcy's equation. His development, as follows, assumes that the medium is incompressible and that the continuity equation for flow through a homogeneous medium as shown in Figure 2 is

$$\frac{\partial \rho^1}{\partial t} = - \frac{\partial \rho V_x}{\partial x} - \frac{\partial \rho V_y}{\partial y} - \frac{\partial \rho V_z}{\partial z} \quad (5)$$

where ρ^1 = mass of fluid per unit volume
 t = time
 V = volume of fluid flowing through the unit cross section per unit time (flow rate)
 p = fluid density.

Equation (5) written in vectorial form is

$$\frac{\partial \rho^1}{\partial t} = - \text{div} (p \mathbf{V}) = - \mathbf{V} \cdot (\nabla p) \quad (6)$$

Substituting Equation (4) into Equation (6) gives

$$\frac{\partial \rho^1}{\partial t} = + \nabla \cdot (\rho L \nabla \phi) \quad (7)$$

For a medium saturated with water ρ^1 is constant and ρ is constant assuming water is incompressible and the temperature is constant. Then Equation (7) can be expressed.

$$\nabla \cdot (L \nabla \phi) = 0. \quad (8)$$

FIGURE 2 Flow Into and Out of Each Face of an Infinitesimal Parallelepiped of the Soil Medium

This describes the flow of water through a saturated medium.
Rewriting Equation (5)

$$\frac{\partial(\rho\theta)}{\partial t} = \nabla \cdot (\rho L \nabla \phi) \quad (9)$$

where θ = volumetric moisture content.

Holding ρ , as a constant yields

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (L \nabla \phi) \quad (10)$$

This is the equation for the general case of water flow through an unsaturated porous medium originally developed by Richards (1931).

Klute (1952) divided Φ into two components

$$\Phi = \psi + z \quad (11)$$

where ψ = capillary potential

and z = gravitational potential

this delineates the flow in a vertical direction in the medium.

Regarding L and ψ as single valued functions of θ ,

$$\begin{aligned} \frac{\partial \theta}{\partial t} &= \nabla \cdot (L \nabla \Phi) = \nabla \cdot [L \nabla (\psi + z)] \\ &= \nabla \cdot (L \nabla \psi + L). \end{aligned} \quad (12)$$

Thus

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (L \nabla \psi) + \frac{\partial L}{\partial z} \quad (13)$$

Equation (13) may be rewritten as

$$\begin{aligned} \frac{\partial \theta}{\partial t} &= \nabla \cdot (L \frac{\partial \psi}{\partial \theta}) + \frac{\partial L}{\partial z} \\ &= \nabla \cdot (L \frac{\partial \psi}{\partial \theta} \cdot \frac{\partial \theta}{\partial z}) + \frac{\partial L}{\partial z} \end{aligned} \quad (14)$$

where $L(\theta) \frac{\partial \psi}{\partial \theta} = D$ which is defined as the diffusion coefficient or diffusivity. Equation (14) is the differential equation

that expresses water movement in a vertical column and may be written as

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial \theta}{\partial z} + \frac{\partial L}{\partial z} \right). \quad (15)$$

Considering diffusivity as a constant and disregarding the gravity term Equation (15) becomes

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial z^2}. \quad (16)$$

Flow rates are radically changed as the soil becomes unsaturated. With a decrease in water content in the soil pores, the capillary potential decreases (increases negatively) as a result of the increasing effect of the absorptive forces of the soil. In very dry soils, the capillary potential can attain very great negative values and for most cases concerning water flow in the unsaturated regions above the water table the capillary potential is the predominant driving force included in the water potential.

Simultaneous Flow

The preceding discussion has been directed to the simple case where the only substance moving in the system is pure water. The isothermal theory has limited application in nature since there are few water flow problems that occur in an isothermal manner. Heat is evolved at the wetting front when water infiltrates a dry soil (Anderson, 1960). When water is evaporated from soil, the evaporating site is cooled by the evaporation process (Wiegand and Taylor, 1962). Also, radiation at the soil surface and chemical or biological activity within the soil may cause temperature gradients. Thus, an equation is needed that will incorporate the temperature gradient into the flow equation in order to describe and explain such natural processes.

If a soil system initially at equilibrium (uniform water content with a constant water potential at constant temperature throughout) is subjected to a temperature gradient, water will flow from the warm region to the cool region (Gurr, Marshall, and Hutton, 1952; Taylor and Cavazza, 1954; Woodside and Cliffe, 1959). When the soil is saturated or near saturation, the flow occurs primarily in the liquid phase (Taylor and Cary, 1960). Water movement occurs primarily in the vapor phase when the soil is relatively dry. At intermediate soil water contents, however, movement is by a combination of liquid and vapor water flow (Cary and Taylor, 1962a; Cary and Taylor, 1962b; and Taylor and Cary, 1962).

The energy state of the water molecules in soil changes when a temperature gradient is imposed in the system, and water will move in response to this energy gradient. For the duration of the imposed temperature gradient, an irreversible and spontaneous flow of heat occurs. Thus, both flow processes will interact with each other and cannot be considered as independent processes but must be considered together in terms of the interaction. Where there is simultaneous movement of more than one component in the system, isothermal flow equations and simple equilibrium thermodynamics cannot be used to predict or describe the flow.

ANALYSIS OF SIMULTANEOUS WATER AND HEAT FLOW

Two approaches have been developed in an attempt to describe the phenomenon of simultaneous flow where water is moved by a thermal gradient. In the first, theory and equations were developed to describe heat and water transfer in porous medium, in terms of the classical mechanisms of vapor diffusion and liquid movement by capillarity and further defined to account for heat flow. The second approach used irreversible thermodynamic theory to develop general equations for the simultaneous flow of water and heat in the soil system.

Phillip and de Vries Theory

In an attempt to expand on the previous theory of water vapor diffusion in a porous medium under temperature gradients, Phillip and de Vries (1957) were apparently the first to include the interaction of vapor, liquid and solid phases, and the difference between average temperature gradients in the air-filled pores and in the soil as a whole. Taking these factors into account, an approximate analysis was developed which would predict orders of magnitude and general behavior that was in satisfactory agreement with the experimental facts of Gurr, Marshall, and Hutton (1952); Rollins, Sprangler, and Kirkham (1954); Smith (1943) and Jones and Kohnke (1952); Staple and Lehane (1954).

Phillip and de Vries (1957) have taken the "simple" theory of vapor diffusion which may be shown by the equation (Penman, 1940; van Bavel, 1952; Rollins and others, 1954)

$$q_{\text{vap}} = - D_{\text{atm}} \cdot v \alpha a \nabla \rho^* \quad (17)$$

where

q_{vap} = vapor flux

D_{atm} = diffusion coefficient of water vapor in air

a = dimensionless factor depending on the structure

a = volumetric air content of the medium

ρ^* = density of water vapor

v = "mass flow factor" introduced to allow for the mass flow arising from the differences in boundary conditions governing the air and vapor components of the diffusion systems.

and extended it to (a) separate the isothermal and thermal components of vapor transfer and (b) to show the effect of relative humidity on the transfer. As they pointed out, the developments depend only on the proportionality of the vapor flux to the vapor-density gradient.

By the introduction of the thermodynamic relationship as given in Edlefsen and Anderson (1943) and considering the influence of temperature on relative humidity for a constant value of θ , they were able to show that the density of saturated water vapor was a function of temperatures only and that the relative humidity was a function of θ only. They were able then to separate the flux into two components, that due to the temperature gradient and that due to the moisture gradient and illustrate it by the equation

$$\frac{q_{\text{vap}}}{\rho_w} = - D_{T\text{vap}} \nabla T - D_{\theta\text{vap}} \nabla \theta \quad (18)$$

where ρ_w = density of water = 1
 D_T = thermal vapor diffusivity
 D_θ = isothermal vapor diffusivity.

To account for the liquid flow of water due to temperature and water gradients, Darcy's equation for liquid flow in unsaturated media was combined with Equation (11).

In the water content range where liquid transfer occurs ($L > 0$), water pressure is determined by capillarity, thus

$$\frac{\partial \psi}{\partial T} = \frac{\psi}{\sigma^*} \frac{d\sigma^*}{dT} = \gamma \psi \quad (19)$$

where γ = temperature coefficients of surface tension of water
 σ^* = surface tension.

Using Equation (19) and (11) in Darcy's equation gives

$$\frac{q_{\text{liq}}}{\rho_w} = - L \gamma \psi \nabla T - L \frac{\partial \psi}{\partial \theta} \nabla \theta - Li \quad (20)$$

where i = unit vector in a positive z direction.

Thus, the liquid flux was separated into three components, that caused by temperature gradients, that caused by the water gradient and that caused by gravity.

Thus, if $\theta = f(\psi)$ and is single valued then it is easily seen that Equation (20) is of the form

$$\frac{q_{liq}}{\rho_w} = - D_{Tliq} \nabla T - D_{\theta liq} \nabla \theta - Li. \quad (21)$$

In describing the interaction of vapor and liquid phases where liquid continuity no longer existed, there still remained water molecules adsorbed on the surface of the matrix of the soil. These water molecules formed bridges between the isolated wedges of liquid water. Thus, when a vapor pressure gradient due to a temperature gradient produces a vapor flux water vapor would condense on one side of the liquid wedges and be transported by capillarity to the other side where evaporation would take place. The liquid wedge would be at "equilibrium" when the rate of condensation equaled the rate of evaporation. These regions would permit the rapid transport of water since the changes produced in the curvature of the menisci resulted in essentially no resistance to liquid flow through the wedge.

Since evaluation would involve a detailed analysis of the fine structure of the vapor and temperature fields in the pore system, an alternate method using the thermal properties of the system was used for approximating the parameters. The thermal properties were denoted by the ratio of the average temperature gradient in the air-filled pore spaces to the overall temperature gradient. Large differences in thermal conductivity and heat capacity of the liquid, vapor, and solid phases were noted which could cause temperature changes in the solid phase to occur more rapidly than those in the pores. With the increased thermal conductivity due to the evaporation-condensation process, the overall differences in thermal

conductivity of the liquid, vapor, and solid phases were such that the average pore temperature gradient may be three times the overall temperature gradient of the system.

Evaluation of flow in a closed system was done realizing that the observations were of net water transfer and not of total water transfer. In the case where the average water content is so low that no liquid continuity exists, the net water transfer would be a measure of the total water flow because the water transfer was in vapor phase. The vapor phase transfer would increase rapidly with increased water content up to the point where liquid continuity is established. Then a liquid phase return flow produced by the water gradient will tend to balance the thermal vapor phase flow and reduce the net water transfer. It then follows that maximum net transfer occurs at some point below where liquid continuity is established and that net water transfer will gradually decrease above the liquid continuity point until at some given point it will essentially become zero. It is apparent that a static equilibrium cannot exist under these conditions but that a cyclic flow of water in the liquid and vapor phase is accompanied by a transfer of heat.

The pressure component and the general influence of temperature on the flow system were accounted for in the diffusivity terms. Then for describing the water and heat transfer an equation was developed. Using Equation (18) for vapor phase transfer and redescribing the diffusivities in terms of the Phillip and de Vries theory gave

$$D_{\theta \text{vap}} = \frac{D_{\text{atm}}}{\rho_w} \frac{v_{\text{ag}} \rho}{RT} \frac{\partial \psi}{\partial \theta} . \quad (22)$$

The thermal transfer mechanism, however, failed in this case since the vapor pressure gradient is due solely to the water

gradient and very small changes in the curvature of the meniscus would cause a reversal in the direction of water vapor movement.

Using the combination of Equations (18) and (21) yields

$$\frac{q}{\rho_w} = - D_T \nabla T - D_\theta \nabla \theta - Li \quad (23)$$

where q is the quantity that describes the total water flux and

$$D_T = D_{Tliq} + D_{Tvap} \quad (24)$$

and

$$D_\theta = D_{\theta liq} + D_{\theta vap} \quad (25)$$

where D_T = thermal water diffusivity

D_θ = isothermal water diffusivity.

Differentiation of Equation (23) and combining with the equation of continuity yields an equation for describing water transfer under the combined influence of water and temperature gradients.

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (D_T \nabla T) + \nabla \cdot (D_\theta \nabla \theta) + - \frac{\partial L}{\partial z}. \quad (26)$$

The existence of hysteresis in $\psi(\theta)$, which could occur if a portion of the system was decreasing in water content while another portion was increasing, could invalidate the use of Equation (23).

Equation (26) neglecting gravity and the influence of salts may be written

$$J_w = - (D_T \nabla T) - (D_\theta \nabla \theta) \quad (27)$$

where J_w = water flux

∇T = temperature gradient

$\nabla \theta$ = water content gradient

$$D_T = D_{T\text{vap}} + D_{T\text{liq}} = \frac{a + f(a) \cdot \theta D_o v h}{\rho_w} \frac{\partial \rho_o}{\partial T} \frac{(\nabla T)_a}{(\nabla T)} - k \gamma \psi$$

$$D_\theta = D_{\theta\text{vap}} + D_{\theta\text{liq}} = \frac{D_o \alpha a}{\rho_w} \frac{\partial \rho}{\partial \theta} + k \frac{\partial \psi}{\partial \theta}$$

D_T = thermal moisture diffusivity

D_θ = isothermal moisture diffusivity

$D_{T\text{vap}}$ = thermal vapor diffusivity

$D_{T\text{liq}}$ = thermal liquid diffusivity

$D_{\theta\text{vap}}$ = isothermal vapor diffusivity

$D_{\theta\text{liq}}$ = isothermal liquid diffusivity

θ = volumetric water content

a = volumetric air content

$f(a) = a/a_k$, for $\theta \leq a \leq a_k$ as a first approximation;

$f(a) = 1$ for $a \geq a_k$

a_k = value of a at which "liquid continuity" no longer exists

D_o = molecular diffusivity of water vapor in air

$v = P/(P-p)$ = mass flow factor (approximately 1 for most soil systems) where P = air pressure;

p = soil water vapor pressure

$h = p/p_o$ = relative vapor pressure of the soil air

ρ_θ = density of saturated water vapor

$(\nabla T)_a$ = average temperature gradient in the air filled pores

∇T = overall temperature gradient

$\gamma = 1/a \, d \sigma/dT$ = temperature coefficient of the surface tension of water, a

L = unsaturated hydraulic conductivity

- α = tortuosity factor allowing for the extra path length
- p = density of soil water vapor
- ρ_w = density of liquid water
- ψ = index of water potential (capillary potential)
- R = specific gas constant for water vapor.

An extensive analysis of the soil water characteristics must be made for the evaluation of Equation (27). The water content at which liquid continuity no longer exists must be estimated as well as the water potential and the diffusivity as a function of water content in the water content range of interest. The thermal properties as influenced by the water in the system must be estimated to evaluate the $\frac{\Delta T_a}{\Delta T}$ term. Values for this term for water contents and different porosities were presented. An elaborate analysis pertaining to the thermal conductivities of the gas, solid, and liquid phases of a hypothetical porous system was used for these data. Thus, the values only held in the 10 to 30 °C range and were regarded only as first approximations (Phillip and de Vries, 1957).

Irreversible Thermodynamics

Taylor and Cary (1964) developed a theory for describing water flow caused by a thermal gradient. Their general approach of describing flow was based on thermodynamic considerations using nonequilibrium systems. The standard works of Prigogine (1961); de Groot (1959); and de Groot and Mazur (1962) review the general theory of nonequilibrium thermodynamics. A discussion follows that gives the general theory and a systematic guide for setting up interrelated equations that describe the transport of one or more components through the soil-water system.

Consider a soil which remains unchanged in the x - y plane though moisture, heat, salt and air fluxes may occur in the z plane. Thermal, osmotic, attractive forces between soil water

and soil solids, and gravitational force fields may cause these gradients. If this is so, the continuity equation may be written as

$$\rho \frac{dC_k}{dt} = - \frac{dJ_k}{dz} \quad (28)$$

where ρ = total mass of material in a unit bulk volume

$C_k = \frac{\rho_k}{\rho} = \frac{M_k}{M}$ = mass of component k per unit total mass of the system (concentration)

ρ_k = mass of component k in a unit bulk volume

J_k = flow of component k

t = time.

Equation (28) shows that the total mass per unit volume multiplied by the rate of change with time of the unit mass of a component is equal to the rate of change of the flow component (k) of the mass with respect to distance.

Taylor and Cary (1964) have written the equations for the conservation of energy per unit mass given by de Groot (1951) as

$$\rho \frac{d(1/2 v'^2 + u)}{dt} = \rho v \frac{dv}{dt} + \rho \frac{du}{dt} = - \frac{d}{dz} (Pv + J_u) \quad (29)$$

$$+ \sum_{k=1}^n F_k v_k \rho_k$$

where v = velocity of the center of mass of the system

J_u = flow of energy

F_k = any external force acting on the component k

v_k = velocity of component k

Choosing the fluxes with respect to the center of mass, the velocity of the center of mass is zero. If it is assumed that the acceleration of the center of mass ($\frac{dv}{dt}$) is

insignificant when compared to the acceleration due to the gravitational force in the term F_k , then the kinetic energy term and the flow energy terms are very small and approximately zero. Thus, Equation (29) may be simplified to

$$\rho \frac{du}{dz} = - \frac{dJ_u}{dz} + \sum_{k=1}^n F_k v_k \rho_k \quad (30)$$

Application of this theory to the flow problem of either open or closed systems can be started with the Gibbs equation of equilibrium thermodynamics which states

$$T dS = dU + P dV - \sum_{k=1}^n \mu_k dM_k \quad (31)$$

where

- T = absolute temperature
- S = internal entropy
- U = internal energy
- P = pressure
- V = volume
- M_k = mass of k at a point in the system
- n = number of components
- μ_k = chemical potential of the k component

The instantaneous thermodynamic state at any point in the system can be described by this equation. The assumption is made in theory that the molecules only deviate slightly from equilibrium, even though the system is not in an equilibrium condition. The internal entropy is produced when the molecules return to the equilibrium condition. The basis for the determination of the fluxes in the phenomenological laws that describe the flow system is the entropy production.

Fourier's law used for heat flow, Darcy's equation used for saturated water flow, and Ohm's law used for electrical current flow show that flow may be described as being

proportional to the driving force. Laws which describe irreversible processes are sometimes termed phenomenological laws. If the system has two or more of these natural flows occurring simultaneously, the strict proportionality between the individual driving forces and the flux no longer applies.

The theory of irreversible thermodynamics assumes that a linear equation will describe the flow as a summation of the individual driving forces, so

$$J_i = L_{i1} X_1 + \cdot \cdot \cdot + L_{in} X_n = \sum_{k=1}^n L_{ik} X_k \quad (32)$$

where J_i = flux of the i -th component formerly noted as v in Equation (1)
 L = phenomenological coefficient
 X = driving force
 n = number of driving forces.

This equation, if applicable to flow in porous media, resolves the difficulty of interference through the assumption that the driving forces are independent and linearly related to the flux. Thus, Equation (32) is general and will describe the flow of any component as a linear relationship between the flow of that component and the driving forces involved. Therefore, mass transfer could be evaluated with this analysis.

An understanding of the interrelationship between the phenomenological coefficients (proportionality constants) is necessary to solve the equations which describe this interaction of forces. Onsager's reciprocal relations

$$L_{ik} = L_{ki}$$

are based on the concept of microscopic reversibility under nearly equilibrium conditions and requires that any molecular process and the reverse of that process will on the average

take place at the same rate. In the case at hand of heat and water flow, the reciprocal relationship provides the information that the coefficient of water flow resulting from a unit water content gradient is equal to the coefficient for water flow resulting from a unit thermal gradient.

In an irreversible flow system, the general relationship for entropy production is

$$T \frac{\partial S}{\partial t} = \sum_{i=1}^n J_i X_i \quad (33)$$

where T = absolute temperature
 $\frac{\partial S}{\partial t}$ = rate of entropy production.

Combining the laws of conservation of mass, energy, and momentum with Equation (31) the entropy production of a system can be calculated. Entropy production depends upon the heat flow at a given temperature, and heat flow is a function of the temperature gradient ($\frac{\Delta T}{\Delta z}$), the temperature at which the heat flow occurs, and the thermal conductivity (K) of the material.

Writing the equation for entropy production, or the irreversible component in the notation of Taylor and Cary (1964) gives

$$T\sigma' = - J_u \frac{d \ln T}{dz} + \sum_{k=1}^n J_k \left[F_k - T \frac{d(\mu_k/T)}{dz} \right] \quad (34)$$

where σ' is the entropy produced and other terms are as previously defined.

A linear combination of the forces will describe a first approximation of the fluxes in Equation (34). Then upon application of Onsager's theory the phenomenological equations take the form

$$J_i = \sum_{k=1}^n L_{ik} \left[F_k - T \frac{d(\mu_k/T)}{dz} \right] - L_{iu} \frac{d \ln T}{dz} \quad (35)$$

$$J_u = \sum_{k=1}^n L_{uk} \left[F_k - T \frac{d(\mu_k/T)}{dz} \right] - L_{uu} \frac{d \ln T}{dz} \quad (36)$$

where the Onsager reciprocal relations (phenomenological coefficients) are

$$L_{ik} = L_{ki}$$

and

$$L_{iu} = L_{ui}.$$

The subscript *i* refers to any of the *n* components of the system that contain *k* kinds of materials. Taylor and Cary (1964) have demonstrated that this theory can be applied to a porous medium and show that generalized flow equations can be written for a soil system where fluxes of water, heat, salt or other components may exist.

For a porous system in which the simultaneous flow of heat and only one component, water, are considered, the appropriate equations may be written

$$J_w = L_{ww} \left[F_w - \left(\frac{d\mu_w}{dz} \right)_T \right] - L_{wq} \frac{d \ln T}{dz} \quad (37)$$

and

$$J_q = L_{qw} \left[F_w - \left(\frac{d\mu_w}{dz} \right)_T \right] - L_{qq} \frac{d \ln T}{dz} \quad (38).$$

where J_w = water flux

J_q = calorimetric heat flux

L_{ww} = phenomenological coefficient due to water flux

$L_{wq} = L_{qw}$ = interaction coefficients

L_{qq} = phenomenological coefficient due to heat flux .

Equation (38) expresses the flux in terms of calorimetric heat flow rather than in the thermodynamic energy flux as given in Equation (36).

Taylor (1958) and Babcock and Overstreet (1955) have shown that the soil water potential can be defined as the difference in potential between soil water and pure water, thus

$$\Phi = \mu_w - \mu_w^0 . \quad (39)$$

Since the potential for pure water is a constant then

$$\frac{d\Phi}{dz} = d \frac{\mu_w}{dz} . \quad (40)$$

Consider a closed system that is a mixture of air, water, and soil which is subjected to a constant temperature gradient and where only heat is allowed to flow in and out of the system. Where the potential distributions vary in only one direction, the water and heat flux equations will reduce to

$$J_w = - L_{ww} \frac{d\Phi}{dx} - L_{wq} \frac{d \ln T}{dx} \quad (41)$$

• and

$$J_q = - L_{qw} \frac{d\Phi}{dx} - \frac{L_{qq}}{T} \left(\frac{dT}{dx} \right) \quad (42)$$

where L_{ww} = unsaturated conductivity

L_{qq} = Fourier heat conductivity coefficient.

Cary (1964) was successful in testing the validity of the Onsager relationship for vapor diffusion in air under thermal gradients. Apparently it is also applicable for water movement in soil (Taylor and Cary, 1965; Cary, 1965). This can be demonstrated by an independent measurement of the heat flux and the two conductivities (heat and capillary).

Placement of a constant thermal gradient across a horizontal column of soils will cause heat to flow. This will induce

water flow which will continue until a steady state condition has been reached. At this point $J = 0$ and Equation (41) becomes

$$J = 0 = - L_{ww} \frac{d\phi}{dx} - L_{wq} \frac{d \ln T}{dx} \quad (43)$$

which leads to the relation

$$\frac{d\phi}{d \ln T} = - \frac{L_{wq}}{L_{ww}} = - \frac{L_{qw}}{L_{ww}} = - \beta . \quad (44)$$

Then β , the apparent heat of transfer, can be obtained by plotting ϕ against the $\ln T$ and evaluating the slope of the curve. If β can be found, it is then possible to solve the flow equation.

If it is more desirable to measure soil water content (θ) than water potential (ϕ) as the independent variable, Equation (43) becomes

$$J_w = - D \frac{d\theta}{dx} - L_{wq} \frac{d \ln T}{dx} \quad (45)$$

where $D = L_{ww} \left(\frac{d\phi}{d\theta} \right)$ = coefficient of diffusivity

Expressing Equation (45) in a steady state ($J_w = 0$) when no flux is occurring

$$J_w = 0 = - D \frac{d\theta}{dx} - L_{wq} \frac{d \ln T}{dx} \quad (46)$$

which upon rearrangement becomes

$$\frac{d\theta}{d \ln T} = \frac{L_{wq}}{D} = - \beta^* \quad (47)$$

where β^* is defined as $\beta \frac{d\phi}{d\theta}$ at constant temperature, pressure, and composition or sometimes as the diffusion transfer coefficient.

Applying Equation (47) to Equation (45) and rearranging gives

$$J_w = - D \left(\frac{d\theta}{dx} + \beta^* \frac{d \ln T}{dx} \right) \quad (48)$$

and also using Equations (42) and (47), and remembering the phenomenological coefficients leads to

$$J_q = - D\beta \frac{d\theta}{dx} - L_{qq} \frac{d \ln T}{dx} \quad (49)$$

which gives a set of simultaneous equations that can be solved after making appropriate measurements.

This development suggests that two coefficients, β^* and $D\beta$, should be related by the slope of the Φ vs θ curve as a consequence of the phenomenological coefficients. This same system may be more readily described by Equations (41) and (42) with the use of only three coefficients. It may be possible to expand the commonly used flow equations to account for the influence of temperature gradients simply by measuring the temperature and evaluating the ratio, β or β^* which may prove to be constant over rather wide ranges of water contents (Taylor and Cary, 1964). If β and β^* are independent of the applied temperature and constant over a significant portion of the water content range, then for conditions where a constant thermal gradient exists, it would be possible to account for the thermally induced water flow by adding a constant term to the usual flow equations.

The conductivities and coefficients which have been used in the above equations represent the sum of the individual vapor, liquid and in some instances the absorbed phase of water flow. The flow equations assume that the driving forces for flow in each individual phase was the same or at least directly proportional. It is also well to keep in mind the following

conditions which must be met, in addition to the general assumption inherent with the general theory of irreversible thermodynamics:

- a. The soil is inert and no chemical reactions take place in it.
- b. The system is never far from equilibrium.
- c. The flow can be adequately described by linear equations.
- d. All fluxes of matter and energy are specifically accounted for.
- e. If the "diffusion" form is used, it must further be assumed that the water potential is a unique function of water content.

The conductivities and coefficients represent a composite of the individual conductivities, therefore the mechanisms for flow are masked and a more detailed analysis must be made to evaluate the contributions of the individual phases to the total flow. Jackson (1965) has reported work where the vapor and liquid flow components have been separated in near air dry soil and the temperature and pressure dependence of the diffusivities measured. Cary (1965) has been able to separate the liquid and vapor flow in a loam soil under suctions from 5 to 34 cm of Hg.

Additional analyses of this nature are needed on the entire water content range for a more adequate understanding of the flow mechanisms and their dependence upon water content and temperature.

SIMULTANEOUS FLOW OF WATER AND SALT

Interaction of water and salt movement in soils is of interest from many points of view. The salt concentration in arid and semiarid soil water is often high. Since salts move only in the liquid phase high salt concentration gradients develop in these soils, and may effect water movement.

Qayyam and Kemper (1962) demonstrated that evaporation rates from soil are influenced by salt accumulation at the surface. Kemper and Rollins (1966) introduced a term called Osmotic Efficiency (a) which relates the effectiveness of osmotic pressure gradients to move water versus hydraulic pressure gradients. If this osmotic efficiency term is not equal to one (1), psychrometers are not adequate for measuring water driving forces.

Equations to describe simultaneous movement of water and salt in soil and quantitative data on the movement are needed for the above mentioned considerations. The theory of non-equilibrium thermodynamics has been applied to several systems where two or more simultaneous moving components exist.

The rate of entropy production, or the dissipation function (rate of entropy production times the temperature), is equal to the sum of the products of the fluxes and forces in the system. The equation representing the dissipation function for a porous plug or membrane separating solutions of various solute concentration is:

$$\phi^* = J_s \nabla \mu_s + J_w \nabla \mu_w \quad (50)$$

where ϕ^* is the dissipation function, J is the flux, and μ is the chemical potential. The subscript "s" refers to solute (salt) and "w" to solvent (water). Other equations involving $\nabla \mu$ for the solute or water components are as follows:

$$\nabla \mu_w = \bar{V}_w (\nabla P - \nabla \pi) \quad (51)$$

$$\nabla \mu_s = \bar{V}_s \nabla P + \nabla \pi / C_s \quad (52)$$

where $\bar{V}$ is the partial molar volume, P is pressure, π is osmotic pressure, and C_s is the average solute concentration.

Substitution of (51) and (52) into (50) and collecting terms results in:

$$\phi = (J_w \bar{V}_w + J_s \bar{V}_s) \nabla P + [(J_s / C_s) - \bar{V}_w J_w] \nabla \pi . \quad (53)$$

The first term in parentheses is the total volume flow, J_v . Since $J_s \bar{V}_s$ is small compared to $J_w \bar{V}_w$, assume J_v is, for practical purposes, equal to the flux of the solvent. The second term in parentheses represents the velocity of the solute relative to the velocity of the solvent. Because of its similarity to diffusion flow, it will be designated to J_D . Substitution of the volume flow and diffusional velocity into (53) results in the transformed dissipation function

$$\phi = J_v \nabla P + J_D \nabla \pi . \quad (54)$$

The dissipation function has been transformed from the expression as stated in Equation (50) to the expression in Equation (54). Equation (54) is preferable to Equation (50) because the forces are more directly measurable. Because the effect of gravity has been neglected, the derivation is restricted to horizontal flow. For vertical flow, the force due to gravity is added to ∇P to represent the force acting upon volume flow. In the development of nonequilibrium thermodynamics, the fluxes are related to the forces in linear equations as follows:

$$J_v = + L_{ww} \nabla P + L_{wD} \nabla \pi \quad (55)$$

$$J_D = L_{Dw} \nabla P + L_{DD} \nabla \pi . \quad (56)$$

Where L is called the phenomenological coefficient and represents the constant of proportionality between the flux and force, L_{ww} is the hydraulic conductivity of the medium, and L_{wD} is the coefficient relating the flow of water caused by an osmotic pressure gradient. The restriction in movement of the solute relative to movement of the solvent (as a pressure gradient) is applied and is represented by L_{Dw} . The solute

diffusion coefficient is related to L_{ww} but L_{DD} must also account for increased movement along concentration gradients due to hydrodynamic dispersion.

The Onsager reciprocal relation for the system is

$$L_{wD} = L_{Dw} \quad .$$

The solute flux, (J_s) , is easier to measure than J_D . It is, therefore, necessary to have an equation relating the solute flux to the phenomenological coefficients. By definition [Equation (53) and following context],

$$J_D + J_v = J_s/C_s - \bar{V}_w J_w + \bar{V}_w J_w + \bar{V}_s J_s \quad . \quad (57)$$

Since, according to Letey and Kemper (1969), $\bar{V}_s \ll 1/C_s$ we can use Equations (55) and (56) for J_v and J_D respectively. Thus,

$$J_s/C_s = (+L_{ww} + L_{Dw}) \nabla P + (+L_{DD} + L_{wD}) \nabla \pi \quad . \quad (58)$$

Equations (55), (56), and (58) are the flux equations that can be used in the analysis of water and salt fluxes through soil.

Most of the experimental data on the effect of osmotic pressure gradients on water movement have been collected on pure clay systems completely saturated with water. Abd-El-Aziz and Taylor (1965) measured movement in an unsaturated soil system and found that the osmotic pressure gradient had a very small effect upon water movement. Kemper and Rollins (1966) estimated that the soil water suction must be greater than about 5 bars before osmotic pressure gradients could be very effective in causing water movement. Their data would indicate that the effect would be greater at lower average salt concentrations as compared to higher average salt concentrations. Letey, Kemper and Noonan (1969) concluded that at low suctions

both L_{wD} and $\sigma = L_{wD}/L_{wW}$ are low and, for practical purposes, the osmotic gradient can be neglected in the consideration of water flow through the soil. They also concluded that the value of L_{wD} is still low at high suctions so that the amount of water moved by an osmotic gradient is not great. The data presented in their paper indicated that under most conditions L_{wD} is considerably different than L_{wW} . The net conclusion would be that, since the psychrometer measures a combined matric function and osmotic function, there are few, if any, cases in which the psychrometer results in themselves can be used in water flow analysis.

LIST OF SYMBOLS

- a = volumetric air content of the medium
 a_k = value of a at which "liquid continuity" no longer exists
 C_k = mass of component k per unit total mass of the system (concentration)
 D = diffusivity
 D_o = molecular diffusivity of water vapor in air
 D_T = thermal moisture diffusivity
 D_t = thermal vapor diffusivity
 D_{atm} = diffusion coefficient of water vapor in air
 D_{Tliq} = thermal liquid diffusivity
 D_{Tvap} = thermal vapor diffusivity
 D_θ = isothermal moisture diffusivity
 $D_{\theta liq}$ = isothermal liquid diffusivity
 $D_{\theta vap}$ = isothermal vapor diffusivity
 F_k = any external force acting on the component k
 λ = relative vapor pressure of the soil air
 J_i = flux of the i -th component
 J_k = flow (flux) of component k
 J_q = calorimetric heat flux
 J_s = solute flux
 J_u = flow of energy
 J_w = water flux
 L = transmission coefficient - unsaturated hydraulic conductivity
 L_{qq} = phenomenological coefficient due to heat flux - Fourier heat conductivity coefficient.

- $L_{wq} = L_{qw}$ = interaction coefficients
 L_{ww} = phenomenological coefficient due to water flux -
 unsaturated hydraulic conductivity
 M_k = mass of k at a point in the system
 n = number of driving forces acting - number of components
 P = pressure
 q_{vap} = vapor flux
 R = specific gas constant for water vapor
 v = "mass flow factor"
 S = internal entropy
 T = temperature - absolute temperature
 t = time
 U = internal energy
 V = volume of fluid flowing through the unit cross section
 per unit time
 v = flow rate of water or water flux velocity of center
 of mass
 $\bar{V}$ = partial molar volume
 v_k = velocity of component k
 X = driving force
 x = length
 ∇T = temperature gradient
 $(\nabla T)_a$ = average temperature gradient in the air filled pores
 $\nabla \theta$ = water content gradient
 a = dimensionless factor depending on the structure
 (tortuosity factor)
 β = apparent heat transfer
 β^* = diffusion transfer coefficient
 y = temperature coefficient of surface tension of water
 θ = volumetric water content
 μ_k = chemical component of component k
 μ_s = chemical potential of salt

μ_w = chemical potential of water

π = osmotic pressure

ρ = fluid density or mass density

ρ' = mass of fluid per unit volume

ρ^* = density of water vapor

ρ_k = mass of component k in a unit bulk volume

ρ_w = density of water

ρ_θ = density of saturated water vapor

a = osmotic efficiency

σ^* = surface tension

a' = entropy produced

ϕ = soil water potential = $\psi + z$

ϕ^* = dissipation function

ψ_m = capillary potential

z = gravitational potential

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