5-1964

The Interaction of Water and Salt Flow in Unsaturated Soils

Mahmoud Hassan Abd-el Aziz
Utah State University

Recommended Citation

Abd-el Aziz, Mahmoud Hassan, "The Interaction of Water and Salt Flow in Unsaturated Soils" (1964). *All Graduate Theses and Dissertations*. 3646.
https://digitalcommons.usu.edu/etd/3646

THE INTERACTION OF WATER AND SALT FLOW IN UNSATURATED SOILS

by

Mahmoud Hassan Abd-el Aziz

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Soil Physics

UTAH STATE UNIVERSITY
Logan, Utah

1964

ACKNOWLEDGMENTS

I am indebted to Dr. Sterling A. Taylor for his interest and stimulating suggestions throughout the course of this research. I wish also to thank my committee members, Drs. W. M. Moore, A. A. Bishop, R. L. Smith, and G. L. Ashcroft for their encouragement, suggestions, and criticisms. Discussions with Dr. R. H. Boyd and Dr. J. W. Cary contributed to the clarification of thought on many occasions.

The Egyptian government is gratefully acknowledged for the financial support necessary for the completion of my graduate program.

My wife, Yosria, has done a most admirable and unselfish job of being mother and helpmate through four years of challenge and sacrifice.

Mahmoud Hassan Abd-el Aziz

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The movements of salt and water, particularly in fairly dry soils or compacted shales, are important processes in both agronomic studies and hydraulics of deep ground water which is important in the location of oil.

In agronomic studies water movement in soil has received considerable attention. Movement of water to plant roots and hence through the plant is essential for the synthesis of plant tissue, which in turn is the basic material for sustaining animal life.

In addition to its importance in agriculture, water movement in porous media is of interest in many other areas. Drainage is essential in highway and airport construction. Water movement in and out of clay layers underneath building foundations can cause their settlement. The living cells are surrounded by a cell wall made of porous materials. The movement of water solutions through these walls is a vital process.

There are several good reviews of the subject of water movement in the literature (Klute, 1952; Philip, 1955, 1958; Scheideggar, 1960; Collins, 1961). However, most of the studies have been concerned with flow under saturated conditions. Since this case is much easier to solve, considerable progress has been made; and it is no longer of as much research importance as problems dealing with unsaturated flow.

The movement of salts in the soil medium is of prime importance in the application of fertilizers because the roots of a plant must come in contact with the fertilizer elements before adsorption occurs. The environments of active metabolism of plant roots and microorganisms are largely dependent upon the diffusion process occurring in the soil medium. This has long been appreciated and emphasized by various studies dealing with ionic diffusion (Bouldin and Black, 1954; Bloksma, 1957; Heslep and Black, 1954; etc.).

One of the most characteristic features of arid and semi-arid soils is their tendency to develop salinity. This is due to the movement of soil water carrying salts with it from deep soil to the surface by capillary rise where the water evaporates and salt accumulates.

The removal of the salts by leaching is well known in reclamation programs. Accordingly, the problem of simultaneous movement of water and salts in soils has been recognized and studied by soil scientists and hydrologists, among whom may be mentioned Biggar and Nielsen (1960, 1961, 1962), Kemper (1961b), Day (1956), Shapiro et al. (1960), and Qayyum and Kemper (1962). Because of the problems encountered in solving equations for flow of water in unsaturated soils, particularly when salts and water are considered to move simultaneously, no satisfactory solution has been obtained at the present time.

In the last three decades a thermodynamic theory of irreversible processes has been developed (Onsager, 1931; Denbigh, 1951; Prigogine, 1961; de Groot, 1959; de Groot and Mazur, 1962). The most important consequence of this theory is Onsager's reciprocal relation, which was derived by using the postulate of microscopic reversibility.

The theory of irreversible processes and Onsager's relation have been successful in treating several types of irreversible phenomena and for analyzing the kinetics of systems in which two or more processes occur simultaneously. The processes could be a combination of several fluxes such as water, salt, heat, and electricity that flow simultaneously in the system.

With this understanding, Taylor and Cary (1960) applied the theory of irreversible thermodynamics to the simultaneous flow of heat, salt, electricity, and water in Millville silt loam. The analysis verified the validity of applying the theory to soil systems. They also concluded that the theory will make possible the understanding of some processes connected with water transfer that have not been understood previously.

It is the purpose of this investigation to study the interaction of water and salt flow under unsaturated conditions using the theory of irreversible processes and also to find out if these two phenomena can be related by means of Onsager's reciprocal relation.

REVIEW OF LITERATURE

Conventional Transport Equations in Unsaturated Soils

The conventional description of transport of matter through unsaturated soils makes use of two equations, one for solute flow, and the other for flow of soil solution.

Solutes are usually transported from one part to another through the water in unsaturated soil as a result of random molecular motion known as diffusion.

The mathematical theory of diffusion in isotropic substance is based on the hypothesis that the rate of movement of the diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section. Thus, for diffusion in a horizontal column of porous medium from a reservoir containing a solution at one concentration into a reservoir containing a solution at another concentration where a steady state is ultimately attained, the rate of transfer of diffusing substance J could be determined by Fick's first law

$$J = -DA \frac{\partial c}{\partial x} \qquad (1)$$

where D is the coefficient of diffusion, A is the cross sectional area, c is the concentration of diffusing substance, and x is the space coordinate normal to the cross section.

Generally, it is not possible to investigate diffusion under conditions of constant concentration gradient, which implies the establishment of a steady state. One, therefore, has to determine the change of concentration with time. The flow of any substance must obey the principle of conservation of matter. This is usually expressed as

> the net excess of mass flux per unit time into or out of any infinitesimal volume element in the fluid is equal to the time rate of change of matter concentration in the volume element.

Mathematically, this is expressed as

$$\frac{\partial c}{\partial t} = - \nabla J \tag{2}$$

where ∇ is the "del" operator = $\partial/\partial x + \partial/\partial y + \partial/\partial z$. Combining equations (1) and (2) for a one dimensional horizontal flow gives

$$\frac{\partial c}{\partial t} = DA \frac{\partial^2 c}{\partial x^2} \tag{3}$$

which is Fick's second law of diffusion, derived on the assumption that D is constant, i.e. independent of the concentration and of the position. If this is not the case, we have

$$\frac{\partial c}{\partial t} = A \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x}\right) . \tag{4}$$

It is usually inconvenient to use equation (4), but one is compelled to make use of it when the diffusion coefficient shows a marked variation in space.

In a steady state there is no change of concentration with time. The steady state, therefore, is characterized by the condition

$$\frac{\partial c}{\partial t} = 0 \quad . \tag{5}$$

According to the special case of linear flow expressed by equation (3)

$$DA \frac{\partial^2 c}{\partial x^2} = 0 \quad , \quad \frac{\partial c}{\partial x} = \text{constant} \quad . \tag{6}$$

Consequently, a constant concentration gradient and a linear distribution of concentration exist if the diffusion coefficient can be treated as a constant.

When a solute is allowed to diffuse in free water medium, a plot of solute concentration against distance from the source may be represented by a smooth curve. The work of Bouldin and Black (1954), however, showed that this was not the case when diffusion of phosphorus took place in soil. Heslep and Black (1954) explained that these irregularities might be a result of the reaction between diffusing phosphorus and soil through which it was moving.

Porter et al. (1960) studied the rate of chloride diffusion in medium and fine textured soils at moisture tensions from 1/3 to 15 atmospheres. The measured rates of diffusion ranged from 0.133 - 0.003 times the diffusion rate which would occur in bulk solutions with the same concentration gradients. From the data collected, they obtained parameters for estimating the rates of ionic diffusion in soils. They showed that when diffusion takes place through water in a porous system, several geometric and interaction factors must be considered in the diffusion law. Since the interaction between the diffusing ions associated with the charged media act to decrease the diffusivity, an interaction parameter γ was considered. They also accounted for the turtuosity effect and the fraction of the volume occupied by water. Taking these factors into consideration, Fick's first law (1) was modified for a porous media to be

$$J = -D\ \gamma\ (\frac{L}{L_e})^2\ \theta\ A\ \frac{dc}{dx} \qquad (7)$$

$$= -D_e\ A\ \theta\ \frac{dc}{dx}$$

where θ is the volumetric moisture content, $(L/L_e)^2$ is a factor due to the turtuosity and directions of paths, γ is a factor which takes into account ionic interaction. The term $D\gamma(L/L_e)^2$ was called the effective diffusivity and is represented by the symbol D_e. In the same manner, Fick's second law (3) for a porous media will be

$$\frac{\partial c}{\partial t} = D_e \; A \; \theta \frac{\partial^2 c}{\partial x^2} \quad . \tag{8}$$

In applying equation (8) to the diffusion of ions in soils, they assumed that D_e is independent of concentration. However, they reported that these equations should give a good estimate of movement of nitrates, sulfates, and halides in soils; also the treatment should be valid for calcium movement in Ca-saturated soil, sodium movement in Na-saturated soil etc.

Counter ion

In the paper by Husted and Low (1954), it was shown that the diffusion of a given ion is practically controlled by the rate of diffusion of the counter (co-diffusing) ion. The diffusion of one ion is coupled to that of the other ion to maintain neutrality. The results of their study indicate that the adsorbed ions do not diffuse at the immediate surface of the clay particles, but diffuse in the diffuse ionic layer with the same relative rates as in true solutions. It is postulated, therefore, that the diffusion coefficients vary with the proximity to the clay mineral surface, being zero at the surface and increasing outward from the surface until it attains a value equal to that in true solutions.

Dutt and Low (1962a, b) determined the apparent diffusion coefficients for the steady state of LiCl, and NaCl in pastes of Li clay and Na clay respectively. They found that these coefficients decreased with increasing salt concentration. The decrease was ascribed to a salt-induced change in the fractions of cations and anions in the more viscous, adsorbed water. They also reported that the integral[1] diffusion coefficients were much lower for diffusion through the paste than diffusion within the paste. Therefore, it was concluded that salt diffusion was slowed down at paste-solutions interfaces. The postulate was made that the negatively charged clay pastes repelled the anion, reducing its diffusion rate at the inlet interface, and attracted the cations reducing their diffusion rate at the outlet interface. This is in accordance with Kemper's experiment (1960) by which he showed that a clay paste will filter salts from a solution which is forced through it.

Potassium and chloride transference numbers and apparent mobilities were measured in three soil materials at various concentrations by Letey and Klute (1959a, b). They found that the potassium transference number decreased, whereas its apparent mobility increased as the salt concentration increased. On the other hand, the apparent mobility of chloride decreased with increasing salt concentration. The results were explained on the basis of the ionic distribution with respect to the charged clay surface and how they are influenced by the soil colloid charge and viscosity of water. From the apparent mobilities salt diffusion coefficients were calculated, and they were found to increase with salt concentrations. This is in contradiction with the results of Dutt and Low (1962b).

The theory of moisture flow through unsaturated soil is based on the assumption that, at a given moisture content, volume flux of water per unit area is directly proportional to the potential gradient (Richards, 1931; and Childs and George, 1950). This gives an expression analogous to

---

[1] See derivation and definition in Dutt and Low (1962b).

Darcy's law

$$v = -K_{(\theta)} \nabla \phi \tag{9}$$

where v is the volume flux per unit area, $\nabla\phi$ is the driving force causing movement, and $K_{(\theta)}$ is a parameter which is called the capillary conductivity or unsaturated permeability. Mathematically, this expression differs from Darcy's law only in that the quantity $K_{(\theta)}$ is not constant but is a function of the soil water content (θ). Analytical proof of the validity of equation (9) depends on the assumption that the drag between the phases in the unsaturated media is negligibly small (Philip, 1957).

In addition to the law of motion, i.e. equation (9), the flow of fluids must obey the principle of conservation of matter, equation (2), which if considered for a unit volume of fluid, gives

$$\frac{\partial \rho}{\partial t} = - \nabla \rho v \tag{10}$$

where ρ is the fluid density and v is the volume flux per unit cross sectional area.

In a porous medium (soil) equation (10) must be modified to consider the fact that not all the space per unit volume is available for fluid flow. Hence, it may be written as

$$\frac{\partial(\rho_B \theta)}{\partial t} = - \nabla \rho v \tag{11}$$

where ρ_B is the bulk density and θ is the soil moisture content on a volume basis. Combining equations (9) and (11) gives the following equation

$$\frac{\partial(\rho_B \theta)}{\partial t} = \nabla(\rho k \nabla \phi) \tag{12}$$

which is called the general equation of fluid flow. It is usually convenient to separate the total potential ϕ into capillary (ψ) and gravitational potentials (gz)

$$\frac{\partial(\rho_B\ \theta)}{\partial t} = \nabla(\rho k \nabla \psi) + \rho g \frac{\partial k}{\partial z} \quad . \tag{13}$$

In 1936 Childs suggested that moisture movement in porous materials is a diffusion phenomenon. From Fick's first law (1) and the equation of continuity (2), he showed that for one dimensional flow

$$\frac{\partial c}{\partial t} = \left(\frac{k}{\rho_B}\right) \frac{\partial^2 c}{\partial x^2} \tag{14}$$

where c in this case is the ratio of mass of water to mass of dry matter, and k is the diffusion coefficient assumed by Childs to be constant. Later Kirkham and Feng (1949) showed that the linear flow case expressed by equation (14) is not an acceptable mathematic model for the movement of water in unsaturated soils. In 1950 the concentration-dependent diffusivity was developed by Childs and George. This development implied the existence of a general partial differential equation describing water movement in the liquid phase which would prove to be of the diffusion type, i.e. parabolic second order.

When diffusion type equations are used to express flow theory of unsaturated soil, the capillary potential ψ and the moisture content θ are related by a single valued function, that is the hysteresis effect is disregarded. Klute (1952) developed a nonlinear diffusion equation, which for one dimensional, horizontal flow is

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[D_{(\theta)} \frac{\partial \theta}{\partial x}\right] \tag{15}$$

where $D_{(\theta)} = K_{(\theta)} \frac{\partial \psi}{\partial \theta}$ and is called diffusivity. Although in practice it is not feasible to attempt a complete analytical solution of the diffusion equation (15), it seems to be suitable for describing isothermal moisture movement in unsaturated soils for some applications.

This does not, however, imply that the mechanism of water transfer is diffusion in the same sense as diffusion in gases, liquids, and solids due to random molecular motion. Several mechanisms are probably involved, depending upon the water content and the nature of soil particles and their arrangement. Vapor movement may be included in the equation to the extent that the water vapor tends toward equilibrium with the liquid water surrounding the pore.

Several different approaches have been utilized in order to obtain a solution of the diffusion equation (15). Each of these approaches requires assumptions that limit the application of the solutions. One approach limits the solution to a steady state flow where $\frac{\partial \theta}{\partial t} = 0$, a condition that is seldom met in soil. Methods of solving the diffusion equation for transient state flow that assumes a constant diffusivity have been shown to be generally unaccepted (Kirkham and Feng, 1949). Numerical or graphical methods of solution are necessary when diffusivity varies. The Boltzmann transformation was used by Bruce and Klute (1956) to convert the non-linear partial differential equation (13) into an ordinary differential equation. However, the transformation limits the solution to a uniform medium, semi-infinite in extent, and containing a uniform concentration initially (Crank, 1956). For finite systems, with arbitrary initial moisture concentration, a numerical approach seems to provide a promising method of solution (Philip, 1955, 1957; Ashcroft et al., 1962).

Gardner (1956) and Staple and Lehane (1954) have also suggested methods to determine the capillary conductivity for flow in a transient state. These methods can only give approximate results because of the generalization and assumptions inherent in them.

Kemper (1961a) modified the viscous and diffusive laws of water movement to account for the effects of turtuosities, diffuse layer of adsorbed cations, and variable viscosity of water near particle surfaces. Equations representing the two types of flow were combined to give a general equation for flow in thin films.

Transition state theory of Eyring has been applied to a study of the diffusion constant (Wang et al., 1953). Eyring's equation for diffusivity is written

$$D_o = K' \, T \exp \left(-\Delta F^{\dagger}/RT\right) \qquad (16)$$

where D_o is the diffusivity, K' is a constant involving Boltzmann's constant, Plank's constant and lattice factors, and $\Delta F^{\dagger}$ is the free energy of activation. Experimental evidence gathered by Wang and his co-workers verified the validity of Eyring's equation (16) (Glasstone et al., 1941).

An interaction between flow of chloride ions and soil water has been shown by Biggar and Nielsen (1962). Day (1956) reported that the flow of a solute may occur at much greater rate than can be expected by ion diffusion. He attributed this effect to a mechanism referred to as hydrodynamic dispersion. Biggar and Nielsen (1960, 1961, 1962) have verified experimentally that both diffusion and hydrodynamic dispersion must be included in the theory of solute and water transfer in soil.

Salt concentration differences can be a major factor in causing water flow in soils. Kemper (1961b) compared experimentally a solute induced free energy gradient with a pressure-induced free energy gradient in causing water to flow. Qayyum and Kemper (1962) studied the effect of salt concentration gradients on movement of moisture within soil profiles at five different moisture contents. Their data indicate a definite movement of moisture to the salt-bearing surface of these profiles. There was also greater evaporation from soil containing low levels of salt than from those having no salt. Taylor and Cary (1960) have shown that moisture movement may occur in saturated soil when gradients of temperature, salt, electricity, or pressure are imposed across a soil sample.

Thermodynamic Preliminaries

Of all the macroscopic theories of chemistry and physics, classical thermodynamics is both the most powerful and the best founded in experiment (Lewis and Randall, 1961). The foundation of this theory was laid before the middle of the nineteenth century. The work of Black, Rumford, Carnot, Joule, Kelvin, and Helmholtz established the basic principles of the theory of energy. Next came the task of building from these principles a great body of thermodynamic theorems. This was the work of many men, among whom may be mentioned Vont Hoff and Williard Gibbs. Thereafter came the stage of thermodynamic development which is characterized by the design of more specific thermodynamic methods and their application to particular physical or chemical processes.

Through the application of classical thermodynamics, scientists were able to develop the necessary and sufficient conditions for only equilibrium processes. This was due to the fact that classical thermodynamics is essentially a theory of equilibria and is largely concerned with closed systems which do not exchange matter with the surroundings. Soil or living organisms, on the other hand, are open systems in a state of constant flux. Therefore, for the description of biological processes in such open systems, a thermodynamic theory of flow in open systems is needed (Taylor, 1963).

An advancement toward this goal was made during the last thirty years through the establishment of the theory of thermodynamics of irreversible processes.[2] This theory is based upon the idea that flow occurs as a result of molecules in the system deviating from equilibrium, and that, on the average, the return of molecules to equilibrium follows the usual phenomenological laws. It is assumed that if these deviations are small enough, the Gibbs equation of equilibrium thermodynamics (classical) will express the instantaneous thermodynamic state at any point in the system. These conditions are obviously correct if the system is near enough to equilibrium and incorrect if it is far from equilibrium. This assumption has been shown to be valid provided the gradients in the system are small (Prigogine, 1961; de Groot, 1959).

As early as 1850 Clausius introduced the concept of non-compensated heat, which characterizes irreversible processes by an increase of entropy

$$dS > \sum \frac{\delta q}{T} \tag{17}$$

---

[2] The derivations and proof of the theory upon which thermodynamics of irreversible processes is based are found in the statistical mechanical considerations of fluctuation theory, microscopic reversibility, and regression of fluctuations which are assumed to follow ordinary phenomenological laws. The proof is given by de Groot (1959).

for irreversible processes, where S is the entropy, q is the heat transported across the boundaries of the system, T is the absolute temperature of the surroundings at the boundaries, and δ refers to an inexact differential. Equation (17) could be turned into an equality such as

$$dS = \sum \frac{\delta q}{T} + dS_i \qquad (18)$$

where dS_i is called the entropy created internally due to the irreversible process.

In non-equilibrium thermodynamics, the so-called entropy balance plays a central role. This expresses the fact that the entropy of a volume element changes with time for two reasons. First, it changes because entropy flows into the volume element, second because there is an entropy source due to irreversible phenomena inside the volume element (Prigogine, 1961). The rate of change of entropy source (dS_i) with respect to time ($\frac{dS_i}{dt}$) is called the entropy production (σ).

When $T \frac{dS_i}{dt}$ (the dissipation function) is calculated for any system, it turns out to be a sum of terms each being a product of a flux characterizing an irreversible process J_i, and a quantity called thermodynamic force X_i

$$T\sigma = T \frac{dS_i}{dt} = \sum J_i \, X_i \quad . \qquad (19)$$

The entropy production is thus chosen as the fundamental magnitude characterizing the irreversible processes occurring in a system (de Groot and Mazur, 1962).

Since equation (19) contains the irreversible fluxes as unknown parameters and therefore cannot be solved with given initial and boundary conditions for the state of the system, an additional set of phenomenological equations which relate the irreversible fluxes and the thermodynamic forces appearing in the entropy production have to be established. Actually, as early as the beginning of the nineteenth century, several phenomenological laws describing irreversible processes in the form of proportionalities existed, e.g. Fourier's law relates heat flow and temperature gradient, Ohm's law relates electrical current and electrical potential gradient, Newton's law relates shearing force and velocity gradient, the chemical reaction law relates reaction rate and chemical potentials, and two laws of particular interest to soil scientists and biologists; Fick's law relates flow of a component of a mixture and its concentration gradient, and Darcy's law relates flow of water and its hydraulic gradient. When two or more of these phenomena occur simultaneously, they interfere and give rise to new effects. Such cross phenomena were realized as early as 1801 in the electro-osmotic flow where a volume flow of liquid is produced by an electrical driving force. Other well-known examples of intereference are the Seebeck effect, where a temperature difference in a thermocouple produces a flow of electricity, and the Soret effect, where a coupling of diffusion and heat conduction gives rise to thermal diffusion, etc. (Taylor, 1963).

In general, if there is more than one irreversible process occurring, it is found experimentally that each flow J_i is not only linearly related to its conjugate force X_j, but is also linearly related to all other forces found in the entropy production expression. Accordingly, if the general linear coefficient is denoted by L_{ij}, the general form for J_i is

$$J_i = \sum_{i=1}^{n} L_{ij} X_j \quad . \tag{20}$$

The straight coefficients L_{ii} (i=j) are always positive while the cross coefficients L_{ij} ($i \neq j$) may be either positive, negative, or zero.

The most important step added to the irreversible thermodynamics theory is the so-called reciprocity theorem presented by Onsager (1931a, b). This principle states that

> provided a proper choice is made for the fluxes J_i and forces X_i, the matrix of phenomenological coefficients L_{ij} is symmetrical or that the cross coefficients are related by

$$L_{ij} = L_{ji} \quad . \tag{21}$$

Onsager's proof[3] of the validity of equation (21) is based on the idea of connecting macroscopic and microscopic properties by means of statistical mechanics of fluctuations of an aged system; that is a system which has been isolated for a sufficient length of time to come close to equilibrium. The importance of the Onsager Reciprocal Relation expressed in equation (21) is that it reduces considerably the number of experimental quantities necessary to describe the irreversible flows. Thus, the experimental verification of (21) is of great interest in current literature.

Dunlop (1959a, b) studied the isothermal diffusion process for four compositions for the ternary system in which NaCl-KCl diffused simultaneously in water at 25° C. He analyzed activity coefficient data in the literature and combined them with the diffusion data to test the Onsager reciprocal relation. He found that this relation is valid within experimental error for the four compositions. Miller (1959) has also reported several tests of Onsager's relation, but he used estimates rather than experimental values for the solute activity coefficients.

---

[3] The proof and derivations of Onsager's theorem are not given in this dissertation, and the interested reader is referred to de Groot (1959), chapters 2 and 11.

In 1960 the validity of Onsager's theory was thoroughly checked by Miller for various systems, e.g. thermoelectricity, electrokinetics, isothermal diffusion, and aniostropic heat conduction. The experimental checks were sufficiently good that the validity of the theory seemed to be unquestionable.

Wendt (1962), Woolf et al. (1962), among many others, studied the isothermal diffusion for binary and ternary systems. In each case, the experimental evidence was overwhelming in favor of the validity of Onsager's relation.

At that time very little has been done to apply the theory to either soil or biological systems. However, numerous speculations have been made by various authors on the application of the theory to describe transfer processes through porous media or membranes. Hutcheson, Nixon, and Denbigh (1948) had discussed the possibility of such an application to analyze the thermo-osmosis of liquids through porous material. Winterkorn (1958) pointed out that any mass transfer through a moist soil might undergo coupling with a number of different potentials and suggested that analysis with the theory of irreversible processes might be useful. Spiegler (1958) also speculated that the theory could be applicable for porous materials such as base exchange columns, natural soil aggregates, shales, plug of fibers, etc.

Staverman (1952) has used the theory of irreversible thermodynamics to obtain expressions for the osmotic pressure measurements in membrane processes. However, these expressions could not be applied directly to the physiological measurements described in the literature. Kedem and Katchalsky (1958, 1961) extended the work of Staverman and modified the equations derived by the methods of thermodynamics of irreversible processes in order to apply them to biological permeability data. Michaeli and Kedem (1961) have described the transport of ions and solvent through a membrane in terms of the transfer coefficients. Haase (1959) and Haase and Steinert (1959) have developed equations to evaluate and interpret the measurements of osmosis, thermo-osmosis across permeable and semi-permeable membranes of cellophane sheets and cellophane with a precipitate of copper ferrocyanide respectively. Their results did not confirm Onsager's relation. They ascribed that to certain experimental difficulties in the membranes.

Cary and Taylor (1962) were the first to apply the theory of irreversible processes in the analysis of simultaneous flows of heat and water in soils. The analysis confirmed the validity of Onsager's relation.

In light of the previous review, there is not yet experimental verification for the application of the theory to the more complicated system of simultaneous movement of water and salts in porous media which is considered in this investigation.

Table 1. Definition of symbols.

Symbol	Definition
Δ	difference between vessels A and A'
i, k (subscripts)	chemical components
ln	natural logarithm
R	universal gas constant
L	phenomenological coefficient
t	time
T	absolute temperature (°K)
μ	chemical potential
E	electricity
p	total pressure
V and subscript v	volume
$\bar{v}$	specific volume
S	entropy
S_i	internal entropy of the system
s subscript	salt
w subscript	water
L_{ik}	linked phenomenological coefficient
J	flux
α	relative activity at constant temperature and pressure
γ	activity coefficient
X	thermodynamic affinity (driving force)
σ	entropy production per unit time
x	mole fraction

Table 2. continued.

Symbol	Definition
C	concentration
ρ	density
η	viscosity of water

THEORY DEVELOPMENT

Consider a system (figure 1) in which an electrolytic solution (KCl) is contained in each of two vessels A and A' and separated by a porous body B. The system is under isothermal condition, and the porous plug is at constant moisture content. The two reservoirs are at different pressures and contain solutions of different concentrations. Consider changes in the two vessels and neglect reactions and processes that occur within the porous body. Such a system is called discontinuous because we neglect reactions within the porous body. The expression for the entropy production (σ) is given by equation (19). The two driving forces operating in the system are the difference in chemical potential of water and salt. However, the flow of ions may induce an electric potential difference ($\Delta\mu_E$), and an additional flow of electrical current J_E. The fluxes corresponding to these three driving forces operating in the system are respectively the solvent flux J_w, the flux of solute J_s, and the electric current J_E. The thermodynamic driving forces on a single salt (KCl), water, and electricity are $\Delta\mu_s$, $\Delta\mu_w$, and $\Delta\mu_E$ respectively (de Groot, 1959). For a constant temperature, the entropy production (19) for flow of water (J_w), KCl (J_s), and electricity (J_E) is

$$\sigma = J_w \frac{\Delta\mu_w}{T} + J_s \frac{\Delta\mu_s}{T} + J_E \frac{\Delta\mu_E}{T} \quad . \qquad (22)$$

Since electric flow does not occur in this study, the system was simplified by considering only the case where the electric gradient does

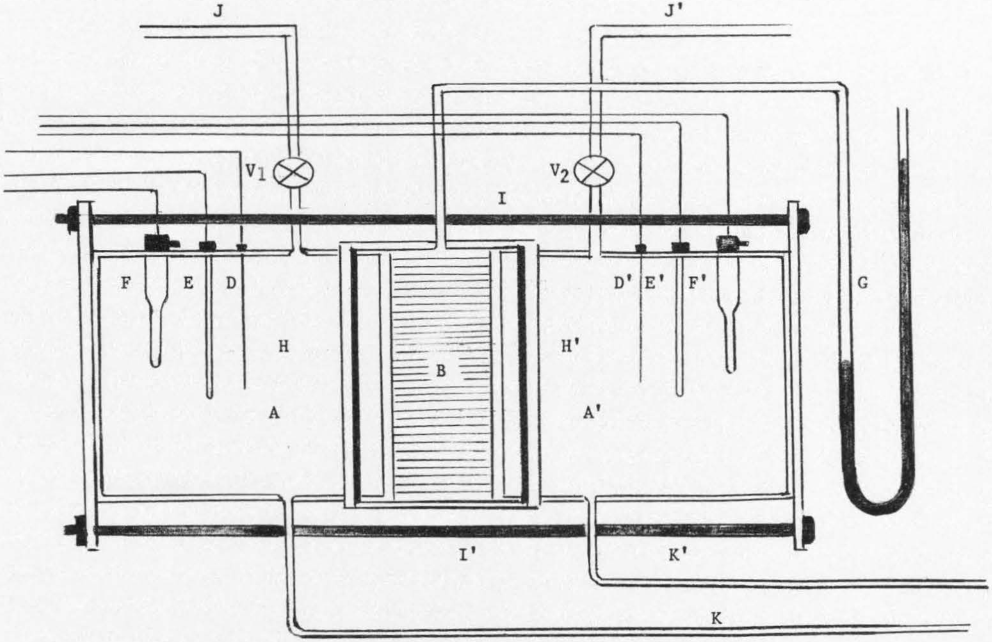

Figure 1. Diagram of the experimental diffusion cell where A, A' are solution compartments, B is porous material (soil or kaolinite), C,C' are glass-bead porous plates, D, D' are platinum electrodes, E,E' are silver-silver chloride electrodes, F,F' are calomel electrodes, G is the mercury manometer, H,H' are the O rings, I,I' are the brass bolts, J,J' are the solutions inlet tubes, K,K' are capillary flow tubes, and V_1 and V_2 are the valves.

not exist.[4] Thus, equation (22) becomes

$$T\sigma = J_w \, \Delta\mu_w + J_s \, \Delta\mu_s \quad . \qquad (23)$$

In the following, we shall make the approximation that the chemical potential for ideal solutions may be used, so that at constant temperature

$$\Delta\mu_i = \mu_i^{II} - \mu_i^{I} = \bar{v}_i \Delta p + RT \, \Delta \ln \alpha_i \qquad (24)$$

where $\bar{v}_i$ is the partial specific volume of the constituent i, Δp is the difference in pressure between the two vessels, and α_i is the relative activity of the constituent i at constant pressure (Kedem and Katchalsky, 1961). Thus, equation (24) for KCl becomes

$$\Delta\mu_s = \mu_s^{II} - \mu_s^{I} = \bar{v}_s \Delta p + RT \, \Delta \ln \alpha_s \qquad (25)$$

and the corresponding equation for water is

$$\Delta\mu_w = \mu_w^{II} - \mu_w^{I} = \bar{v}_w \Delta p + RT \, \Delta \ln \alpha_w \quad . \qquad (26)$$

The three forces (Δp, $\Delta \ln\alpha_w$, and $\Delta \ln\alpha_s$) are not independent parameters but are related by the Gibbs-Duhem equation (Lewis and Randall, 1961, p. 261)

$$C_w \, \Delta \, \mu_w + C_s \, \Delta \, \mu_s - \Delta p = 0 \qquad (27)$$

where C_w and C_s are the concentration (moles/liter) of the water and salt respectively.

Introducing equations (25) and (26) into (27), the Gibbs-Duhem relation is given by

---

[4] This was provided for in the system. See Experimental Procedure.

$$C_w(RT \; \Delta \; \ln \; \alpha_w) + C_s(RT \; \Delta \; \ln \; \alpha_s) = 0 \qquad (28)$$

since

$$\overline{v}_w + \overline{v}_s = 1 \quad . \qquad (29)$$

We define the ratio

$$r = \frac{\Delta \; \ln \; \alpha_w}{\Delta \; \ln \; \alpha_s} = - \frac{C_s}{C_w} \qquad (30)$$

from equation (29).

Corresponding to the two driving forces, $\Delta\mu_w$ and $\Delta\mu_s$, we have a flow of water J_w, a flow of salt J_s, and a volume change J_v resulting from a net flow of water and salt. Since these three flows are not independent, we have a restricting condition upon them (Michaeli and Kedem, 1961)

$$J_v = \overline{v}_w \; J_w + \overline{v}_s \; J_s \quad . \qquad (31)$$

In the case of dilute solutions used in this study, the partial specific volume ($\overline{v}_s$) for the KCl is small and is assumed to be zero, while $\overline{v}_w$ is considered to be the specific volume of pure water (Lewis and Randall, 1961, p. 208). Thus equation (31) reduces to

$$J_v = J_w \quad . \qquad (32)$$

Using the same argument, equation (25) becomes

$$\Delta\mu_s = RT \; \Delta \; \ln \; \alpha_s \quad . \qquad (33)$$

Introducing equations (26), (32), and (33) into equation (23), we get

$$\begin{aligned} T\sigma &= J_w(\bar{v}_w \Delta p + RT\ \Delta\ \ln\ \alpha_w) + J_s(RT\ \Delta\ \ln\ \alpha_s) \\ &= J_w\ \bar{v}_w \Delta p + J_w\ RT\ \Delta\ \ln\ \alpha_w + J_s(RT\ \Delta\ \ln\ \alpha_s) \quad . \end{aligned} \tag{34}$$

According to partial Gibbs potential (Taylor, 1963), RT Δ ln α_w is not independent of the salt concentration difference. At constant temperature and pressure and with a single salt in the system, the dependence of water activity on salt concentration is given by Taylor (1963)

$$RT\ \Delta\ \ln\ \alpha_w = \int_{C_{s1}}^{C_{s2}} \left(\frac{\partial \mu_w}{\partial C_s}\right)_{T,P,\theta} d\ C_s \quad . \tag{35}$$

Since $\Delta\mu_w$ and $\Delta\mu_s$ are not mutually independent, we will arbitrarily introduce the two independent driving forces Δp and Δ ln α_s into the entropy equation (19) and determine the appropriate conjugate fluxes. The flux $J_w = J_v$ corresponds to the pressure difference and a new flux J_χ corresponds to Δ ln α_s. This is expressed mathematically from (19) as

$$T\sigma = J_w(\bar{v}_w \Delta p) + J_\chi(RT\ \Delta\ \ln\ \alpha_s) \quad . \tag{36}$$

By equating (23) and (36) and considering (30), the flux J_χ is defined by

$$J_\chi = J_w\ r + J_s \quad . \tag{37}$$

According to the Onsager theory (Onsager, 1931a, b), the fluxes are related to the driving forces by

$$\begin{aligned} TJ_w &= -L_{ww}(\bar{v}_w \Delta p) - L_{ws}\ (RT\ \Delta\ \ln\ \alpha_s) \qquad \text{(a)} \\ TJ_\chi &= -L_{sw}(\bar{v}_w \Delta p) - L_{ss}(RT\ \Delta\ \ln\ \alpha_s) \qquad \text{(b)} \end{aligned} \tag{38}$$

and

$$L_{ws} = L_{sw} \quad . \tag{39}$$

The physical meaning of equation (38) may be seen in the following way. Each of the fluxes is determined by its conjugate driving force [J_w by pressure difference (Δp) and J_χ by the difference in logarithms of salt activity ($\Delta \ln \alpha_s$)] plus a linked flow wherein the difference in salt activity produces a water flux known as osmotic flow and a pressure difference causes a solute flux known as ultrafiltration. This interdependence is explained by the coefficients L_{ws} and L_{sw}.

Substituting (38a) into (37), we get

$$J_\chi = r[-L_{ww} \frac{\bar{v}_w \Delta p}{T} - L_{ws} R \Delta \ln \alpha_s] + J_s \quad . \tag{40}$$

Equating (38b) and (40), then solving for J_s, gives

$$J_s = [r L_{ww} - L_{sw}] \frac{\bar{v}_w \Delta p}{T} + [r L_{ws} - L_{ss}] R \Delta \ln \alpha_s \tag{41}$$

and (38a) for the flow of water remains unchanged.

We now have our flux equations in terms of measurable variables of water flux J_w and salt flux J_s with equations (38a) and (41) as follows

$$\begin{aligned} -TJ_w &= L_{ww} \bar{v}_w \Delta p + L_{ws} RT \Delta \ln \alpha_s & \text{(a)} \\ -TJ_s &= [L_{sw} - r L_{ww}] \bar{v}_w \Delta p + [L_{ss} - r L_{ws}] RT \Delta \ln \alpha_s \ . & \text{(b)} \end{aligned} \tag{42}$$

Our problem is to test equation (42) to see if $L_{sw} = L_{ws}$. Using the appropriate experimental data which relate the flux terms to the driving forces in the system, also determining the magnitude of the coefficient r and that of the driving forces,[5] equation (42a) and (42b) contain four

---

[5] An example of calculation is shown in Appendix B.

unknown coefficients (L_{ww}, L_{ws}, L_{sw}, L_{ss}) which must be evaluated. Since there are two equations and four unknowns, two of the phenomenological coefficients must be evaluated independently of the driving forces in the system. In this study a range of salt concentration gradient was selected, such that L_{ww} was constant and independent of salt concentration. Thus L_{ww} and L_{ws} could be evaluated by relating the experimental data of water flux to the corresponding driving force. The other phenomenological coefficients L_{ss} and L_{sw} could be determined by simultaneously solving equation (42b) with experimental data relating salt flux to driving forces in a way that the salt driving force vector is considered for two opposite directions. This makes it possible to solve the equations and see if $L_{ws} = L_{sw}$ as predicted.

Units of the components in the rate equations (42a) and (42b) are as follows:

J_w, J_s = gm $\sec^{-1}$ cm^{-2}

$\bar{v}_w = \text{cm}^3\ \text{gm}^{-1}$

Δp = dyne cm^{-2} = gm cm^{-1} $\sec^{-2}$

R = erg. gm^{-1} deg^{-1} = cm^2 $\sec^{-2}$ deg^{-1}

T = deg K°

$\Delta \ln \alpha = \dfrac{\ln \alpha_{II}}{\ln \alpha_I}$ = dimensionless quantity

$r = \dfrac{\Delta \ln \alpha_w}{\Delta \ln \alpha_s}$ = dimensionless quantity

L_{ww}, L_{ws}, L_{ss}, L_{sw} = gm. sec. deg. cm^{-4}.

EXPERIMENTAL PROCEDURE

Apparatus

The evaluation of the phenomenological coefficients L_{ww}, L_{ws}, L_{sw}, L_{ss}, and the consequential test of Onsager's reciprocal relations are achieved by solving each of the rate equations (42a), (42b), with appropriate salt and water flux data. Diffusion cells were constructed so that solutions of different salt concentrations could be brought into contact with opposite ends of the soil plug, as shown in figure 1. The cells were made from lucite tubing. Solution compartments A and A' were cylinders 7.6 cm inside diameter and 11.5 cm long, and contained a cross-sectional area of 45.341 cm^2 and a volume of 521.421 cm^3. Fritted glass-bead porous plates were connected to compartments A and A' at the ends next to a porous plug column through which diffusion took place. The porous media was confined between the two porous plates in compartment B, which was a cylinder 8.8 cm inside diameter and 2.86 cm long. O rings were used to achieve tight seals, and the whole diffusion cell unit was held together with brass bolts which were inserted through corresponding holes. The entire system was placed inside a specially designed air bath which controlled temperature to ± 0.1° C.

Each end compartment had an opening in the top for introducing solutions and was connected from the bottom to a calibrated capillary tube 100 cm long. It was necessary to keep the solutions on either side of the porous plug at uniform pressure and at constant composition. This was achieved by continuously stirring the solutions in chambers A and A' with magnetic stirrers. Pressure was introduced into the porous plug column between the fritted glass plates in order to keep the soil unsaturated. This pressure was measured with a mercury manometer attached to the system. In order to maintain the unsaturated media at constant moisture content, constant pressure of 23.4 cm Hg was applied to the porous media during the course of the experiment.

The apparatus (figure 1) was designed so that a variable pressure difference could be established across the system from compartment A to A' simultaneously with the salt concentration difference.

Sample Preparation

The porous materials used in this study were Millville silt loam and kaolinite.[6] Both samples were saturated with potassium chloride. This was accomplished by preparing suspensions of soil and clay in a 3 N KCl solution. The suspensions were allowed to equilibrate with KCl solutions for a 15-day period, after which the supernatant liquid was removed. Following this treatment, suspensions were then prepared with fresh 3 N KCl solutions, stirred, and allowed to settle until the supernatant liquid was clear; then it was discarded. This process was repeated four times. To remove the excess salts, the samples were then washed free of chloride with alcohol. The soil was passed through a 2 mm round-hole sieve, thereafter both soil and kaolinite were saturated with distilled water for a period of four hours. The saturated samples were transferred to pressure chambers and a desired moisture potential was

---

[6] Kaolinite samples were obtained from Wards National Science Establishment, P. O. Box 1712, Rochester 3, New York, and are listed as Catalog #5 from Lamar pit.

obtained by extraction of water. Soil and kaolinite samples were compacted in compartment B of the diffusion cell at bulk densities of 1.328 and .853 g cm^{-3} respectively.

Temperature Control

All measurements were carried out in a room at ± 0.5° C. In addition, the diffusion cells were placed in a constant temperature air bath, figure 2. Temperature was controlled in the bath by a continuous cooling and intermittent heating arrangement. The control circuit consisted of a mercury thermoregulator, an electronic relay, a resistance heating coil which was inserted inside the inlet opening of an electric blower to provide a uniform heat distribution, and a heat exchanger from an automobile through which cool water was circulating. A thermometer sensitive to ± 0.1° C was placed in the air bath. Since observations revealed no temperature variation, it is reasonable to expect that temperature variations were less than 0.1° C. All experiments were conducted at three constant temperatures, 15, 25, and 35° C.

Flux Measurements

The fluid velocity was measured by means of air bubbles introduced into both the inflow and outflow capillary tubes connected to the solution chambers. The water flux J_w was evaluated by multiplying the measured velocity by the cross sectional area of the capillary. The salt flux J_s was determined by measuring the voltage developed between silver-silver chloride and calomel electrodes installed in each solution compartment. Silver-silver chloride electrodes were constructed in the soil physics laboratory using the standard method of Daniel et al. (1956, p. 178). Electrodes were calibrated before installation, and calibration curves

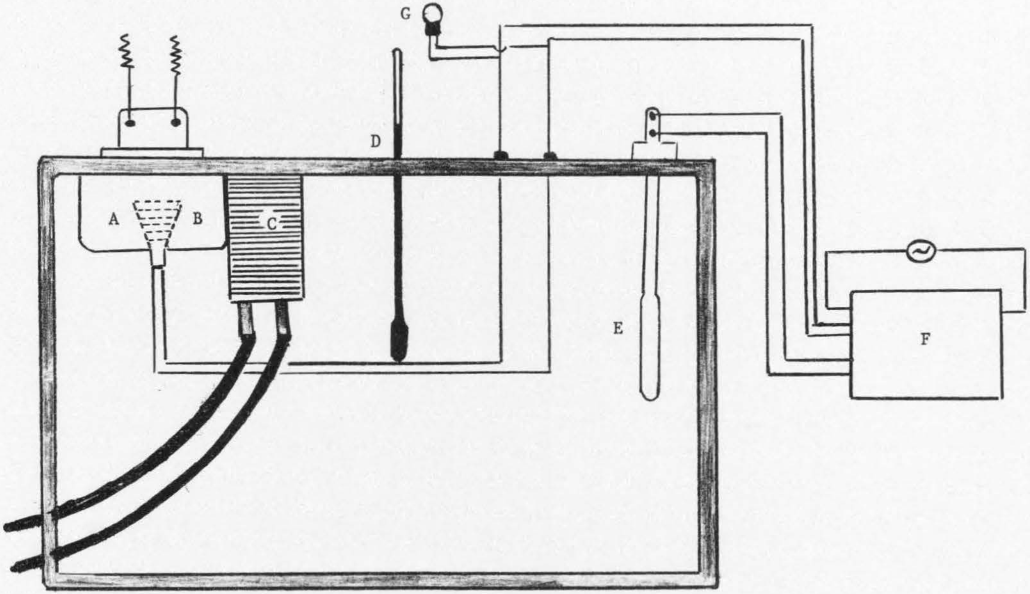

Figure 2. Air bath for temperature control where A is electric blower, B is resistance heating coil, C is car heater radiator, D is the thermometer, E is mercury thermoregulator, F is electronic relay, and G is a light bulb indicating open or closed circuit.

(figures 3, 4, 5, and 6) were obtained by plotting voltage readings as a function of concentration at 15, 25, and 35° C. Considering the concentration and volume of each chamber at the beginning and at the end of each run, the net amount of salt transferred was evaluated by subtracting the initial salt content from the final salt content.

Electric Potential Elimination

A gradient of electrical potential develops in the system because of the transport of ions. Furthermore, this potential may develop if the flow in the system takes place by diffusion. Electrical potential, however, could be eliminated if electrodes are placed in the solution chambers and their electrical potential difference externally maintained equal to zero. In the system under study an electrical potential equal and opposite in polarity to that developed in the system was introduced. The opposing potential was achieved through a slide wire potentiometer connected to two platinum electrodes, one of which is located in solution compartments at either end of the porous column (figures 1 and 7).

Preliminary Experiment

The objective of the preliminary experiment was to determine a region where the phenomenological coefficient L_{ww} is independent of pressure difference gradient and salt concentration.

Consider the system in which two chambers of distilled water or potassium chloride solution are communicating by means of a soil or clay column, provided that a salt concentration difference does not exist in the system. If a pressure (or suction) difference is maintained between the chambers, a net flux of water (or fluid) will result, entirely

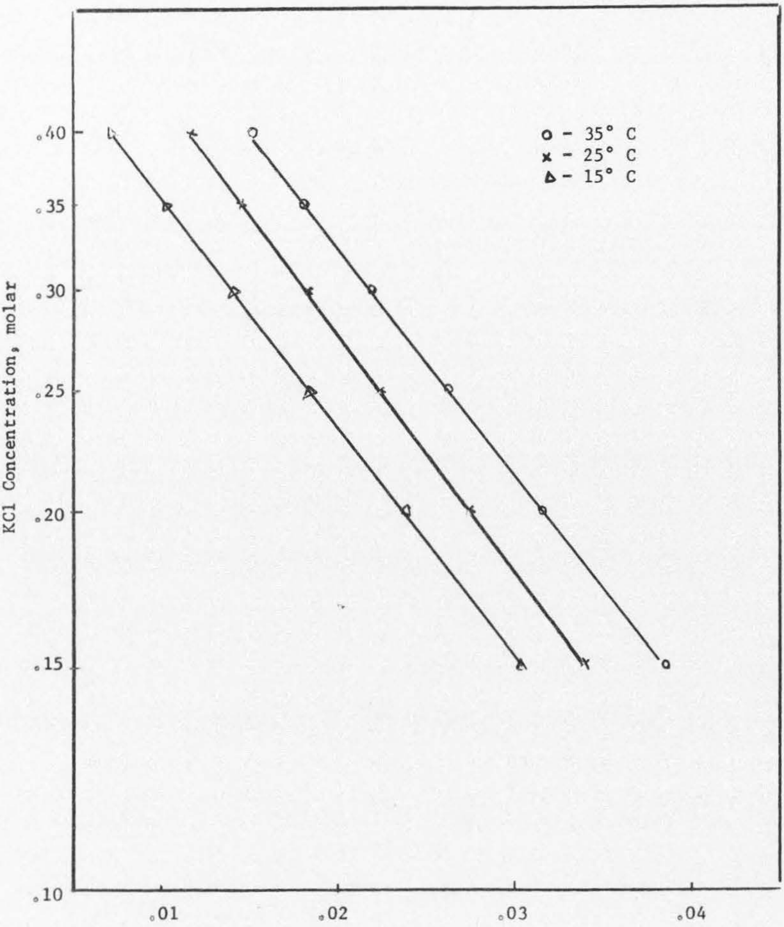

Figure 3. Calibration curve for [silver-silver chloride]-[calomel] electrodes placed in Compartment A of the diffusion cell containing soil.

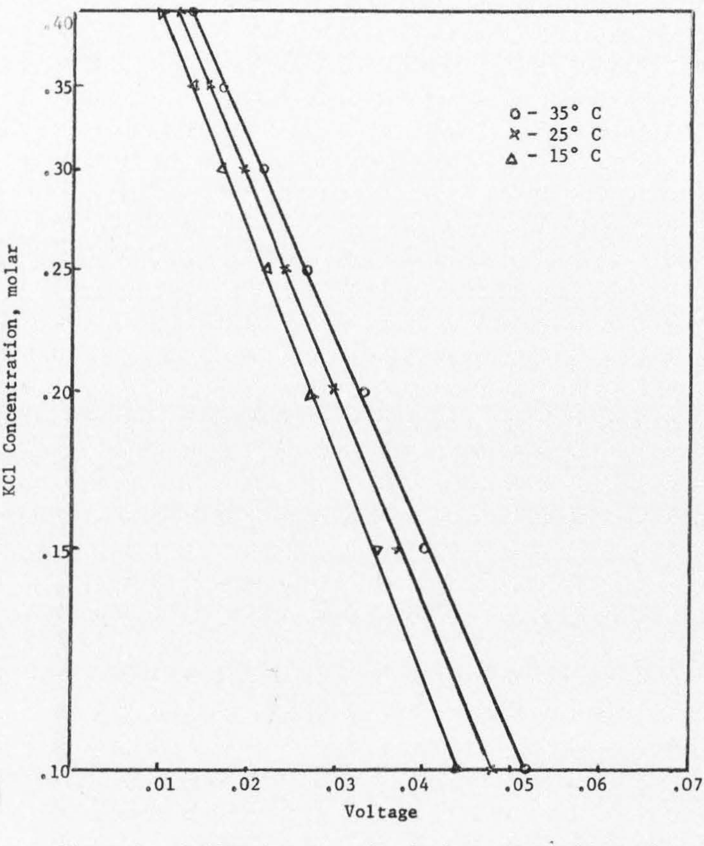

Figure 4. Calibration curve for [silver-silver chloride]-[calomel] electrodes placed in Compartment A' of the diffusion cell containing soil.

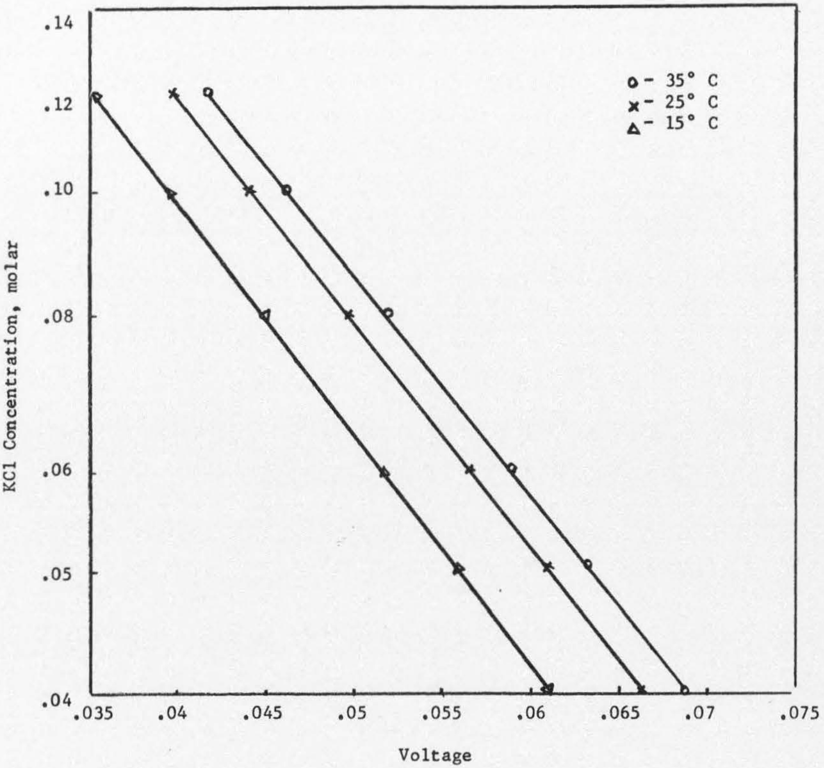

Figure 5. Calibration curve for [silver-silver chloride]-[calomel] electrodes placed in Compartment A of the diffusion cell containing kaolinite.

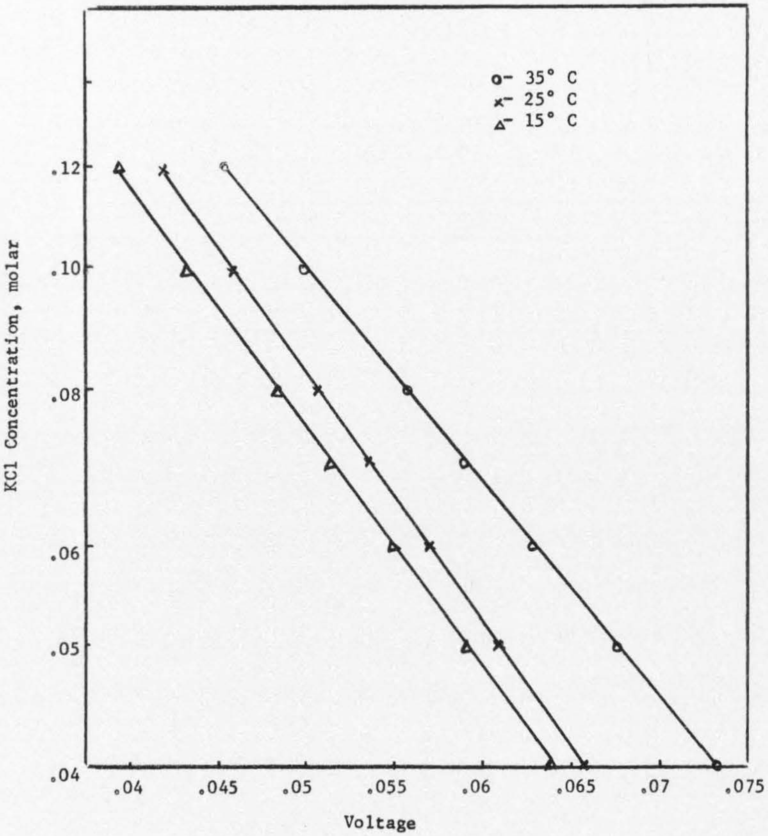

Figure 6. Calibration curve for [silver-silver chloride]-[calomel] electrodes placed in Compartment A' of the diffusion cell containing kaolinite.

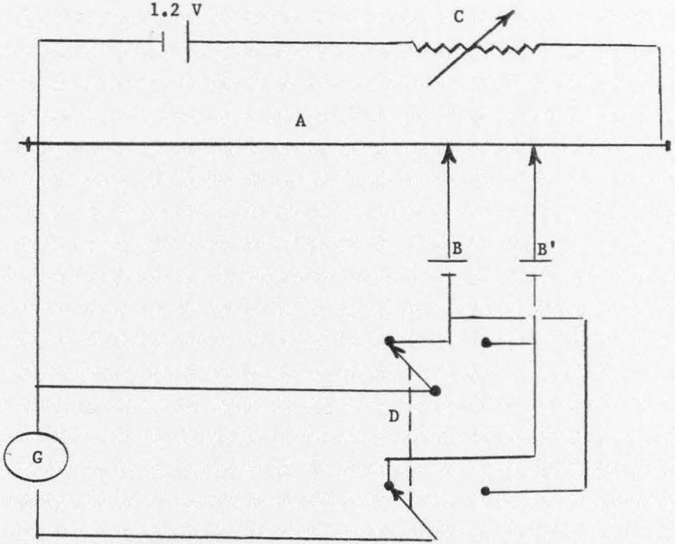

Figure 7. Slide wire potentiometer circuit where A is resistance slide wire, B,B' are e.m.f. developed in systems, C is variable resistance, D is double pole - double through switch, and G is the galvanometer.

due to the pressure (or suction) difference established across the system. The rate equation (42a) reduces in this case to

$$-TJ_w = L_{ww}\ (\bar{v}_w \Delta p) \quad . \qquad (43)$$

Head differences of 10, 20, 40, and 80 cm of water were applied across a sample of soil which was successively in contact on both ends with distilled water, 0.1 N, 0.2 N, and 0.3 N potassium chloride solutions. All experiments were carried out at 15, 25, and 35° C respectively.

Several days were allowed for the experimental media to come to temperature and pressure equilibrium. Generally, a 1-2 day period was sufficient time to establish a flow that was constant with respect to time.

Results

Variations of the phenomenological coefficient L_{ww} with salt concentration as calculated from (43) are shown in figures 8, 9, 10, and 11 for soil and kaolinite with head differences of 10 and 80 cm of water respectively. For soil systems, it is obvious that when salt concentration was increased, L_{ww} increased rapidly until it reached a maximum at 0.2 N KCl, then became constant between 0.2 N and 0.3 N. For kaolinite systems, L_{ww} did not show any change between 0 and 0.1 N KCl, then increased rapidly as concentration increased above 0.1 N.

Although there must exist a region of linearity of flow with driving force, it is not always easy to ascertain how far this region extends for any specific sample. Therefore, the water flux J_w was plotted as a function of head difference. The results are shown in figures 12 and 13 for soil and kaolinite systems. A linear relationship between water flow and

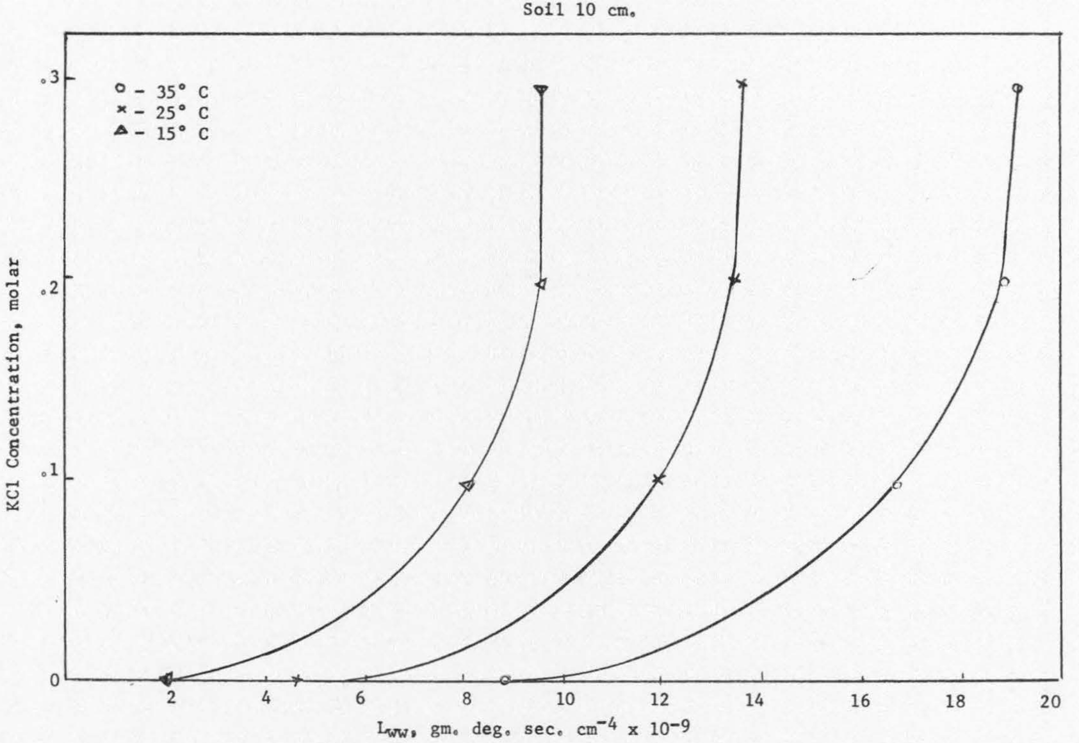

Figure 8. Variation of the coefficient L_{ww}, evaluated at 10 cm water head difference as the concentration of KCl solution increases at 15° C, 25° C, and 35° C (soil water).

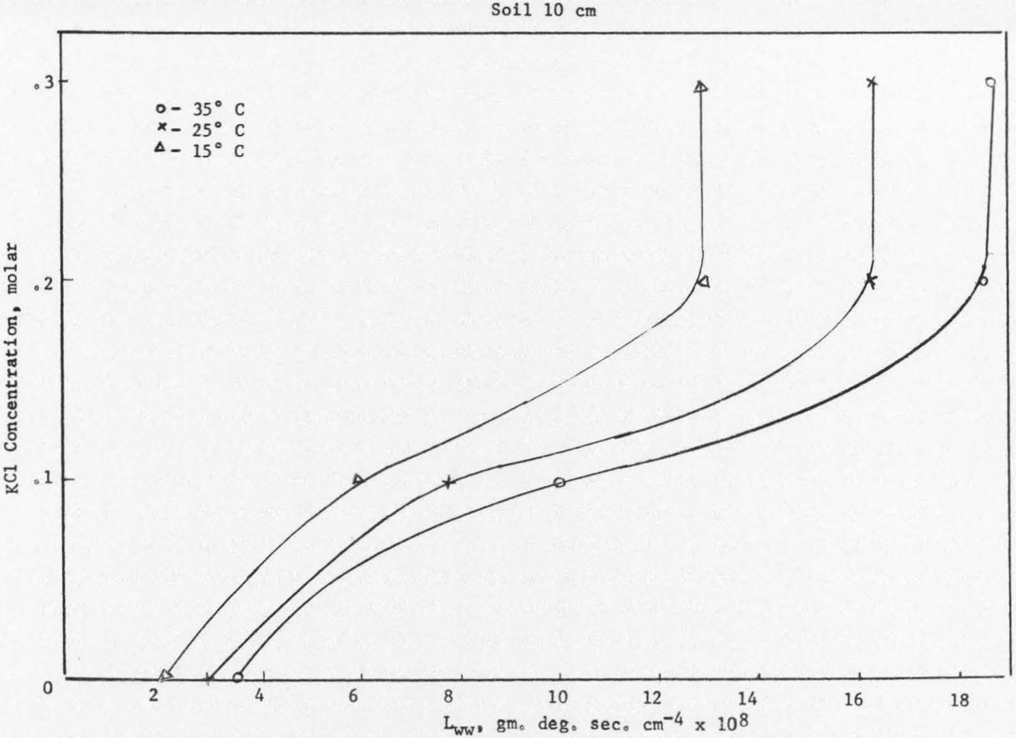

Figure 9. Variation of the coefficient L_{ww}, evaluated at 80 cm water head difference as the concentration of KCl solution increases at 15° C, 25° C, and 35° C (soil system).

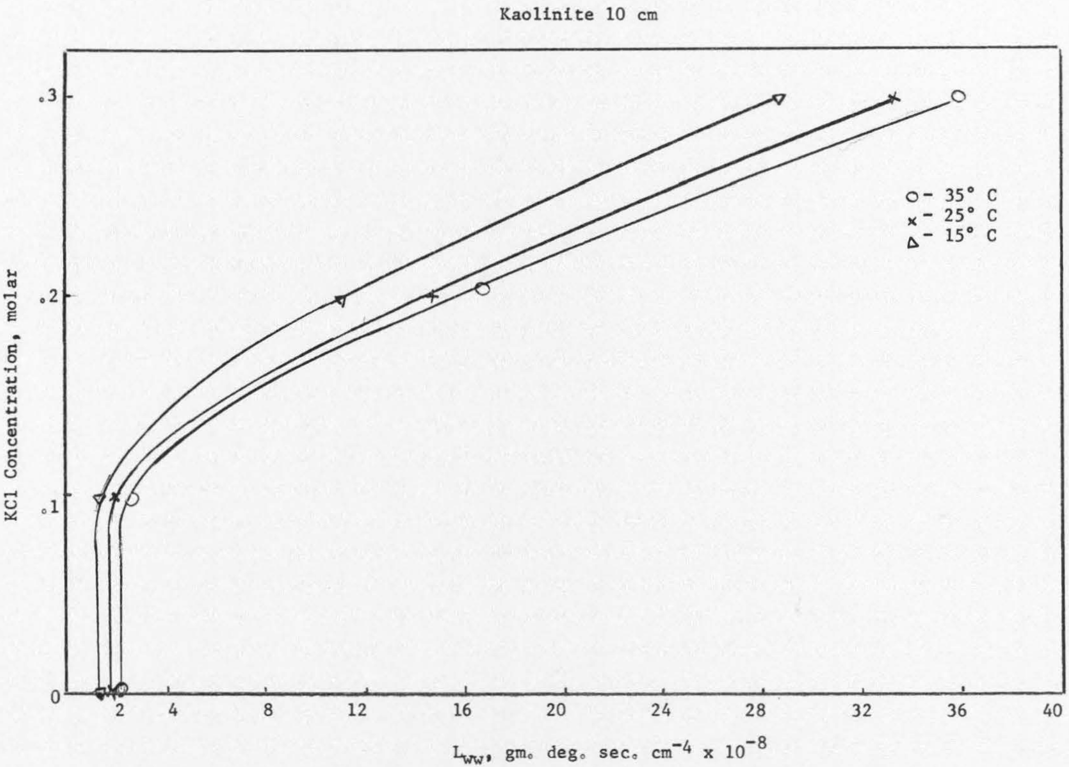

Figure 10. Variation of the coefficient L_{ww}, evaluated at 10 cm water head difference, as the concentration of KCl solution increases at 15° C, 25° C, and 35° C (kaolinite system).

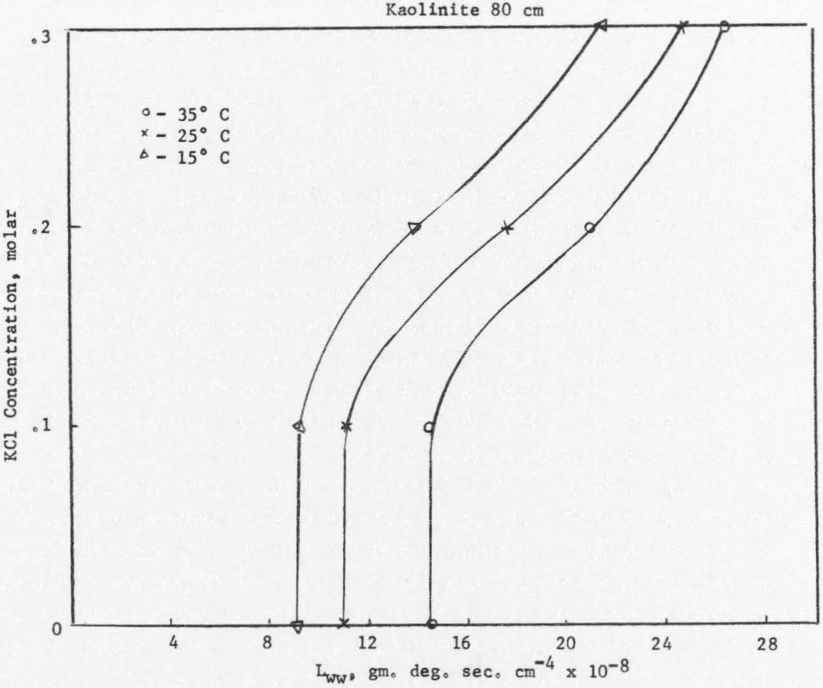

Figure 11. Variation of the coefficient L_{ww}, evaluated at 80 cm water head difference, as the concentration of KCl solution increases, at 15° C, 25° C, and 35° C (kaolinite system).

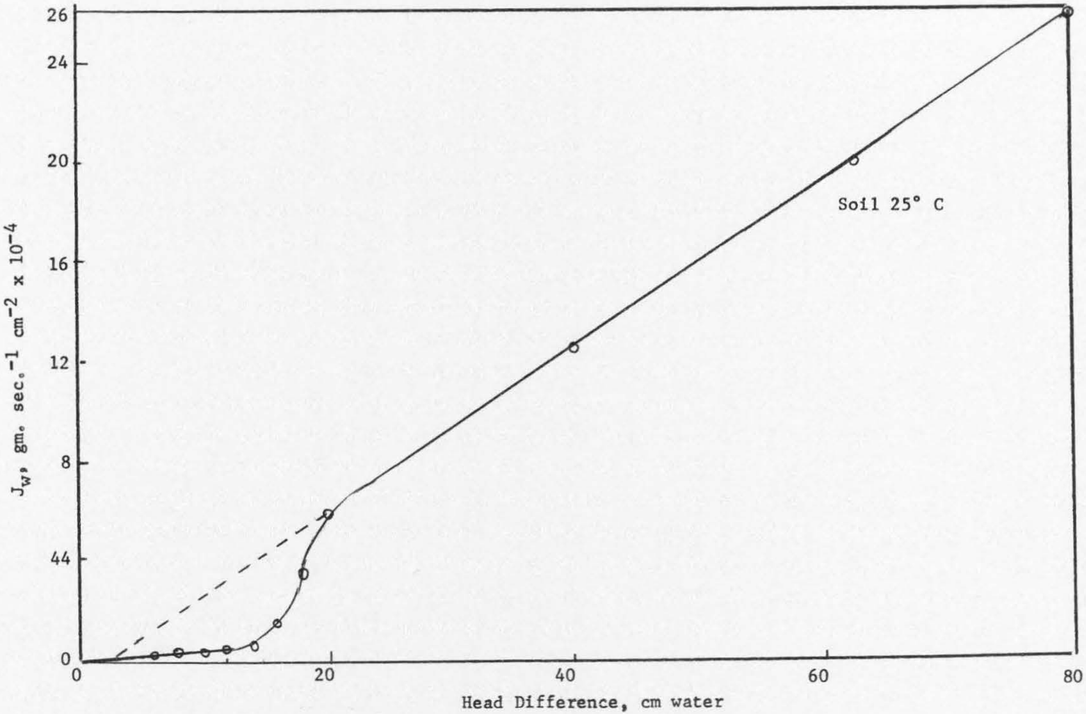

Figure 12. Water flux through soil sample at 25° C and salt concentration of .2 N KCl, plotted as a function of head difference.

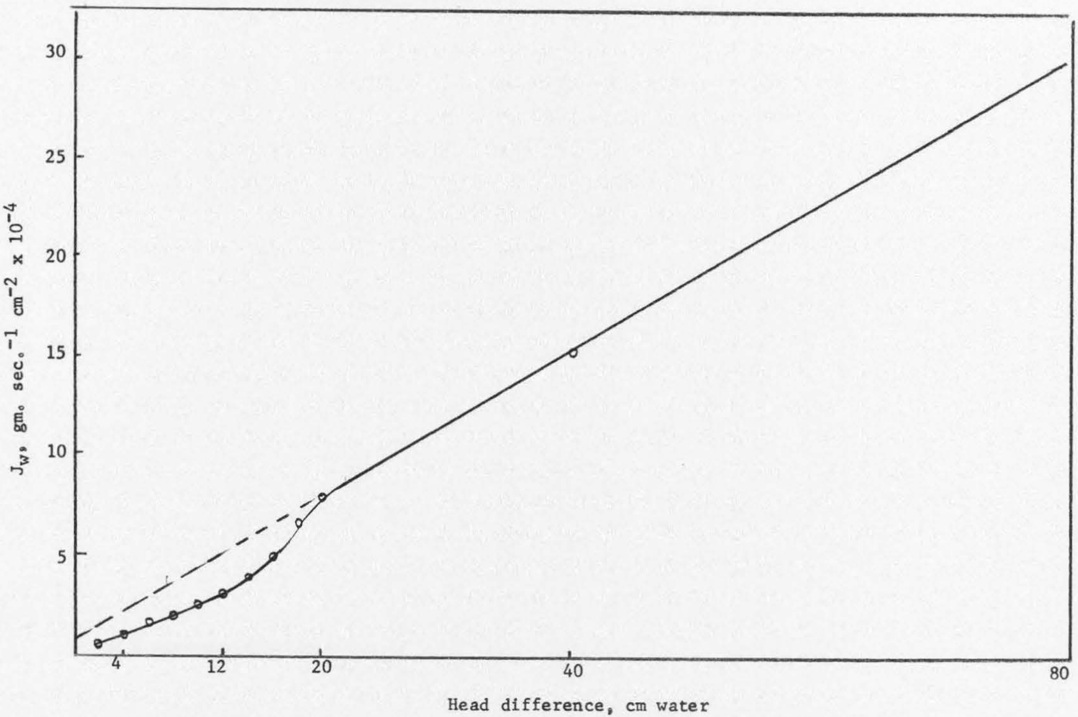

Figure 13. Water flux through kaolinite sample at 25° C and salt concentration of .2 N KCl plotted as a function of head difference.

the driving force seems to fit the data for 2-12 and 20-80 cm water head difference. On the other hand, a rapid increase of water flux is obvious for 12-20 cm water difference in heat (see p.   for further discussion).

The difference in chemical potential of salt (equation 33) may be written as

$$\Delta\mu_s = RT \ln \frac{\gamma^{A'} x^{A'}}{\gamma^{A} x^{A}} \qquad (44)$$

where the superscripts A and A' denote respectively the chamber containing solutions of low and high concentrations of salt. Hence, a zero concentration for any of the solutions yields a trivial case. Consequently, the concentrations of solutions on either side of a kaolinite material were selected to be .05 and 0.1 N KCl, and for soil material they were 0.2 and 0.3 N KCl.

Primary Experiment

The same apparatus with the same soil and kaolinite samples used in the preliminary experiment was used in the primary experiment except that silver-silver chloride and calomel electrodes were installed in the solution chambers. Steady state was reached in both systems within a fifteen day period, during which solutions were changed periodically to avoid any significant change in the concentration differences. This also was done during the course of the experiment so that an assumption of constant concentration difference could be made.

In the first run, a salt driving force vector was operating in the same direction as the pressure difference. In a second run, the forces were operating in opposite directions. Pressure difference was held constant at 9833 ergs gm^{-1} during the experiment for both systems.

During each run, the valves V_1 and V_2 (figure 1) were completely closed. The fluid velocity was recorded periodically. The voltage drop between silver-silver chloride and calomel electrodes was measured once or twice every day by a student potentiometer.[7] Generally, a period of 5-8 days was required to get reasonably accurate data to calculate salt flux J_s.

Each series of runs lasted three months or more in order to develop confidence in the reproducibility of the data and to allow for the time lost from experimental difficulties and changing bath temperature. Leakage of air into the solution chambers sometimes occurred; however, this was easily detected so that its effect was mainly one of experimental delay.

---

[7] Leeds and Northrup Company, Catalog #7651.

EXPERIMENTAL DATA AND ANALYSIS

The net amount of water and salt transferred across the porous plug columns was evaluated by converting the fluid velocity and the voltage measurements to flux of water and flux of salt with dimensions gm $\sec^{-1}$ cm^{-2}. The coefficient L_{ww} was evaluated independently of the driving forces as already described in connection with the preliminary experiment. The salt and water driving forces were calculated in units of ergs gm^{-1}. The ratio (r) was evaluated from equation (30) as

$$r = \frac{\ln \alpha_w^{A'} - \ln \alpha_w^{A}}{\ln \alpha_s^{A'} - \ln \alpha_s^{A}} \tag{45}$$

where the subscripts A and A' denote respectively the solution of low and high salt concentration. The methods used in calculating the previously mentioned parameters (J_w, J_s, $\overline{v}_w \Delta p$, RT $\Delta \ln \alpha_s$, r, and L_{ww}) are shown in Appendix B. Table 2 shows the values of r, salt potential difference (RT $\Delta \ln \alpha_s$), and the difference in water pressure at 15, 25, and 35° C for both soil and kaolinite systems.

In equations 42a and 42b, there are three phenomenological coefficients L_{ws}, L_{sw}, and L_{ss} that are still unknown. In order to find them, experimental measurements were taken when both the pressure and salt activity differences were operating in the same direction and also in opposite directions. The flux was considered to be positive if it was from chamber A to A' and negative if it was in the opposite direction.

Two values of L_{ws} were determined by substituting the known parameters (L_{ww}, $\overline{v}_w \Delta p$, and RT $\Delta \ln \alpha_s$) into equation 42a for each of the two experimental runs where driving forces wereoperating in the same direction for

Table 2. A comparison of the driving forces operating in the soil and kaolinite systems.

Sample	Temp. °K	RT $\frac{ergs}{gm}$	$\bar{v}_w \Delta p$ ergs/gm	RT $\Delta \ln \alpha_s$ ergs/gm	$r = \frac{\Delta \ln \alpha_w}{\Delta \ln \alpha_s}$	RT:$\bar{v}_w \Delta p$ x 10^5	RT:RT$\Delta \ln \alpha_s$
Soil	288	32.1515×10^7	9833	1.17×10^8	-8.803	1:3.05	1:0.3646
	298	33.68×10^7	9833	1.21×10^8	-8.805	1:2.955	1:0.3639
	308	34.384×10^7	9833	1.24×10^8	-8.807	1:2.86	1:0.3611
Kaolinite	288	32.15×10^7	9833	2.06×10^8	-2.2899	1:3.05	1:0.6424
	298	33.268×10^7	9833	2.137×10^8	-2.2901	1:2.955	1:0.6423
	308	34.38×10^7	9833	2.206×10^8	-2.289	1:2.86	1:0.6418

the first run and in the opposite direction for the second. The two values of L_{ws} were in good agreement (table 3). Hence, the average of the two values was used in further calculations.

Equation 42b for the run with both forces operating in the same direction was solved simultaneously with the same equation applied to the run with the forces in the opposite directions to give L_{sw} and L_{ss}.

Under the conditions of this experiment, it was found that the interaction coefficient L_{sw} did not differ significantly from L_{ws} for either soil or clay systems at any temperature studied (table 4). Figure 14 shows the phenomenological coefficients L_{ws} against L_{sw}.

The phenomenological coefficients L_{ww}, $L_{ws} = L_{sw}$, and L_{ss} are plotted as functions of temperature for both soil and kaolinite systems as shown in figures 15, 16, and 17. The plots show that all these coefficients increase with temperature.

Table 3. Average values of the interaction coefficient L_{ws} calculated from equation 42a.

Sample	Temp. °K	$L_{ws} \times 10^{13}$ Forces in Same Direction	$L_{ws} \times 10^{13}$ Forces in Opposite Direction	Average $L_{ws} \times 10^{13}$
Soil	288	3.950	3.987	3.968
	298	5.425	5.558	5.491
	308	6.892	6.863	6.877
Kaolinite	288	5.456	4.812	5.134
	298	5.997	5.999	5.998
	308	7.397	7.026	7.211

Table 4. Summary of the phenomenological coefficients, gm deg. sec. cm^{-4}.

System	Temp. °K	$L_{ww} \times 10^9$	$L_{ss} \times 10^{14}$	$L_{ws} \times 10^{13}$	$L_{sw} \times 10^{13}$	$\frac{L_{ws}}{L_{sw}}$
Soil	277	9.638	2.10	3.97	3.02	1.3
	298	13.56	2.82	5.49	5.08	1.08
	308	19.12	3.82	6.88	6.39	1.08
Kaolinite	288	13.17	.58	5.13	6.72	.812
	298	17.13	.89	6.00	6.5	.923
	308	21.32	1.11	7.21	9.2	.804

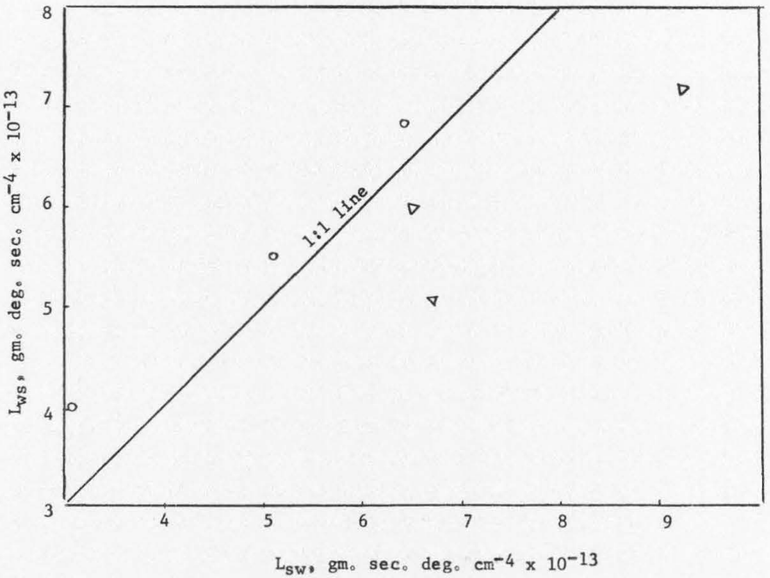

Figure 14. Correlation of the interaction of the coefficients L_{ws} and L_{sw}. Experimentally evaluated coefficients are shown as open points O for soil system and Δ for kaolinite system. The 1:1 line is the relation predicted by Onsager.

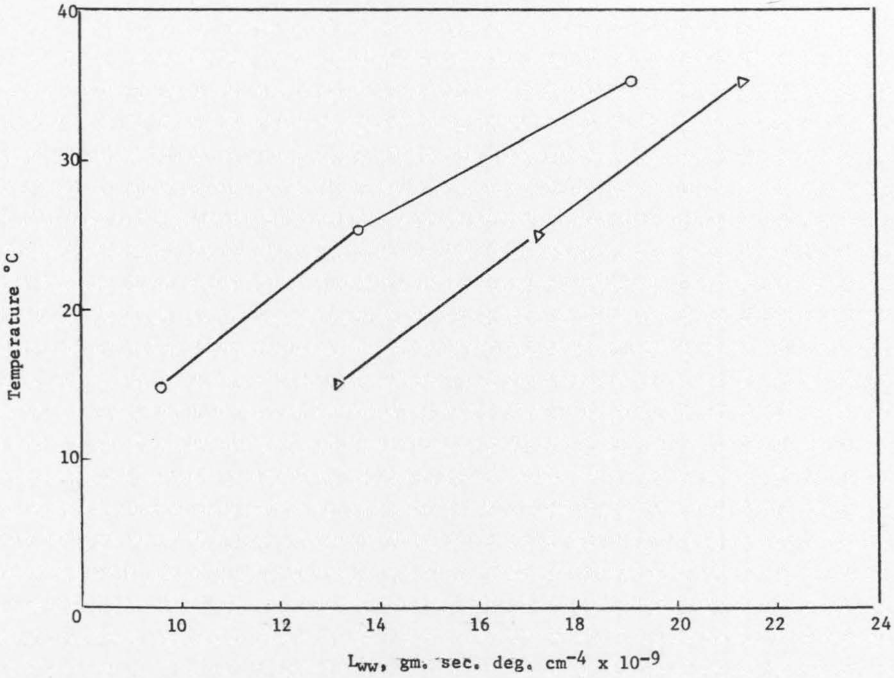

Figure 15. Variation of the coefficient L_{ww} with temperature. The open points, O, indicate soil system and Δ indicates kaolinite system.

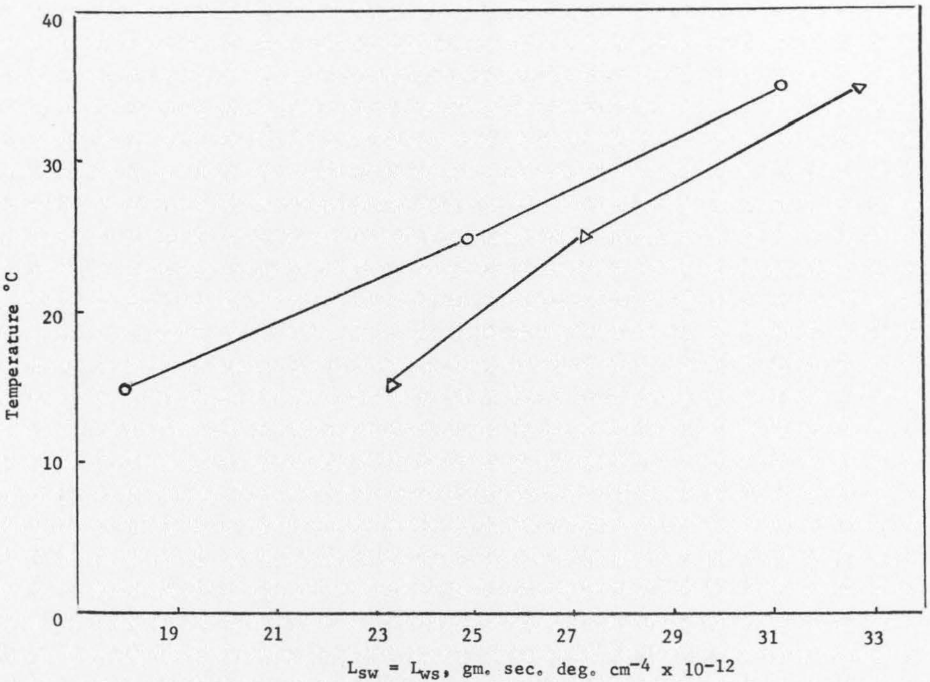

Figure 16. Variation of the coefficient L_{ws} with temperature. The open points O indicate soil system, and Δ indicates kaolinite system.

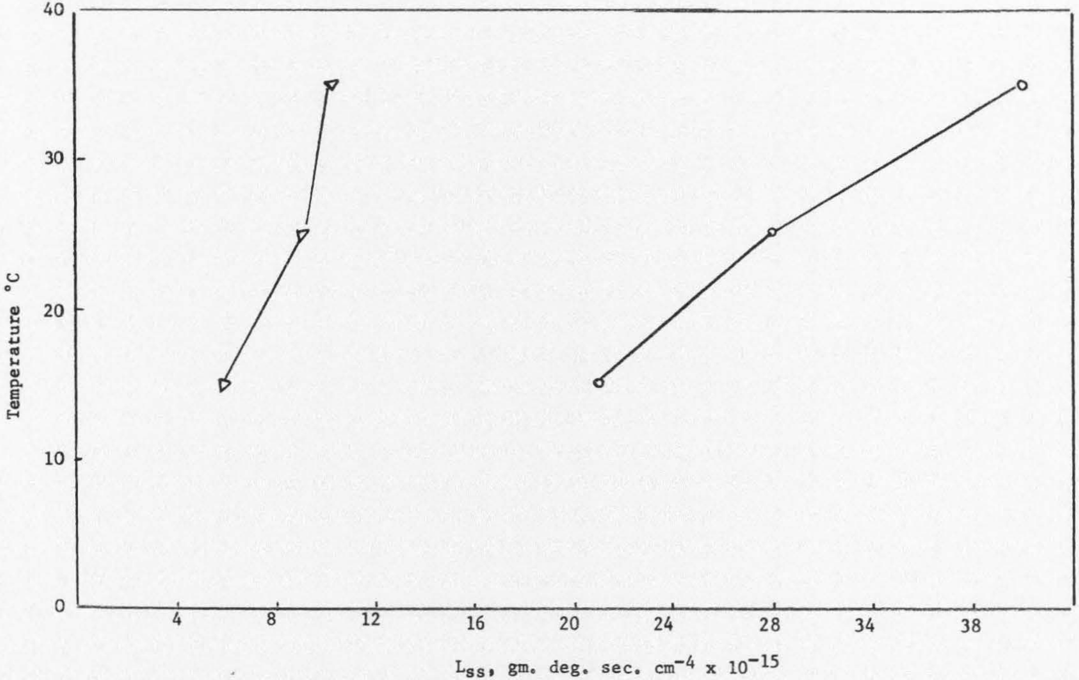

Figure 17. Variation of the coefficient L_{ss} with temperature. The open points, O, indicate soil system and Δ indicates kaolinite system.

DISCUSSION

Assumptions and Conditions

In the application of the theory of irreversible processes and Onsager's reciprocal relation for analysis of the system under study, several assumptions and conditions should be met.

Assumptions inherent in the derivations and proof of the theory of irreversible processes state that the mechanical considerations of fluctuation theory, microscopic reversibility, and regression of fluctuations follow ordinary phenomenological laws. These assumptions have been discussed in detail by de Groot (1959).

The following conditions are discussed in this dissertation because of their particular concern with the system under study:

1. The fluxes and the driving forces developed in equations 42a and 42b are mutually independent.
2. The system is close to equilibrium.
3. The fluxes are linearly related to the driving forces.
4. Equal quantities of the same ion are liberated at a given point if adsorption occurs at that point.
5. The porous plug column (soil, kaolinite) is inert, and no chemical or biological reactions take place to interfere with the transference processes.
6. Partial specific volume for the solute is negligible and can be taken as zero in the range of salt concentration used in this investigation.

Condition 1. The Onsager relation theorem is valid only when either the mutually independent fluxes or the thermodynamic driving forces, or both, are employed in the phenomenological equations developed for the system according to Miller (1960). In order to meet the conditions of mutual independence between fluxes and forces, the rate equations (42a and 42b) were developed to provide that the two driving forces operating in the system; i.e., the matric potential of water ($\overline{v}_w \Delta p$) and the difference in chemical potential of salt ($RT\Delta \ln \alpha_s$), were independent.[8] In addition, an effort was made to select pressure and salt concentration ranges for the system such that the coefficient L_{ww} would be independent of the driving forces.

De Groot and Mazur (1962) showed that one may use the Onsager relation even though the fluxes and/or the driving forces are not independent, provided that they are related by a linear relationship. They proved two theorems which state:

> "Theorem I. A linear homogeneous dependency among the fluxes leaves the validity of the Onsager relation unimpaired.
>
> Theorem II. If linear homogeneous relationships exist between the thermodynamic forces, then the phenomenological coefficients are not uniquely defined, and the Onsager relation is not necessarily fulfilled. It can, however, be shown that the coefficients can always be chosen in such a way that the Onsager relation holds."

Condition 2. The requirement that the system be close to equilibrium is a consequence of the postulate of local equilibrium essential to the basic theory of irreversible processes which states that the Gibbs equation from equilibrium thermodynamics expresses the instantaneous thermodynamic state at any point in the system. Prigogine (1961) showed that,

---

[8] See Theory Development, page of this dissertation.

from a microscopic viewpoint, the postulate of local equilibrium is valid for a nonequilibrium system which is characterized by the statistical mechanical distribution function

$$f = f_o + f_1 \qquad (46)$$

where f_o is the equilibrium molecular distribution function and f_1 is the first order correction. He also stated that if the difference in chemical potentials is small compared to the value of RT; i.e., $\Delta\mu_i << RT$, the system will be close enough to equilibrium to satisfy Onsager's relations. However, Fitts (1962) showed that Onsager's reciprocal relation was valid within the limits of experimental error, for the ternary system $NaCl$-KCl-H_2O even when the salt chemical potential difference $\Delta\mu_s$ was in the same order as RT.

In the system here reported, the ratios of solute chemical potential differences to the value of RT; i.e., $\frac{\Delta\mu_s}{RT}$, were about 1/3 and 2/3 for soil and kaolinite systems respectively (Table 2). The ratios of water chemical potential differences to RT; i.e., $\frac{\Delta\mu_w}{RT}$, were in the order of $\frac{1}{3 \times 10^4}$ for both systems. The relatively high salt concentration differences were used to reduce the error because of the assumption of a constant salt driving force during the course of the experimental run, and to make it possible to detect the small concentration changes in solution compartments.

Condition 3. A linear relationship between the flux and driving force is achieved under a steady state when a solute is allowed to diffuse in a free water medium (Jost, 1952). This linear relationship does not always exist when diffusion takes place through unsaturated soil or clay media (Bouldin and Black, 1954; Heslep and Black, 1954; Letey and Klute, 1959a, b; Porter et al., 1960; Dutt and Low, 1962a, b). The deviation from linearity in soils has been attributed to the interaction between diffusing ions and those associated with clay surfaces (Heslep and Black, 1954).

In most solute diffusion studies using unsaturated porous media, the linearity relationship between flux and concentration gradient has normally been assumed. This assumption is valid whenever the diffusion coefficient does not show a marked dependence on concentration.

Although the validity of Onsager's reciprocal theorem is dependent on the domain of validity of linear phenomenological laws, it may still hold with sufficient precision even though slight nonlinearity exists in the system (Cary and Taylor, 1962). Therefore, an attempt was made to keep the unsaturated system reported herein as nearly linear as possible by imposing the following conditions:

1. Migration of mobile particles (K, Cl ions and water molecules) was allowed to reach a steady state. Also, constant moisture content[9] was maintained during the course of the experiment.

2. Since L_{ws} is independent of the driving forces as will be shown hereafter, a linear relationship between water flux and the driving forces was achieved by selecting a range of pressure and concentration differences where the coefficient L_{ww} was constant.

3. Salt concentration differences were chosen as a compromise between the various experimental conditions; that is, the differences were as small as possible so that an approximation of linearity could be met.

---

[9] Hysteresis effect is not a significant factor here.

At the same time, they were large enough so that the small concentration changes in solution compartments could be detected with the Ag-AgCl electrodes.

Condition 4. In order to insure that equal quantities of the same ion would be released at any point where ionic adsorption occurred, the exchange capacity of the samples was saturated with K^+ ions from KCl solution. The concentration of chloride ions was regarded as being equal to the free salt concentration. This ion has much less tendency to be adsorbed on clay surfaces than potassium ions, particularly when the system had already been brought to equilibrium with KCl solution (Grim, 1953).

Condition 5. The assumption that the porous plug is inert requires that no interaction occur between either the solute or the solvent and the porous plug. However, in dense membranes in which part of the solute is dissolved in the matrix of membrane, as by sieving effect (Maasland and Kemper, 1961), another factor, namely the interaction between the solute and membrane, should be considered (Kedem and Katchalsky, 1958). Under the conditions of this experiment, there is no dissolution of salt in the porous plug (figure 18); that is, the reduction in content of salt in one solution chamber was equal to the increase of salt content in the other chamber of the diffusion cell; hence, there was no source or sink of ions in the membrane.

Under unsaturated conditions, where the flow is known to take place in a thin film of liquid between solid surfaces, Kemper (1961a) reported that there is a force resulting from the electrostatic interaction of ions. This force tends to retard the viscous movement of flowing solutions. The magnitude of this kind of force and its effect on the

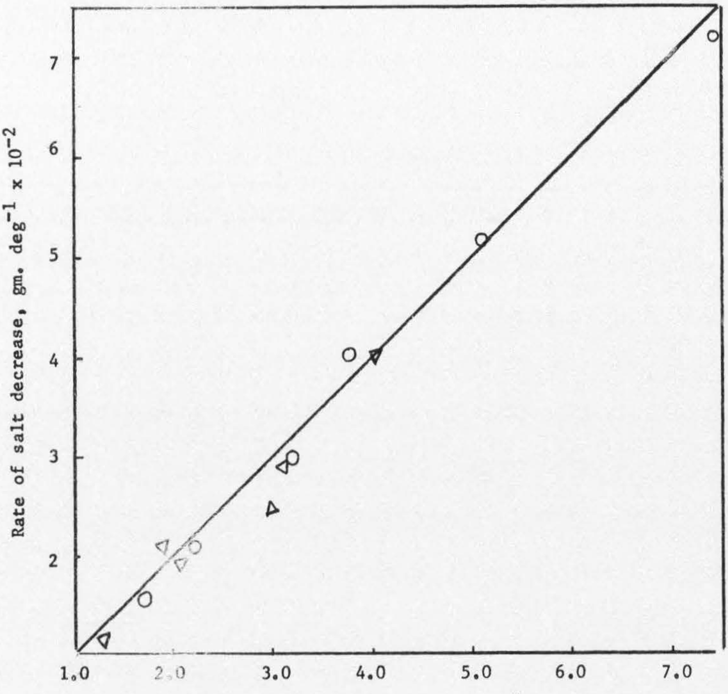

Figure 18. Reduction of salt content in solution Compartment A, correlated with the increase of salt content in solution Compartment A'. The open points, O, indicate soil system and Δ indicates kaolinite system.

migration of mobile particles in the system has been discussed and calculated by Onsager and Fuoss (1932), who concluded that even though the coulombic forces between the ions constitute a potential, the interaction between ions may be disregarded, since it does not affect the validity of the symmetry condition.

It can be shown that chemical reactions in the membrane could not act as a driving force for water or salt since this would be a violation of the Curie principle which states that coupling can take place only between fluxes of the same tensorial order. Hence, a diffusional flow which has a vectorial character and is a tensor of the first order cannot be coupled with the flow of a chemical reaction which is a scalar in nature and is a tensor of zeroth order. On the basis of Curie's principle, it has been stated (de Groot and Mazur, 1961) that no direct coupling is possible between solute flow and chemical reaction proceeding in the system.

Nevertheless, chemical reactions were not likely to take place in the system reported here. This is particularly true after the system reached the steady state. The reason is that the experimental porous media were saturated with the same salt (KCl) that was being transferred and no other salts were present.

Biological reactions in the system were a possibility which was not feasible to overcome since it was not possible to keep all experimental materials continuously sterilized. However, the consistency of data after the steady state has been reached indicates that such reactions, if any, did not interfere with the transference processes.

Condition 6. The partial specific volume of water and KCl was determined using the graphical method of intercepts (Lewis and Randall,

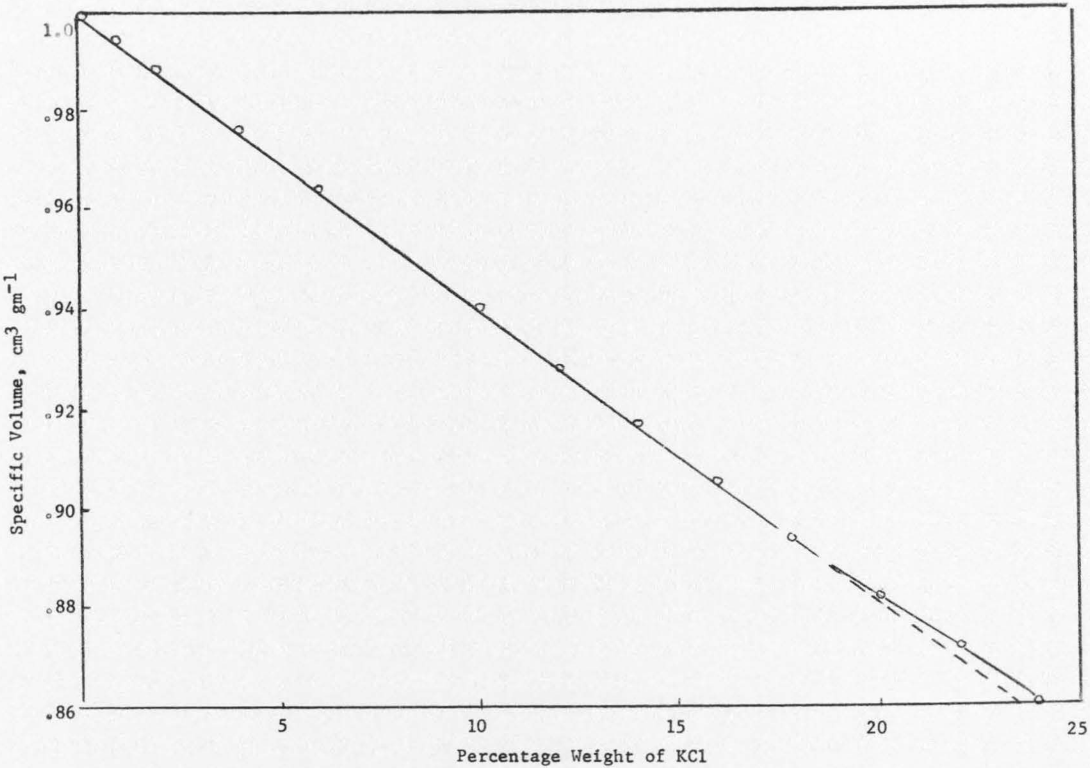

Figure 19. Specific volume of KCl solution at 20° C.

1961). According to the method, the intercepts of the tangent give the partial specific volume of solvent and solute. The specific volume of KCl solutions, which is the reciprocal of the density (taken from the international critical tables), was plotted against the weight percentage of solute (figure 19). It is obvious from that figure that in the range of the concentration used in this study, the tangent of the slope of the line is the line itself which has an intercept of one. Thus, the partial specific volume of water is one; consequently, the partial specific volume of KCl is zero.

Results

Dependence of the coefficient L_{ww} on salt concentration. As the concentration of ions in the fluid increases, the zeta potential value decreases owing to a repressing action of the ions in the solution. This in turn reduces the volume of the dispersed layer of ions and makes the water associated with these ions free to move. This explains the increase of the coefficient L_{ww} with salt concentration (figures 8, 9, 10, and 11).

Dependence of the coefficient L_{ww} on pressure difference. The nonlinear relationship between water flux and the conjugate driving force (head difference), which is shown by the preliminary experiment (figures 12 and 13) is in contradiction with the generalized flow equation. This contradiction may be explained as follows.

Because of the unsaturated conditions imposed on the system (23.4 cm Hg pressure introduced into the porous plug), the flow took place in a thin film of liquid at the solid surfaces. Hence, the interaction between the ions in the moving solution and those associated with the mineral surfaces may retard the viscous movement of the solution. This interaction has been evaluated for several systems by Onsager and Fuoss (1932) and Kemper (1960). The reduction in velocity was found to be generally more marked as the fluid films became thinner and as the electrolyte concentration decreased. Lutz and Kemper (1959) found that in systems where the diffuse double layer would be expected to extend into the flow channels, the intrinsic permeability increased with increased pressure gradient. Their work is in full agreement with the results presented herein for the region of 2-20 cm water head difference (figures 20 and 21). This implies that the magnitude of the effect of ions in retarding fluid flow is negligible at rapid flow of liquid (relatively high pressure differences), whereas, it is considerable at slow flow of liquid (relatively small pressure differences). To account for these changes, Kemper (1960) assumed that the major portion of the hydrated ions associated with the clay particles may be moved out of the flow channel by rapid flow of liquid.

Temperature dependence of phenomenological coefficients. The coefficients L_{ww}, $L_{ws} = L_{sw}$, and L_{ss} are expected to increase with temperature, as shown in figures 15, 16, and 17. This increase is a result of the direct relation that exists between temperature and diffusion in liquids. The relation is expressed by the following equation (Jost, 1952)

$$D = ukT \tag{47}$$

where D is the diffusion coefficient, u is the mobility of the particle under consideration, k is a constant, and T is absolute temperature. The relations between L_{ww} and D and L_{ws} and D are now considered.

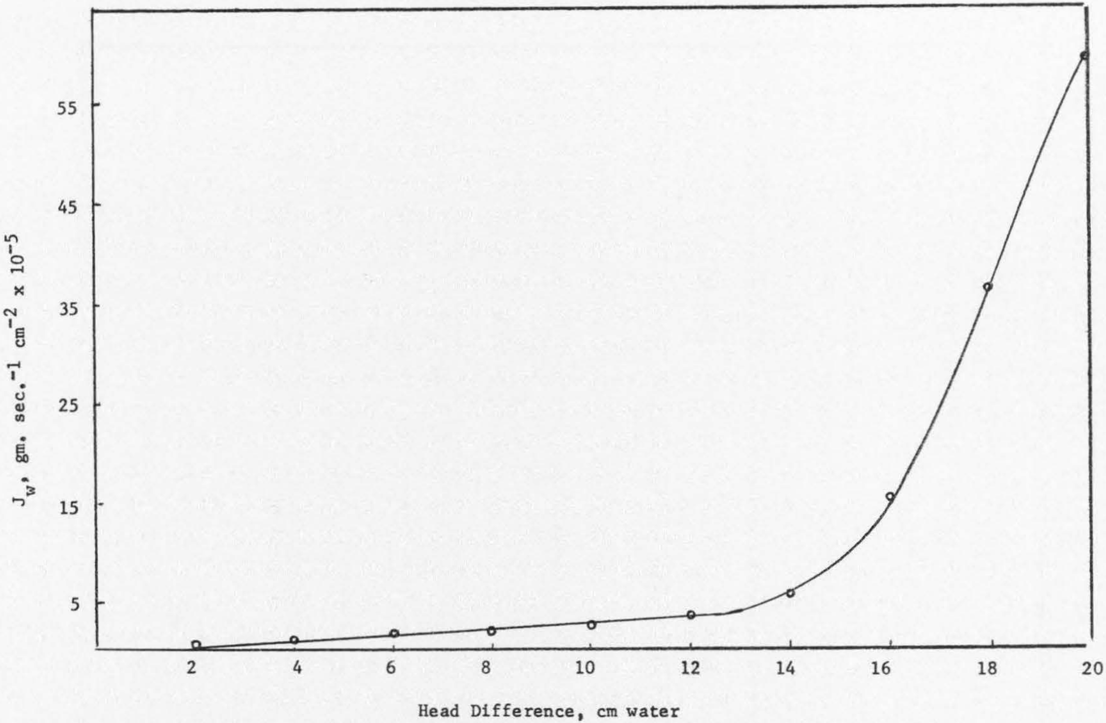

Figure 20. Water flux through soil sample at 25° C and salt concentration of .2 N KCl, plotted as a function of head differences for the range 2-20 cm of water.

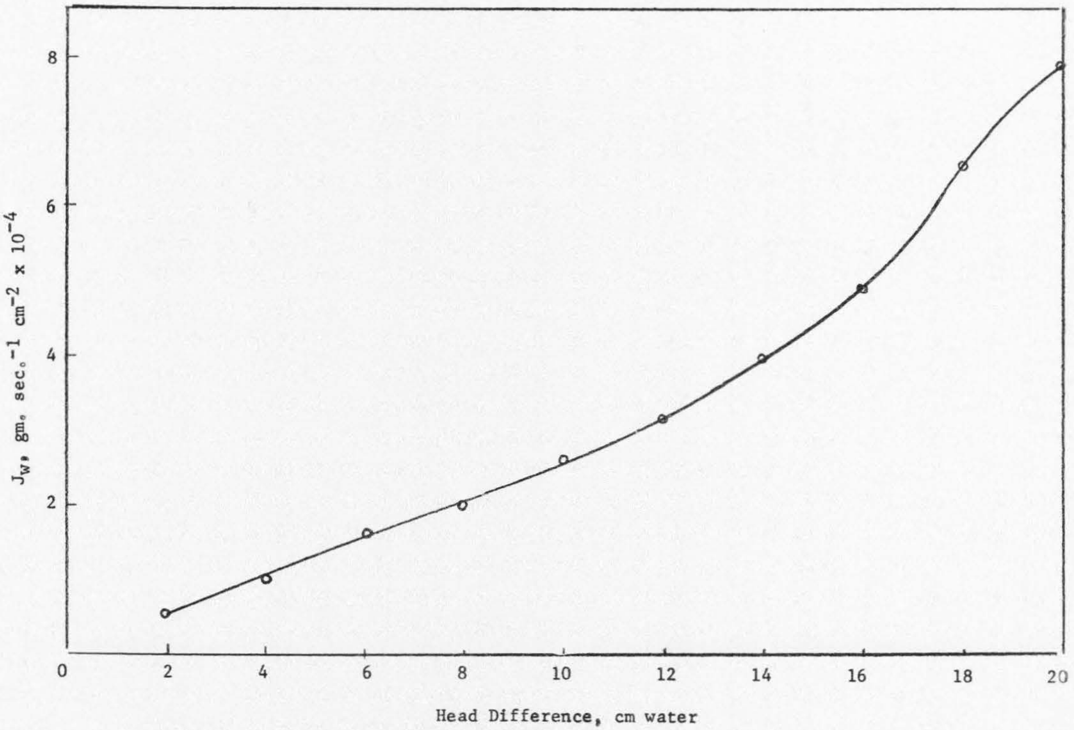

Figure 21. Water flux through kaolinite sample at 25° C and salt concentration of .2 N KCl plotted as a function of head difference for the range 2-20 cm of water.

Suppose that for the system described in figure 1 the water were driven across the porous plug owing to a pressure difference between the solution compartments, as expressed mathematically by equation 43. In this isothermal process, the water flux J_w may also be represented by Darcy's law

$$J_w = - k \frac{\Delta p}{\Delta x} \tag{48}$$

where k (the conductivity coefficient) is directly proportional to the diffusion coefficient of water (equation 15), and $\frac{\Delta p}{\Delta x}$ is the pressure difference. Hence, by combining equation (43) with (48), we get

$$L_{ww} = \frac{kT}{\overline{v}_w \Delta x} \quad . \tag{49}$$

Therefore, at constant temperature, specific volume of water and with a given length of experimental medium (Δx=k), $L_{ww} = \alpha D$, where α is a proportionality constant.

On the other hand, if the water were transferred across the porous plug owing to salt concentration difference between the solution reservoirs, equation (42a) would become

$$J_w = - L_{ws} \; R\Delta \ln \alpha_s \quad . \tag{50}$$

At the same time, the water flux may be expressed by Fick's law

$$J_w = - D \frac{\Delta C_w}{\Delta x} \tag{51}$$

where $\frac{\Delta C_w}{\Delta x}$ is the water concentration gradient. Hence, by equation (50) and (51) and solving for L_{ws}, we get

$$L_{ws} = D \frac{\Delta C_w}{\Delta x(R \Delta \ln \alpha_s)} \quad . \qquad (52)$$

Therefore, $L_{ws} = \alpha D$.

Equations (49) and (52) show that L_{ww} and L_{ws} are directly proportional to the diffusion coefficient D.

Similarly, by using the same argument, it can be shown that L_{sw} and L_{ss} are directly proportional to the diffusion coefficient.

L_{ws} independence of driving forces. Table 3 shows that the values calculated for the coefficient L_{ws} for gradients of salt and pressure in opposite directions were in good agreement. Since the two equations use greatly different driving forces yet give the same values for L_{ws}, the agreement is a good indication that the coefficient L_{ws} is independent of the driving forces operating in the system. This completes the argument of linearity between water flux and driving forces referred to in the discussion of condition (3).

Equality of interaction coefficients. The equality of L_{ws} and L_{sw} (table 4 and figure 14) suggests that the Onsager theorem was met in both kaolinite and soil systems at 15, 25, and 35° C.

The coefficient L_{ws} was slightly higher than L_{sw} for soil and slightly lower for kaolinite systems. It is possible that the linearity required by condition 3 was not perfectly met in the system under study. This may account for the slight differences. Although this possibility exists, the agreement is well within the experimental error so that no significance can be placed on the observed variations.

SUMMARY AND CONCLUSIONS

An experiment has been conducted to evaluate the interaction coefficients of water and salt flow under unsaturated conditions, using the theory of irreversible processes. The consequential test of Onsager's reciprocal relation has been made to determine whether $L_{ws} = L_{sw}$. The phenomenological equations (42a and 42b) for the system under study have been developed from the entropy source.

To gather water and salt flux data, the experimental apparatus was designed so that a suction difference could be established simultaneously with salt concentration difference across a cylindrical soil core. Millville silt loam and kaolinite cores were used as the experimental media through which diffusion took place. The experiment was carried out under isothermal conditions at 15, 25, and 35° C.

The results showed that within the precision of this experiment, the interaction coefficients were equal for both systems at all temperatures. This confirmation of the Onsager proposition was obtained even though a linear relationship between the fluxes and the driving forces was not perfectly obtained in the systems under study.

From this study it can be concluded that:

1. At constant soil moisture content, the diffusivity coefficient of water which is linearly related to the coefficient L_{ww} was dependent on both salt concentration of flowing solution and on the pressure difference between the solutions in the diffusion cell.

2. The interaction coefficients L_{ws} and L_{sw} were equal as predicted by Onsager's theorem.

Further studies should incorporate a more sensitive apparatus for measuring salt flux and if possible smaller salt concentration differences as well as larger ones should be studied. The rate equations should be tested over a wider range of soil water potentials.

The theory appears to be adequate at the present for many but not all applied studies, but techniques need to be developed for accurately and quickly measuring the necessary parameters. Rapid methods for *in situ* determinations of salt potential difference are particularly needed.

Tests should be made on the more complex system wherein the soil water potential is influenced by differences in matric potential and water contents and where free salt accumulates at an evaporating surface.

LITERATURE CITED

(1) Ashcroft, G. L., D. D. Marsh, D. D. Evans, and L. Boersma. Numerical method for solving the diffusion equation: I. Horizontal flow in semi-infinite media. Soil Science Society of America Proceedings 26:522-525. 1962.

(2) Biggar, J. W. and D. R. Nielsen. Diffusion effects in miscible displacement occurring in saturated and unsaturated porous materials. Journal of Geophysical Research 65:2887-2895. 1960.

(3) Biggar, J. W. and D. R. Nielsen. Miscible displacement: II. Behavior of tracers. Soil Science Society of America Proceedings 26:125-128. 1962.

(4) Bloksma, A. H. The diffusion of sodium and iodide ions and of urea in clay pastes. Journal of Colloid Science 12:40-52. 1957.

(5) Bouldin, D. R. and C. A. Black. Phosphorus diffusion in soil. Soil Science Society of America Proceedings 18:255-259. 1954.

(6) Bruce, R. R. and A. Klute. The measurement of soil moisture diffusivity. Soil Science Society of America Proceedings 20:458-462. 1956.

(7) Cary, J. W. and S. A. Taylor. The interaction of the simultaneous diffusion of heat and water vapor. Soil Science Society of America Proceedings 26:413-416. 1962.

(8) Childs, E. C. The transport of water through heavy clay soils. I. The Journal of Agricultural Science 26:527-545. 1936.

(9) Childs, E. C. and N. C. George. The permeability of porous materials. Proceedings of the Royal Society of London, Series A, Mathematical and Physical Sciences 201:392-405. 1950.

(10) Collins, R. E. *Flow of Fluids through Porous Material.* New York. Reinhold, 1961.

(11) Crank, J. *The Mathematics of Diffusion.* London, Oxford Press. 1956.

(12) Daniels, F., J. H. Matthews, J. W. Williams, P. Bender, and R. A. Alberty. *Experimental Physical Chemistry.* New York, McGraw-Hill Book Company, Inc. 1956.

(13) Day, P. R. Dispersion of a moving salt-water boundary advancing through saturated sand. Transactions of American Geophysical Union 37:595-601. 1956.

(14) De Groot, S. R. Thermodynamics of Irreversible Processes. Amsterdam. North Holland Publishing Company. 1959.

(15) De Groot, S. R. and P. Mazur. Non-Equilibrium Thermodynamics. Amsterdam. North Holland Publishing Company. 1962.

(16) Denbigh, K. G. The Thermodynamics of the Steady State. New York. John Wiley and Sons, Inc. 1951.

(17) Dunlop, P. J. Use of diffusion and thermodynamic data to test the Onsager reciprocal relation for isothermal diffusion in the system $NaCl-KCl-H_2O$ at 25° C. Journal of Physical Chemistry 63: 186-193. 1959a.

(18) Dunlop, P. J. Data for diffusion in a concentrated solution of the system $NaCl-KCl-H_2O$ at 25° C. A test of the Onsager reciprocal relation for this composition. Journal of Physical Chemistry 63: 612-615. 1959b.

(19) Dutt, G. R. and P. F. Low. Relationship between the activation energies for deuterium oxide diffusion and exchangeable ion conductance in clay systems. Soil Science 93:195-203. 1962a.

(20) Dutt, G. R. and P. F. Low. Diffusion of alkali chlorides in clay-water systems. Soil Science 93:233-239. 1962b.

(21) Fitts, D. D. Nonequilibrium Thermodynamics. New York. McGraw-Hill Book Company, Inc. 1962.

(22) Gardner, W. R. Calculation of capillary conductivity from pressure plate outflow data. Soil Science Society of America Proceedings 20:317-320. 1956.

(23) Glasstone, S., K. J. Laidler, and H. Eyring. The Theory of Rate Processes. New York. McGraw-Hill Book Company, Inc. 1941.

(24) Grim, R. E. Clay Mineralogy. New York. McGraw-Hill Book Company, Inc. 1953.

(25) Haase, R. Thermoosmose in Flussigkeiten. I. Grundlagen. Zeitschrift fur Physikalische Chemie 21:245-269. 1959.

(26) Haase, R. and C. Steinert. Thermoosmose in Flussigkeiten. II. Messungen. Zeitschrift fur Physikalische Chemie 21:270-297. 1959.

(27) Heslep, J. M. and C. A. Black. Diffusion of fertilizer phosphorus in soils. Soil Science 78:389-401. 1954.

(28) Husted, R. F. and P. F. Low. Ion diffusion in bentonite. Soil Science 77:343-353. 1954.

(29) Hutcheson, H. P., I. S. Nixon, and K. G. Denbigh. Thermo-osmosis of liquids through porous materials. Discussion of the Faraday Society No. 3, Interaction of Water and Porous Materials. 1948.

(30) Jost, W. Diffusion. New York. Academic Press Inc. 1952.

(31) Kedem, O. and A. Katchalsky. Thermodynamic analysis of the permeability of biological membranes to non-electrolytes. Bio Chemica et Bio Physica Acta 27:229-246. 1958.

(32) Kedem, O. and A. Katchalsky. A physical interpretation of the phenomenological coefficients of membrane permeability. Journal of General Physiology 45:143-179. 1961.

(33) Kemper, W. D. Water and ion movement in thin films as influenced by electrostatic charge and diffuse layers of cations associated with clay mineral surfaces. Soil Science Society of America Proceedings 24:10-16. 1960.

(34) Kemper, W. D. Movement of water as affected by free energy and pressure gradients. I. Application of classic equations for viscous and diffusive movements to the liquid phase in finely porous media. Soil Science Society of America Proceedings 25:255-260. 1961a.

(35) Kemper, W. D. Movement of water as affected by free energy and pressure gradients. II. Experimental analysis of porous systems in which free energy and pressure gradients act in opposite directions. Soil Science Society of America Proceedings 25:260-265. 1961b.

(36) Kirkham, D. and C. L. Feng. Some tests of the diffusion theory and laws of capillary flow in soils. Soil Science 67:29-40. 1949.

(37) Klute, A. Some theoretical aspects of the flow of water in unsaturated soils. Soil Science Society of America Proceedings 16:144-148. 1952.

(38) Letey, J. and A. Klute. A modified hittorf method of measuring transference numbers of ions in soil and clay pastes. Soil Science 90:121-128. 1959a.

(39) Letey, J. and A. Klute. Apparent mobility of potassium and chloride ions in soil and clay pastes. Soil Science 90:259-265. 1959b.

(40) Lewis, G. N. and M. Randall. Thermodynamics. New York. McGraw-Hill Book Company, Inc. 1961.

(41) Lutz, J. F. and W. D. Kemper. Intrinsic permeability of clay as affected by clay water interaction. Soil Science 88:83-90. 1959.

(42) Maasland, D. E. and W. D. Kemper. Reduction in salt content of solution on passing through thin films adjacent to charged surfaces. Progress Report. Colorado State University. 1961.

(43) Michaeli, I. and O. Kedem. Description of the transport of solvent and ions through membranes in terms of differential coefficients. Part I. Phenomenological characterization of flows. Transactions of the Faraday Society 57:1185-1190. 1961.

(44) Miller, D. G. Ternary isothermal diffusion and the validity of the Onsager reciprocal relation. Journal of Physical Chemistry 63:570-578. 1959.

(45) Miller, D. G. Thermodynamics of irreversible processes. The experimental verification of the Onsager reciprocal relations. Chemical Review 60:15-37. 1960.

(46) Nielsen, D. R. and J. W. Biggar. Miscible displacement in soils. Soil Science Society of America Proceedings 25:1-5. 1961.

(47) Onsager, L. Reciprocal relations in irreversible processes. I. Physical Review 37:405-426. 1931a.

(48) Onsager, L. Reciprocal relations in irreversible processes. II. Physical Review 38:2265-2279. 1931b.

(49) Onsager, L. and R. M. Fuoss. Irreversible processes in electrolyte. Diffusion, conductance, and viscous flow in arbitrary mixtures of strong electrolytes. Journal of Physical Chemistry 36:2689-2778. 1932.

(50) Philip, J. R. Numerical solution of equations of the diffusion type with diffusivity concentration dependent. Transactions of the Faraday Society 51:885-892. 1955.

(51) Philip, J. R. Remarks on the analytical derivation of the Darcy equation. Transactions of American Geophysical Union 38:782-784. 1957.

(52) Philip, J. R. Physics of water movement in porous solids. National Research Council. Highway Research Board. Water and its Conductance in Soil. (Special Report 40). p. 147-163. 1958.

(53) Porter, L. K., W. D. Kemper, R. D. Jackson, and B. A. Stewart. Chloride diffusion in soils as influenced by moisture content. Soil Science Society of America Proceedings 24:460-463. 1960.

(54) Prigogine, I. <u>Introduction to Thermodynamics of Irreversible</u> Processes. Springfield, Ill. Charles C. Thomas. 1961.

(55) Qayyum, M. A. and W. D. Kemper. Salt concentration gradients in soils and their effect on moisture movement and evaporation. Progress Report. Colorado State University. 1961.

(56) Richards, L. A. Capillary conduction of liquids through porous media. Physics 1:318-333. 1931.

(57) Robinson, R. A. and R. H. Stokes. Electrolyte Solutions. New York. Academic Press Inc. 1955.

(58) Scheideggar, A. E. The Physics of Flow through Porous Media. New York. MacMillan, 1960.

(59) Shapiro, R. E., W. H. Armiger, and M. Fried. The effect of soil water movement vs. phosphate diffusion on growth and phosphorus content of corn and soy beans. Soil Science Society of America Proceedings 24:161-164. 1960.

(60) Spiegler, K. S. Transport processes in ionic membranes. Transactions of the Faraday Society 54:1409. 1958.

(61) Staple, W. J. and J. J. Lehane. Movement of moisture in unsaturated soils. Canadian Journal of Agricultural Science 34:329-342. 1954.

(62) Staverman, A. J. Non-equilibrium thermodynamics of membrane processes. Transactions of the Faraday Society 48:176-185. 1948.

(63) Taylor, S. A. Simultaneous Flow in Soils and Plants. Monograph. Utah State University. 1963.

(64) Taylor, S. A. and J. W. Cary. Analysis of the simultaneous flow of water and heat or electricity with the thermodynamics of irreversible processes. Proceedings of 1960 International Soil Science Congress. Madison, Wisconsin. 1960.

(65). Wang, J. H., C. V. Robinson, and I. S. Edelman. Self diffusion and structure of liquid water with H^2, H^3, and O^{18} as tracers. Journal of American Chemical Society 75:466-470. 1953.

(66) Wendt, R. P. Studies of isothermal diffusion at 25° C in the system: Water-Sodium Sulfate-Sulfuric acid and tests of the Onsager relation. Journal of Physical Chemistry 66:1279-1288. 1962.

(67) Winterkorn, H. F. Mass transport phenomena in moist porous systems as viewed from the thermodynamics of irreversible processes. National Research Council. Highway Research Board. Water and its Conductance in Soil (Special Report 40). p. 324-338.. 1958.

(68) Woolf, L. A., D. G. Miller, and L. J. Gosting. Isothermal diffusion measurements on the system H_2O - Glycine - KCl at 25° C, tests of Onsager reciprocal relation. Journal of American Chemical Society 84:317-331. 1962.

APPENDIX A

Experimental Data

Preliminary Experiment

I.

A. Distilled water is used in both chambers A and A' of diffusion cell.

Table A.1.

Head difference	15° C				25° C				35° C			
	Kaolinite		Soil		Kaolinite		Soil		Kaolinite		Soil	
	T.I[a]	R.M[b]	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.
	2	2.15	2	0.50	2	2.70	2	0.65	2	3.35	2	0.80
	2	2.10	2	0.50	2	2.70	2	0.70	2	3.40	2	0.80
	2	2.10	2	0.55	2	2.65	2	0.65	2	3.50	2	0.80
	2	2.00	2	0.50	2	2.65	2	0.65	2	3.40	2	0.75
80 cm	2	2.05	50	0.51	2	2.75	2	0.65	2	3.40	2	0.80
	20	2.10	2	0.50	2	2.70	20	0.65	2	3.50	2	0.85
	2	2.10	10	0.52	2	2.73	2	0.70	2	3.35	2	0.85
	2	2.15	2	0.50	20	2.67	2	0.70	2	3.35	50	0.80
	2	2.10	---	----	30	2.68	50	0.65	20	3.38	20	0.81
		2.10		0.52		2.7		0.68		3.38		0.80
	10	0.042	10	0.010	100	0.051	100	0.013	100	0.060	100	0.020
	100	0.041	100	0.009	100	0.050	100	0.014	100	0.060	100	0.021
	100	0.042	300	0.010	100	0.051	100	0.014	100	0.062	100	0.020
10 cm	100	0.041	300	0.009	200	0.051	200	0.014	300	0.061	300	0.021
	100	0.042	200	0.010	100	0.050	100	0.015	100	0.062	100	0.021
	100	0.043	100	0.010	100	0.050	100	0.014	100	0.060	100	0.022
	100	0.041	100	0.009	100	0.050	100	0.014	100	0.061	100	0.021
	100	0.043	100	0.01	100	0.050	100	0.015	100	0.061	100	0.022
	100	0.042	400	0.009	100	0.051	100	0.014	100	0.062	100	0.021
	---	--	---	--	100	0.051	---	--	100	0.062	100	0.020
	---	--	---	--	100	0.051	---	--	100	0.061	100	0.021
		0.042		0.0095		0.0505		0.014		0.061		0.021

[a] T.I. is time interval in minutes.

[b] R.M. is rate of fluid movement in the capillary flow tube (cm/minute).

I.

B. KCl solution (0.1N) is used in both chambers A and A' of diffusion cell.

Table A.2.

Head difference	15° C				25° C				35° C			
	Kaolinite		Soil		Kaolinite		Soil		Kaolinite		Soil	
	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.
80 cm	2	2.05	2	1.35	2	2.65	2	1.60	2	3.15	2	2.25
	2	2.00	2	1.35	2	2.70	2	1.60	2	3.20	2	2.30
	2	2.10	2	1.35	2	2.70	2	1.55	2	3.25	2	2.30
	2	2.05	2	1.30	2	2.65	2	1.61	2	3.20	2	2.30
	2	2.05	2	1.35	2	2.70	10	1.55	2	3.25	2	2.35
	4	2.03	2	1.35	10	2.73	2	1.60	2	3.20	2	2.35
	2	2.05	2	1.40	2	2.60	2	1.70	2	3.20	2	2.30
	10	2.00	10	1.35	2	2.55	2	1.65	10	3.21	10	2.30
	1	2.10	10	1.40	2	2.55	--	--	10	3.22	10	2.31
	--	--	--	--	2	2.55	--	--	2	3.20	2	2.30
		2.05		1.35		2.60		1.60		3.20		2.30
10 cm	100	0.042	100	0.0275	114	0.051	100	0.035	100	0.061	100	0.048
	100	0.043	100	0.0280	54	0.050	100	0.036	100	0.062	100	0.048
	100	0.043	100	0.0270	23	0.052	100	0.034	100	0.062	100	0.048
	50	0.044	50	0.0280	22	0.051	100	0.034	100	0.061	100	0.047
	100	0.043	100	0.0280	90	0.050	100	0.035	100	0.061	100	0.048
	100	0.042	100	0.0290	100	01052	100	0.035	100	0.062	100	0.048
	200	0.043	200	0.0280	100	0.051	100	0.035	100	0.063	100	0.048
	100	0.043	100	0.0280	--	--	100	0.036	100	0.062	100	0.048
	--	--	--	--	--	--	--	--	100	0.061	100	0.048
									100	0.062	--	
		0.043		0.028		0.051		0.035		0.062		0.048

I.

C. KCl solution (0.2N) is used in both chambers A and A' of diffusion cell.

Table A.3.

Head difference	15° C				25° C				35° C			
	Kaolinite		Soil		Kaolinite		Soil		Kaolinite		Soil	
	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.	T.I.	R.M.
	2	3.4	2	3.3	1	4.60	1	3.9	1	5.3	1	4.30
	1	3.4	2	3.4	1	4.60	1	3.9	1	5.1	1	4.30
	1	3.5	1	3.3	1	4.70	1	3.9	1	5.2	1	4.20
	1	3.6	1	3.3	1	4.60	1	3.9	1	5.2	5	4.25
	1	3.6	1	3.4	2	4.60	2	3.9	1	5.1	2	4.3
80 cm	1	3.6	1	3.4	10	4.55	10	3.9	10	5.2	1	4.2
	10	3.6	10	3.3	2	4.6	2	3.9	1	5.2	1	4.3
	1	3.7	1	3.5		--	--	--	1	5.2	1	4.4
	1	3.6	1	3.2		--	--	--	--	--	1	4.3
		3.6		3.3		4.6		3.9		5.2		4.3
	20	0.350	20	0.035	2	0.450	2	0.035	10	0.58	10	0.055
	10	0.340	10	0.032	2	0.450	2	0.04	10	0.56	20	0.055
	60	0.345	60	0.033	110	0.450	110	0.045	10	0.56	10	0.057
10 cm	10	0.35	10	0.030	2	0.50	2	0.04	10	0.56	60	0.055
	100	0.34	100	0.033	2	0.45	2	0.04	10	0.56	30	0.055
	50	0.34	50	0.035	1	0.45	1	0.04	10	0.56	10	0.055
	100	0.345	100	0.033	31	0.43	31	0.045	10	0.55	--	--
	--	--	--	--	10	0.45	10	0.04	--	--	--	--
		0.345		0.033		0.45		0.04		0.56		0.055

II.

A. KCl solution is used at concentration of .3 N in chamber A and .2N in chamber A' for soil system.

Table A.4.

15° C					25° C					35° C				
			Voltage					Voltage					Voltage	
T.I.	R.M.	Date and Time	Chamb. A	Chamb. A'	T.I.	R.M.	Date and Time	Chamb. I	Chamb. II	T.I.	R.M.	Date and Time	Chamb. A	Chamb. A'
70	.043	11 A.M.	.0136	.0285	40	.06	10 A.M.	.0175	.0299	24	.08	10 A.M.	.0215	.0315
60	.045	1-2			50	.065	1-9			24	.08	1-19		
30	.043	11 A.M.	.0137	.0285	130	.06	10 A.M.	.0175	.0299	25	.085	10 A.M.	.0217	.0315
60	.043	1-3			22	.06	1-10			20	.082	1-20		
100	.044	11 A.M.	.0138	.0285	20	.06	10 A.M.	.0176	.0299	20	.08	10 A.M.	.0219	.0315
50	.044	1-4			120	.055	1-11			14	.082	1-21		
30	.042	11 A.M.	.0139	.0285	80	.06	10 A.M.	.0177	.0299	36	.08	10 A.M.	.0222	.0314
50	.044	1-5			40	.06	1-12			100	.081	1-22		
20	.042	11 A.M.	.014	.0285	28	.62	10 A.M.	.0178	.0299	50	.083	10 A.M.	.0224	.0314
60	.043	1-6			100	.06	1-13			76	.082	1-23		
10	.044	11 A.M.	.0141	.0284	--	--	10 A.M.	.0179	.0299	25	.082	10 A.M.	.0226	.0314
20	.045	1-7			--	--	1-14			10	.08	1-24		
		11 A.M.			30	.06	10 A.M.	.0178	.0295	10	.08	10 A.M.	.0215	.0315
		1-8			40	.06	1-15			43	.08	1-26		
					180	.06	10 A.M.	.0178	.0295	10	.08	10 A.M.	.0218	.0315
					100	.061	1-16			34	.081	1-27		
					100	.06	10 A.M.	.0179	.0295	30	.08	10 A.M.	.0221	.0315
					50	.06	1-17			50	.08	1-28		
					30	.06	10 A.M.	.018	.0295		--	10 A.M.	.0223	.0315
						.06	1-17				.08	1-29		

II.

B. KCl solution is used at concentration of 0.2 N in chamber A and 0.3 N in Chamber A' for soil system.

Table A.5.

15° C					25° C					35° C				
		Date and Time	Voltage				Date and Time	Voltage				Date and Time	Voltage	
T.I.	R.M.		Chamb. A	Chamb. A'	T.I.	R.M.		Chamb. A	Chamb. A'	T.I.	R.M.		Chamb. A	Chamb. A'
100	0.015	10 A.M. 2-28	.0235	.0185	27	.021	10 A.M. 2-16	.0275	.0196	116	.033	10 A.M. 2-11	.0271	
50	0.016				100	.022				144	.04			
37	0.14	10 A.M. 3-1	.0234	.0185	70	.021	10 A.M. 2-17	.0274	.0197	52	.04	5 P.M. 2-11	.0271	
145	.014				122	.022				140	.03			
76	.015	10 A.M. 3-2	.0233	.0186	267	.020	10 A.M. 2-18	.0272	.0197	33	.03	10 A.M. 2-12	.027	
102	.016				60	.021				100	.033			
100	.015	10 A.M. 3-3	.0232	.0186	40	.021	10 A.M. 2-19	.0271	.0197	50	.032	10 A.M. 2-13	.0269	
100	.014				100	.021				120	.03			
50	.015	10 A.M. 3-4	.0231	.0187	150	.021	10 A.M. 2-20	.0269	.0198	40	.033	10 A.M. 2-14	.0268	
100	.015									30	.03			
--	--	10 A.M. 3-5	.0230	.0187		--	10 A.M. 2-21	.0268	.0198	10	.03	10 A.M. 2-16	.0261	
	.015					.021					.031			
							10 A.M. 2-21	.0275	.0185	120	.03			
										100	.031			
							10 A.M. 2-22	.0274	.0186	50	.031			
										72	.03			
							10 A.M. 2-23	.0273	.0188	265	.031			
										50	.03			
							10 A.M. 2-24	.0272	.019		--			
											.031			

III.

A. KCl solution is used at concentration of 0.05 N in Chamber A and 0.1 N in Chamber A' for kaolinite system.

Table A.6.

15° C					25° C					35° C				
		Date and	Voltage				Date and	Voltage				Date and	Voltage	
T.I.	R.M.	Time	Chamb. A	Chamb. A'	T.I.	R.M.	Time	Chamb. A	Chamb. A'	T.I.	R.M.	Time	Chamb. A	Chamb. A'
100	0.077	10 A.M.	0.0558	.0431	100	.089	10 A.M.	0.061	0.0456	20	.11	10 A.M.	.0625	.05
90	0.076	6-17			20	.09	6-27			20	.105	7-6		
30	0.077	10 A.M.	.0558	.0431	20	.09	10 A.M.	0.061	.0456	20	.11	10 A.M.	.0625	.05
20	0.075	6-18			20	.09	6-28			20	.112	7-7		
50	0.076	10 A.M.	.0558	.0431	20	.095	10 A.M.	0.061	0.0456	100	.11	10 A.M.	.063	.05
100	0.077	6-19			20	.09	6-29			20	.103	7-8		
40	0.075	10 A.M.	.0557	.0431	20	.09	10 A.M.	0.060	.0457	40	.11	10 A.M.	.0625	.0501
30	0.075	6-20			20	.09	6-30			40	.105	7-9		
60	0.076	10 A.M.	.0558	.0432	100	.09	10 A.M.	0.060	.0457	20	.11	10 A.M.	.0625	.0501
20	0.075	6-21			60	.091	7-1			20	.11	7-10		
20	0.076	10 A.M.	.0558	.0432	20	.085	10 A.M.	0.061	.0457			10 A.M.	.063	.0501
		6-22			100	.09	7-2					7-11		
		10 A.M.	.0558	.0433	100	.09	10 A.M.	--	.0458			10 A.M.	.063	.0502
		6-23					7-3					7-12		
		10 A.M.	.0538	.0433			10 A.M.	0.061	.0458			10 A.M.	.063	.0502
		6-24					7-4					7-13		
		10 A.M.	.0558	.0433			10 A.M.	0.061	0.0458			10 A.M.	.063	.0502
	0.076	6-25				.09	7-5				.11	7-14		

III.

B. KCl solution is used at concentration of 0.1 N in Chamber A and 0.05 N in Chamber A' for kaolinite system.

Table A.7.

15° C					25° C					35° C				
		Date and	Voltage				Date and	Voltage				Date and	Voltage	
T.I.	R.M.	Time	Chamb. A	Chamb. A'	T.I.	R.M.	Time	Chamb. A	Chamb. A'	T.I.	R.M.	Time	Chamb. A	Chamb. A'
200	.01	10 A.M. 7-27	.0395	.0592	100	.011	10 A.M. 7-21	.044	.061	100	.015	10 A.M. 7-15	.046	.068
200	.0095				100	.012				100	.014			
200	.01	10 A.M. 7-28	.0395	.059	300	.012	10 A.M. 7-22	.0441	.06	100	.016	10 A.M. 7-16	.046	.067
100	.009				100	.013				100	.015			
300	.0092	10 A.M. 7-29	.0394	.0585	100	.012	10 A.M. 7-23	.0442	.0595	100	.017	10 A.M. 7-17	.047	.066
300	.0042				100	.013				100	.015			
100	.01	10 A.M. 7-30	.0394	.058	100	.012	10 A.M. 7-24	.0442	.0592	100	.014	10 A.M. 7-18	.047	.065
400	.0097				100	.0125				100	.015			
		10 A.M. 7-31	.0393	.058	300	.012	10 A.M. 7-25	.0443	.059	100	.018	10 A.M. 7-19	.047	--
					100	.012								
		10 A.M. 8-1	.0393	.0577			10 A.M. 7-26	.0444	.0588			10 A.M. 7-20	.0475	.064
	.0095					.012					.015			

APPENDIX B

Example of Calculation and Analysis of Experimental Data for Soil System at 25° C

I. Calculation of driving forces

A. The driving force on the water is $\overline{v}_w \Delta p$ where $\overline{v}_w$ is the partial specific volume of water and Δp is the pressure difference between chambers A and A'.

Ten centimeters of water head difference = 9833 dyne cm^{-2}; $\overline{v}_w$ is taken to be 1 gm. cm^{-3}; hence, $\overline{v}_w \Delta p$ erg. gm^{-1}.

B. The salt driving force is $RT\Delta \ln \alpha_s$, where R is the universal gas constant (erg. gm^{-1} deg^{-1} = cm^2 sec^{-2} deg^{-1}), T is the absolute temperature (deg. °K), and $\Delta \ln \alpha_s$ (dimensionless quantity) = $\ln \frac{\alpha_s^{A'}}{\alpha_s^{A}} = \ln \frac{\gamma^{A'} x^{A'}}{\gamma^{A} \gamma^{A}}$. α_s is the activity of salt, γ is the activity coefficient,[1] x is the mole fraction, and A and A' denote respectively the solutions of low and high concentration. Calculation of $\Delta \ln \alpha_s$ is shown in table B.1.

II. Calculation of the ratio r (eq. 30) is shown in table B.2, where the logarithmic of water activity ($\log \alpha_w$) is taken from Stokes and Robinson (1955), at .3 N and .2 N KCl concentration.

III. Calculation of the coefficient L_{ww} from preliminary experiments at pressure differences of 10 cm; KCl solution (0.2 N) is used in Chambers A and A' of soil system. Cross sectional area of capillary (a) is 0.0303 cm^2, and reference surface cross sectional area (A) is 45.34 cm^2.

From table A.3, Appendix A, the average rate of solution movement at 25° C (298° K) is 0.04 cm min^{-1}. The calculation is shown in table B.3.

---

[1] Activity coefficient (x) is taken from Robinson and Stokes (1955).

IV. Calculation of L_{ws}

The value of L_{ws} is determined by substituting the known parameters, J_w (measured), driving forces (calculated), and L_{ww} (determined from preliminary experiment), into equation (42a).

From table A.4, Appendix A, the average rate of solution movement is 0.06 cm min^{-1}. The calculation is shown in table B.4.

V. Calculating salt flux (gm sec^{-1} cm^{-2})

The salt content in a solution chamber could be determined by multiplying the salt concentration of the solution in the chamber by the chamber volume. Hence, subtracting the initial salt content from the final salt content at the end of an experimental run, the net amount salt transferred to or from the chamber was evaluated. Dividing by the reference surface cross sectional area gives the salt flux term. The net amount of salt transferred was taken as an average of that calculated from the two chambers of a diffusion cell.

From table A.5, Appendix A, the initial voltage readings are 0.0275 and 0.0196 for Chambers A and A' respectively. The final readings for the same chambers are 0.0268 and 0.0198. From calibration curves (figures 3 and 4), the corresponding initial concentrations are .2 N and .3 N respectively, and the corresponding final concentrations are .205 N and .296 N. The initial solution volume in either chamber is 521.41 cm^3. Realizing that there is .916 cm^3 day^{-1} transferred from Chamber A' to Chamber A, therefore, initial and final salt contents may be compiled by multiplying the initial and final concentration by the corresponding solution volume. Convert from molar transfer to grams by multiplying by the molecular weight of KCl (74.5 g/mole).

Calculations of salt transfer and salt flux are shown in tables B.5 and B.6 respectively.

VI. Calculation of the coefficients, L_{sw} and L_{ss}

Equation (42b) for two different experimental runs (in the first run, driving forces were operating in the same direction, whereas in the second forces were operating in the opposite direction) was solved simultaneously for L_{sw} and L_{ss} by introducing the known parameters L_{ww}, L_{ws}, $\overline{v}\Delta p$, $RT\Delta \ln \alpha_s$, and the ratio r into the equation. The following is an illustrative example.

From table B.4, $\overline{v}_w$ p is 9833 ergs gm^{-1}, $RT\Delta \ln \alpha_s$ is 1.21×10^8 ergs gm^{-1}, L_{ww} is 1.356×10^{-8} gm sec deg cm^{-4}, and L_{ws} is 5.425×10^{-13} gm sec deg cm^{-4}. The ratio r is 8.805×10^{-3} (table B.2). TJ_s was calculated for the first experimental run to be 4.0129×10^{-6} (table B.5), and for the second run to be 1.6494×10^{-6}.

$$-TJ_s = [-r\ L_{ww} + L_{sw}]\ \overline{v}\Delta p + [-r\ L_{ws} + L_{ss}]\ RT\Delta \ln \alpha_s$$

$$\therefore -4.01 \times 10^{-6} = [(-8.805 \times 10^{-3})(1.356 \times 10^{-8}) + L_{sw}](-9833) + [(-\ 8.805 \times 10^{-3})(5.425 \times 10^{-13}) + L_{ss}](-1.21 \times 10^8)$$

and

$$1.65 \times 10^{-6} = [(-8.805 \times 10^{-3})(1.356 \times 10^{-8}) + L_{sw}](-9833) - [(-8.805 \times 10^{-3})(5.425 \times 10^{-13}) + L_{ss}](-1.21 \times 10^8) \quad .$$

Adding the two equations gives

$$-2.36 \times 10^{-6} = 2[(-11.7401 \times 10^{-7}) - 9833\ L_{sw}]$$

and

$$-2.36 \times 10^{-6} + 2.35 \times 10^{-6} = -19666\ L_{sw}$$

$$\therefore \frac{.01 \times 10^{-6}}{19666} = 5.08 \times 10^{-13} \quad .$$

The coefficient L_{ss} was evaluated by introducing the value of L_{sw} in either equation as follows:

$$1.65 \times 10^{-6} = -11.74 \times 10^{-7} - .05 \times 10^{-7} - 5.78 \times 10^{-7} + 1.21 \times 10^{8}\ L_{ss}$$

$$\therefore 3.45 \times 10^{-6} = 1.21 \times 10^{8}\ L_{ss}$$

$$\therefore L_{ss} = \frac{3.41 \times 10^{-6}}{1.21 \times 10^{8}} = 2.82 \times 10^{-14} \text{ gm sec deg cm}^{-4} \quad .$$

Table B.1. Calculation of $\Delta \ln \alpha_s$ for KCl.

RT ergs/g	x^A Molar	$x^{A'}$ Molar	$\gamma A'$	$\gamma A'$	α_s^A	$\alpha_s^{A'}$	$\frac{\alpha_s^{A'}}{\alpha_s^A}$	$\ln \frac{\alpha_s^{A'}}{\alpha_s^A}$	$RT\Delta \ln \alpha_s$ ergs/g
33.268×10^7	0.2	0.3	0.718	0.688	0.1436	0.2064	1.437	0.3639	1.21×10^8

Table B.2. Calculation of r.

$-\log \alpha_w^A$	$-\log \alpha_w^{A'}$	$\log \alpha_w^{A'} - \log \alpha_w^A$	$\ln \alpha_w^{A'} - \ln \alpha_w^A$	$\ln \frac{\alpha_s^{A'}}{\alpha_s^A}$ From table B.1	$r = \frac{\Delta \ln \alpha_w}{\Delta \ln \alpha_s}$
0.002863	0.004256	-0.001393	-3.2039×10^{-3}	.3639	-8.805×10^{-3}

Table B.3. Calculation of L_{ww}.

Temp. °K	Velocity		$J_w = \frac{V_a \rho_w}{A}$ (gm sec^{-1} cm^{-2})	TJ_w deg gm sec^{-1} cm^{-2}	$-\bar{v}_w \Delta p$ ergs gm^{-1}	$L_{ww} = \frac{-TJ_w}{-(J_w \Delta p)}$ deg gm sec cm^{-4}
	cm min^{-1}	cm sec^{-1}				
298	4×10^{-2}	6.7×10^{-4}	44.7×10^{-8}	1.33×10^{-4}	-9833	1.36×10^{-8}

Table B.4. Calculation of L_{ws}.

Temp °K	Velocity		J_w gm sec^{-1} cm^{-2}	TJ_w deg gm sec^{-1} cm^{-2}	L_{ww} (Table B.3)	$-\bar{v}_w \Delta p$	$-RT\Delta \ln \alpha_s$ (Table B.1)	L_{ws} gm deg sec cm^{-4}
	cm min^{-1}	cm sec^{-1}						
298	6×10^{-2}	1×10^{-3}	6.683×10^{-7}	1.99×10^{-4}	1.36×10^{-8}	-9833	-1.21×10^{8}	5.42×10^{-13}

Table B.5. Calculation of salt transfer.

Temp °K	Chamber A							Chamber A'						
	Initial			Final (5 days)			Salt transf. 3/5 days	Initial			Final (5 days)			Salt transf. 3/5 days
	Volume cm^3	Conc. m/1	Salt Cont. grams	Volume	Conc. m/1	Salt Cont. grams		Volume	Conc. m/1	Salt Cont. grams	Volume	Conc. m/1	Salt Cont. grams	
298	521.41	.2	7.769	526.07	.205	8.033	.264	521.41	.3	11.6535	516.83	.296	11.390	.2635

Table B.6. Calculation of salt flux.

Temp °K	Salt transferred gm/day			$J_s = \frac{gm}{sec\ cm^2} = \frac{\text{Salt transferred}}{A}$	TJ_s $\frac{gm\ deg}{sec\ cm^2}$
	Cham. A	Cham. A'	Average		
298	.0528	- .0527	.05275	1.35×10^{-8}	4.013×10^{-6}

APPENDIX C

Propositions

The following propositions were submitted for defense as a part of the final Ph.D. examination. Three of them were selected to defend.

1. Some of the derivations of thermodynamics equations that are given in physical chemistry texts are confusing and need a more careful identification and notation of symbols.

2. Addition of organic matter during the process of reclaiming black alkali soils could be harmful to the physical properties of sub-layer soil.

3. The existence of Israel in the Middle East constitutes a greater military and economic threat to the neighboring Arab countries than would be present if Palestine were under Arab control.

4. The use of water of poor quality; i.e., water of high salt content and a high proportion of sodium, would be helpful in reclaiming the large areas of impermeable sodic soils in the Nile Delta.

5. Underground water flow into Bear Lake is an important source of the water which is stored in the lake.

6. The entropy of the first molecular layer of water that is adsorbed on soil particles is higher than that of pure free water for all known soils.

7. Agricultural benefits, in addition to the electrical power that will be generated, might result in the western desert of Egypt from the Natron depression project.

8. Exchangeable ions on the clay particles and the ion concentration in the pore water affect the Atterberg limits, consolidation tests, and shear strength tests of soil materials.

Proposition I

Some thermodynamics equations that are given in physical chemistry texts are confusing and need a more careful identification and notation.

Probably most students have more difficulty in understanding thermodynamics than any other phase of chemistry. The fundamental difficulty is in the lack of clarity and the confusing terminology often used in textbooks, especially for the beginning courses in physical chemistry.

This point will be established by the following four examples:

A. The first law of thermodynamics as it is expressed mathematically in equation (1) postulates that for any variation in a closed system, the difference in heat absorbed and the work done by the system is independent of the method used and of the path followed.

$$\begin{array}{lll} dE = d(q-w) & a & \\ dE = Dq - Dw & b & \\ dE = Dq - Pdv - D\mu' & c & (1) \\ dE = Dq - Pdv & d & \\ dE = eq - d\mu & e & \end{array}$$

where E is the internal energy of the system, w is the sum of all work terms dealing with magnetic, gravitational, electrical, or surface work as well as the work of expansion (Pdv), q is the heat absorbed or evolved by the system, and d denotes an exact differential where D defines the function as unperfect differential (not a property of the system).

The various mathematical expressions of the first law as shown above (eq. 1) are of doubtful value if we do not carefully define the symbols in them; i.e., to understand these equations we must agree upon what a property of the system is, the physical difference between d and D as well as the meaning of E, q, μ, μ'.

Equation (1e) has been used to express the first law in widely-used text books (Daniel and Alberty, 1959, p. 95; Moore, 1963, p.38). This equation is an example of confusion. These authors define q and μ so that they can not be properties of the system; then when they use the most exact language (mathematics), they present an expression which says that q and w are properties of the system.

B. By definition

$$H = E + pv \tag{2}$$

where H is called in most, if not all, physical chemistry and thermodynamics books (Daniel and Alberty, 1959; Glasstone, 1954; Moore, 1963; Hamilland Williams, 1961; Lewis and Randall, 1961) heat content of the system. As defined by equation (2), H equals two terms of energy: one is the internal energy; the other is a pressure volume energy. Therefore, H is an energy term which is not restricted only to heat.

H is called heat content because when the reaction expressed by equation (3) is carried out at constant pressure without any useful work being done, ΔH is measured by the heat evolved expressed by the system (Ludder, 1946).

$$\left.\begin{array}{rll} dH &= dE + pdv + vdp & \quad a \\ &= Dq - pdv + pdv & \quad b \\ \Delta H &= q_p \quad . & \quad c \end{array}\right\} \quad (3)$$

This is confusing because with a similar argument, it could be claimed that ΔE is also heat content of the system if the same reaction has been carried at constant volume. This is expressed by equation (4).

$$\begin{aligned} dE &= Dq - pdv && \text{a} \\ \Delta E &= q_v \quad . && \text{b} \end{aligned} \qquad (4)$$

C. Unfortunate confusion has arisen in the literature because of the non-uniformity in the use of symbols for the four thermodynamic functions of Gibbs. Some authors use U, H, F, G for the internal energy, enthalpy, work function or Helmholtz free energy, and Gibbs free energy respectively (Guggenheim, 1957) and others use the symbols E, H, A, F (Lewis and Randall, 1961). Recently, Moore (1963) used the symbols E, H, A, G. An agreement to avoid such confusion should be reached at an international level.

D. Another example of confusing equations as they are written in textbooks (Hamill and Williams, 1959; Daniel and Alberty, 1959) is the equation relating the change of internal energy to the change in temperature

$$dE = C_v dT \quad . \qquad (5)$$

This equation is developed from the first law of thermodynamics (eq. 1) by taking the derivative with respect to temperature at constant volume. This gives

$$\left(\frac{\partial E}{\partial T}\right)_v = \left(\frac{Dq}{\partial T}\right)_v = C_v \quad . \qquad (6)$$

Therefore, equation (5) is not true unless the system is at constant volume in which case dE should be denoted with the partial notation v.

By a similar argument, dH should be denoted by the subscript p when we write the equation relating the change of enthalpy to the change in temperature (6)

$$dH = C_p \, dT \quad . \qquad (7)$$

References

(1) Daniels, F. and R. A. Alberty. Physical Chemistry. John Wiley and Sons, Inc. New York. 1959.

(2) Glasstone, S. G. Thermodynamics for Chemists. D. Van Nostrand Company, Inc. New York. 1954.

(3) Guggenheim, E. A. Thermodynamics. North Holland Publishing Company. Amsterdam. 1957.

(4) Hamill, W. H. and R. R. Williams. Principles of Physical Chemistry. Prentice-Hall, Inc. Englewood Cliffs, New Jersey. 1959.

(5) Lewis, G. N. and M. Randall. Thermodynamics. McGraw-Hill Book Company, Inc. New York. 1961.

(6) Ludder, W. F. The semantics of thermodynamics. Part 1. Journal of Chemical Education 23:54-59. 1946.

(7) Moore, W. J. Physical Chemistry. Prentice-Hall Inc. Englewood Cliffs, New Jersey. 1963.

Proposition II

Addition of organic matter during the process of reclaiming black alkali soil could be harmful to the physical properties of sublayer soils.

Black alkali soils is a term used ordinarily to designate a soil in which the exchangeable sodium percentage is greater than 15 and the conductivity of the saturation extract is less than 4 m.mhos per cm at 25° C (Richards, 1954). The pH usually ranges between 8.5 and 10. Dissolved organic matter present in the soil solution is deposited on the soil surface by evaporation, thus causing darkening and giving rise to the term black alkali.

It has been widely confirmed that the reclamation of alkali soils in general requires:

1. Establishment of drainage if a high water table exists.
2. Replacement of exchangeable sodium by calcium or other divalent cations.
3. Removal of excess salts by leaching.
4. Aggregation of soil particles so as to improve soil structure.

To replace the exchangeable sodium with calcium, the treatment most commonly used is the addition of gypsum, sulfur, or organic matter. Sulfur is converted to sulfuric acid and the organic matter to carbonic acid by the microorganisms present in moist soil. If $CaCO_3$ is present in the soil, the following reactions occur

$$H_2SO_4 \text{ (due to oxidation of sulfur)} + 2CaCO_3 + 4Na(ad) \rightarrow$$

$$2Ca(ad) + Na_2SO_4 + 2NaHCO_3$$

$$H_2CO_3 \text{ (due to decomposition of organic matter)} + CaCO_3 + 2Na(ad) \rightarrow Ca(ad) + 2NaHCO_3 \quad .$$

It is known that the decomposed part of organic matter dissolves in alkaline soils and liberates ammonia which converts to NH_4^+ in the presence of water (Kelley, 1951). Sodium ion has a higher flocculation value than NH_4 (Baver, 1959); hence, the ammonia liberated along with that produced by ammonifying microorganisms (Greaves and Jones, 1941) replaces the exchangeable sodium in the surface layer according to the reaction

$$2Na(ad) + (NH_4)_2\ CO_3 \rightarrow 2NH_4(ad) + Na_2CO_3$$

$$Na(ad) + NH_4OH \rightarrow NH_4(ad) + NaOH \quad .$$

Sodium ions move with the leachate as Na^+ to the sublayer. As the concentration of Na ions increases in the sublayer solution, the equilibrium condition between the soil solution and the soil complex will be disturbed, and sodium will replace exchangeable calcium according to the reaction

$$Ca(ad) + 2(Na^+) + CO_3^{--} \rightleftarrows 2Na(ad) + CaCO_3 \quad .$$

The presence of CO_3^{--} tends to force the reaction to the right in the absence of H^+. As the proportion of the exchangeable sodium increases in the soil sublayer, the soil tends to be more dispersed.

The mixture of dispersed clay particles and dissolved organic matter moves to the sublayer where the clay accumulates. This results in a layer that is impervious to water. This further retards the leaching and reclamation of the soil.

3. Under the conditions of high pH value; i.e., more than 8.5, it has been shown by Greaves and Jones (1941) that such reaction increases the activity of reduction bacteria. It has been also shown by Gracie et al. (1934) that sulfate reducing bacteria have been responsible for the formation of sodium carbonate in the Nile Delta of Egypt. This is expressed by the equations

$$Na_2SO_4 \xrightarrow[\text{bacteria}]{\text{reduction}} Na_2S$$

$$Na_2S + H_2CO_3 \longrightarrow H_2S + Na_2SO_4 \quad .$$

The essential conditions for this reduction are lack of oxygen and an abundance of organic matter which serves as a source of energy for the microorganisms. Not only is sodium carbonate harmful to the soil physical condition, but also it is toxic to plants (Kelley, 1951).

Haycock (1963) presented experimental evidence that there was no change in the amount of exchangeable sodium of the soil in plots that received only manure as an amendment in reclaiming alkali soils. In addition, infiltration of water into the soil of some of these plots treated only with manure was impossible.

References

(1) Baver, L. D. Soil Physics. John Wiley & Sons Inc. New York, p. 30, 1959.

(2) Gracie, D. S., M. Rizk, A. Moukhtar, and A. H. Moustafa. The nature of soil determination in Egypt. Ministry of Agriculture. Egypt, Technical and Science Series Bulletin 148, 1-22, 1934.

(3) Greaves, J. E. and L. W. Jones. The survival of microorganisms in alkali soils. Soil Science 52:329-364. 1941.

(4) Haycock, E. B. The effectiveness of leaching and soil amendments in improving a salt-affected soil of the Hooper area of Utah. M.Sc. Thesis. Utah State University. 1963.

(5) Kelley, W. P. Alkali Soils. Reinhold Publishing Corporation. New York. Chapters 4 and 7, 1951.

(6) Richards, L. A. ed. Saline and alkali soils. Agric. Handbook No. 60. U. S. Superintendent of Documents, Washington D. C., pp. 5, 1954.

Proposition III

Underground water flow into Bear Lake is an important source of the water which is stored in the lake.

Bear Lake is located in an elongated, rather narrow valley lying across the Idaho-Utah boundary about 12 miles west of the Wyoming border. Its width is about 7 miles, which is about 1/6 of its length (figure 1). As a reservoir, the lake has a present capacity of 1,421,000 acre-feet.

The water stored in the lake is used in the production of electrical power and for irrigation. The study of the lake storage operation and hydrology presents a most complex problem. At various times throughout the year, water is withdrawn from the lake for power purposes; and in the irrigation season water is also withdrawn for irrigation.

Water is supplied from several creeks that drain into the Bear Lake from the east and the west. Most of these creeks are not gaged, hence their contribution to the water supply of the lake is not measured. The water of these, together with irrigation return flows, natural channel gains, and natural channel losses add to the difficulty in obtaining accurate inflow-outflow data.

To study the hydrology of any lake, we should maintain a water budget; in such studies the hydrologic equation plays a dominating role.

$$\text{Inflow} = \text{outflow} + \Delta\ \text{storage} + \text{evaporation} \qquad (1)$$

that is, during a given time, the total inflow to a given area must equal the total outflow plus the change in storage plus evaporation.

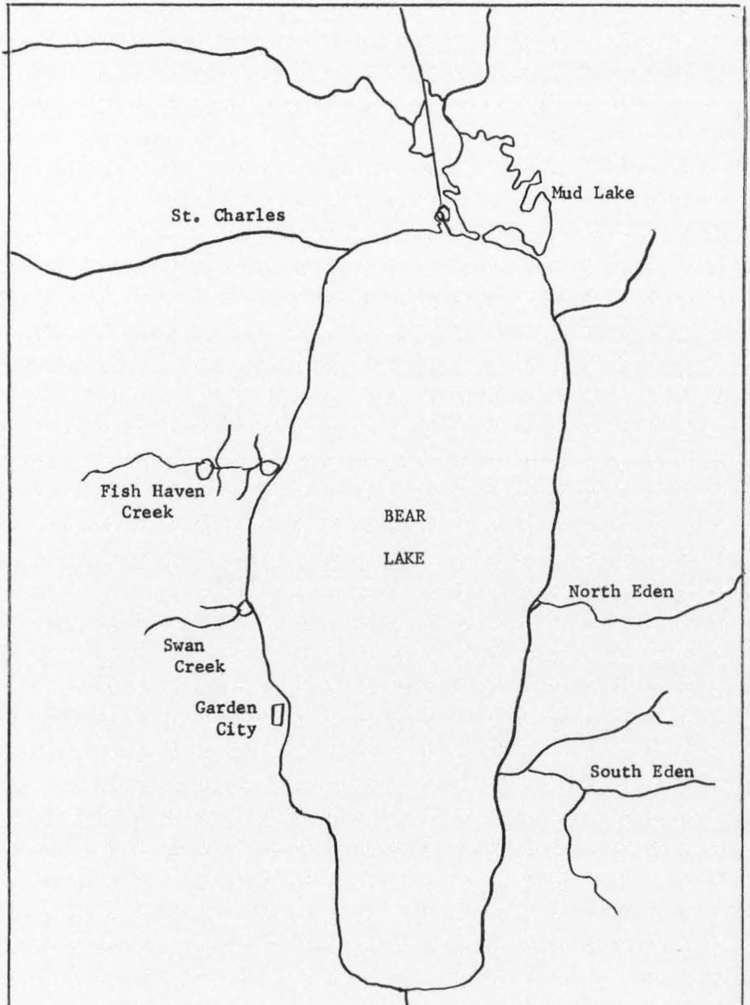

Figure C.1. Bear Lake.

In general, items in that equation are:

I. Inflow: this term includes all kinds of water draining into the area such as:

  a) Surface inflow

  b) Precipitation

  c) Import, defined as water piped or channeled into the area

  d) Ground water inflow.

II. Outflow: this term includes all kinds of water going out of the area:

  a) Surface outflow

  b) Ground water outflow

  c) Export, defined as water piped or channeled out of the area.

III. Change in storage: this occurs as a change in surface reservoir water and depression storage.

IV. Evaporation and transpiration.

Writing the hydrologic equation in detailed, defined terms for Bear Lake conditions gives

$$\Delta S = I_i + I_g + T + P - O_o - E - O_g \qquad (2)$$

where ΔS is the change in storage, I_i is the inflow that passes the inlet canal gage, I_g is ground water inflow, T is the tributary inflow, P is precipitation, O_o is outflow that passes the outflow canal gage, E is evaporation from the lake, and O_g is ground water outflow.

The change in storage is considered to be the difference in the lake content between two successive water years. Precipitation was determined on water year basis. Evaporation was calculated by taking an estimate of 34 inches of water for Bear Lake drainage basin (Iorns, 1955). Multiplying both precipitation and evaporation values by the corresponding surface area of the lake for a particular water year gives the amount of precipitation and evaporation (P, E terms).

Calculations in this study were made for every single water year for the period from 1924-1950. Average values over a period of 25 years are shown in table 1.

Solving equation (2) for the sum of the unknown terms $(T + I_g - O_g)$, it turns out that the amount of water delivered to Bear Lake by the tributaries and the net underground inflow averaged over 25 years to be 137,378 acre feet per year.

The tributary inflow into the lake (T) was determined by considering all but two of the streams that adjoin the lake; these are South and North Eden Creeks for which there is no available data. However, these two streams are of no great significance in contributing to the storage of the lake (Irons, 1950). Data are available above and below diversion during irrigation season only for the following creeks: Swan, Fish Haven, St. Charles, and Cottonwood (figure 1). Bloomington Creek is the only stream which is measured for the whole year.

Since these streams are located in the same basin and exposed to the same climatic conditions, a direct relationship between the discharge of these streams and that of Bloomington was assumed. The monthly diversion of Swan, St. Charles, Fish Haven, and Cottonwood Creeks for the missing data concerning the winter months (October, November, December, January, February, and March) was estimated by taking the ratio of the total diversion during the summer period for each stream to that of Bloomington Creek, then multiplying the ratio into the diversion of every single month during the winter for Bloomington Creek.

Table 1. Averages over a 25-year period in acre-feet.

Surface Area (Acres)	Inflow - $T - I_g$			Outflow - O_g			ΔS	$T + I_g - O_g$	T	$I_g - O_g$
	Inlet Canal	Precip.	$\Sigma\ 1 + 2$	Outlet Canal	Evap.	$\Sigma\ 4 + 5$				
66,444	200,830	56,047	284,500	219,520	175,300	395,200	1,560	137,378	39,372	98,005

The average tributary inflow over the period of study amounted to 39,373 acre-feet per year (table 1). Subtracting this value from that of $(T + I_g - O_g)$, the underground inflow turns out to be 98,005 acre-feet per year as an average over 25 years. This is about 50 per cent of the water diverted from Bear River to the lake and more than 25 per cent of the total inflow to Bear Lake (table 1).

Despite the fact that the underground inflow estimate involves all the errors that might occur in the different measurements, it gives preliminary information which is necessary when a detailed hydrologic study for the lake is conducted.

References

(1) Iorns, W. V. U.S.S.G.S. Water Research Branch. Bear River hydrometric data. Tristate investigation. 1944 and 1945.

(2) Iorns, W. V. Report No. 10. Analysis of Bear Lake. September, 1950.

(3) Iorns, W. V. Evaporation from 17 western states. Professional Paper 272-D. 1955.

(4) Singler, W. F. Bear Lake and its future. 26th Faculty Honor Lecture. U.S.U. 1962.

(5) Williams, J. S. and V. Parker. Recent history of Bear Lake Valley, Utah-Idaho. American Journal of Science 260:24-36. Jan. 1962.