

AN ABSTRACT OF THE DISSERTATION OF

Erick R. Burns for the degree of Doctor of Philosophy in Bioresource Engineering presented on September 27, 2004.

Title: Thermodynamics of Non-Dilute Saline Solutions in Variably Saturated Porous Media.

Abstract approved:

Redacted for Privacy

John S. Selker

Non-dilute salt strength solutions occur in many near surface geologic environments. In order to better understand the occurrence and movement of the water and salt, mathematical models for this non-ideal fluid need to be developed. Initial boundary value problems may then be solved to predict behavior for comparison with observations. Using the principles of equilibrium reversible and irreversible thermodynamics, relationships describing the thermo-physics of non-dilute saline solutions in variably saturated porous media are investigated. Each of four central chapters investigates a particular aspect of the flow of saline solutions through porous media. The first chapter derives the general relationships describing the effects of salt on the vapor content in the gas phase and also on the liquid pressure. The second chapter summarizes an example using the new theory for sodium chloride (NaCl) from zero to saturated strength. Additional terms beyond the dilute approximation are shown to be more important in very dry, fine textured soils with significant salt content. The third chapter derives the salt corrections for Darcy-type flow laws for variably saturated porous media, and an example for NaCl is given. Agreement between theory and experimental data is good, though there appear to be some unaccounted for effects. These effects may be the result of ionic interaction of the salt with the loamy sand used, and/or the effect of hysteresis of the water content-pressure relationship. The final chapter investigates two fundamental assumptions commonly used in process thermodynamics when considering mixtures described by porous media, saline water, and moist air. The first assumption is that temperature is the

generalized intensive variable associated with entropy. The second assumption is that the form of the differential of total energy is known a-priori. It is shown that the first assumption is suspect under some circumstances, and a generalized notion of how to select extensive variables for a given system is introduced for comparison with the second assumption. Examples comparing the “usual” and new theories are accomplished for ideal gases and for isotropic Newtonian liquids, with results being favorable except possibly for the Gibbs-Duhem Relation of the Newtonian liquid for the “usual” theory.

©Copyright by Erick R. Burns

September 27, 2004

All Rights Reserved

Thermodynamics of Non-Dilute Saline Solutions
in Variably Saturated Porous Media.

by
Erick R. Burns

A DISSERTATION

submitted to

Oregon State University

in partial fulfillment
of the requirements for the
degree of

Doctor of Philosophy

Presented September 27, 2004

Commencement June 2005

Doctor of Philosophy dissertation of Erick R. Burns presented on September 27, 2004.

APPROVED:

Redacted for Privacy

Major Professor, representing Bioresource Engineering

Redacted for Privacy

Head of the Department of Bioengineering

Redacted for Privacy

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Redacted for Privacy

Erick R. Burns, Author

ACKNOWLEDGEMENTS

Many people deserve thanks and credit for the successful completion of this dissertation. The research core of my committee is Professors John Selker, Maria Dragila, and Ron Guenther. Each has provided so very much help, and each challenges me in a different way. It has always been my belief that if I can write a dissertation with which they are all happy, then it will be something of which to be very proud. Maria, Ron, and I started working on research topics over four years ago, and with Professors Noam Weisbrod and Larry Boersma's invaluable thoughts and help, we managed to get an EPA STAR (Science to Achieve Results) Fellowship. Even though John Selker was added to the committee later, he has become as thoroughly engaged in the research as Maria and Ron, and for a while, even threatened to pass the others in hours spent with me on this project (I would hate to guess who has spent the most). I have spent many hours one-on-one with John, Maria, and Ron. Each has provided me with so much to think about and so much help. Any success that I can claim comes from the fact that each of them seems as committed to my success as I am. Any student would be lucky to have one such advisor, but I have been blessed three times over.

In addition to the research core, three other scientists deserve thanks. Professor Jean-Yves Parlange hosted me at Cornell University for a month near the beginning of the last year of the fellowship. He generously made ample time for me. I feel that this one month was worth ten months of time spent working on my project alone. Professor Brian Wood was a great surprise-addition as the graduate school representative. His research interests and proclivities towards the mathematical representation of porous media have made him a great resource, and I have enjoyed our discussions immensely. The last member of my committee also deserves my thanks, though not for the reasons I had anticipated when this all began. The research did not progress quite so far down the road towards evaporation (one of Richard's fields of expertise). Instead, I have enjoyed Professor Richard Cuenca's sense of

humor and personal warmth. He has always been there with a kind word and a light joke, and that is worth more than the uninitiated would think.

Lastly, I would express thanks to my wife Mandy, my family, and to God. Certainly, none of these deserves to come last, except in that it seems to make sense to me to write it down in this order (i.e., thanking the technical contributors first). Mandy has always been supportive of my coming back to school. I think she has more faith in me than I have in myself. I know that I will work hard but she seems to know I will succeed. The value of that is beyond measure during times of frustration. I love her, am thankful for her, and am lucky to have her. The rest of my family has always been similarly supportive. Also, they have always let it be known that if we needed anything, that we need only drop the barest of hints. Luckily, this has rarely been the case. Thanks to God for all of my blessings. The aforementioned should convince you that there are many.

CONTRIBUTION OF AUTHORS

Professors Selker, Dragila, Guenther, Parlange, and Weisbrod have each provided different aspects of expertise (subject to their own strengths and research experience) in the areas of mathematical representation of the physics of flow of saline fluids in variably saturated porous media. Professors Dragila, Guenther, and Weisbrod aided greatly in development of the research ideas that eventually resulted in funding for the first author. Professors Selker, Dragila, and Weisbrod have each provided ample feedback, corrections, and new thoughts for inclusion with the journal articles (Professor Dragila for the third and fourth papers and Professor Weisbrod for the third). Their vast collective experience as experimentalists with expertise in unsaturated porous media has greatly improved the resulting papers by ensuring that they are physically grounded and that relevant questions are explored. Professor Guenther has provided thorough review, corrections, and new ideas for the mathematical formulation of the thermo-physical problems. This is especially true for the mixture theory and continuum mechanical notions. Professor Parlange hosted the author at Cornell University for a month, during which time, the foundations for the first paper were firmly laid out. He has continuously been involved in providing review and substantial feedback ever since.

TABLE OF CONTENTS

	<u>Page</u>
Chapter 1 - Introduction.....	1
Chapter 2 - Thermodynamic Correction for Salts in Variably Saturated Porous Media	3
Abstract	4
Introduction.....	4
Derivation of Constitutive Relationships.....	5
Preliminaries and Assumptions.....	5
Derivations	8
Vapor pressure for zero-salt condition with a curved interface:	16
Vapor pressure for dilute solution approximation with a curved interface:	17
Vapor pressure for non-dilute solution with negligible interface curvature: ...	21
Vapor pressure for non-dilute solution with non- negligible interface curvature in an unsaturated porous media:.....	22
Liquid pressure correction for high strength salt solutions.....	24
Derivatives	29
Differential of water vapor pressure	30
Differential of liquid pressure	31
Discussion	32
Conclusion	34
Acknowledgements.....	35
Notation.....	35
References.....	36
Chapter 3 - Effects of Sodium Chloride (NaCl) on Constitutive Relations in Variably Saturated Porous Media.	38
Abstract	39
Introduction.....	39
Constitutive Relationships	40
Approximations to the Constitutive Relations.....	45

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Example: NaCl at 25° C	47
Computation of brine strength salt effects in porous media	48
Evaluation of approximations to the constitutive relations.....	53
Application to the data of Scotter.....	69
Conclusion	76
Acknowledgements.....	77
Notation.....	77
References.....	78
Chapter 4 - Darcy's Law for Flow of Variable Strength Salt Solutions in Variably Saturated Porous Media.	81
Abstract	82
Introduction.....	82
Derivation of Corrections to Darcy's Law.....	83
Salinity Correction to Hydraulic Conductivity	83
Salinity Correction to Hydraulic Diffusivity	84
Comparison with the experimental data of Scotter	89
Discussion	91
Conclusion	94
Acknowledgements.....	95
Notation.....	95
References.....	96
Chapter 5 - Developing an Axiomatic Method for Derivation of the Thermodynamic Relations of Irreversible Processes: Assumptions Reexamined	98
Abstract	99
Introduction.....	99

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Basic Conservation Laws.....	100
Preliminary Notions	100
Derivation of Equations	102
Conservation of Mass.....	105
Conservation of Linear Momentum.....	108
Kinetic Energy Equation.....	110
Conservation of Energy	111
The Usual Results	112
Internal Energy.....	112
Total Energy.....	114
The New Results	115
System Specific Relations.....	120
The “Usual” System Specific Relations.....	121
The System Specific Relations for the New Theory.....	122
Examples – Comparison of the two theories.	123
The Gibbs-Duhem Relation for an Ideal Gas with Zero Advective Velocity....	124
The Gibbs-Duhem Relation for Single Phase Steady Flow with Mass Conserved	126
Steady Flow of an Ideal Gas with Mass Conserved.....	128
Steady Flow of an Idealized Liquid with Mass Conserved.....	129
The Gibbs Relation for Flow of an Idealized Liquid with Mass Conserved	132
Discussion	134
Summary	138
Acknowledgements.....	139
Notation.....	140
References.....	141
Chapter 6 – Conclusion.....	143
Bibliography.....	145

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2.1 Schematic representation of a system composed of both a liquid and a gas.....	9
2.2 Diagram showing the change in state between two arbitrary states A and B, and another path AC followed by CB.	24
2.3 Schematic representation of a partially saturated porous media overlain by a gas filled space.	26
3.1 Surface tension as a function of NaCl(aq).	42
3.2 Integrand of the volume correction term as a function of NaCl(aq).	42
3.3 Liquid pressure as a function of molality for a silt for three different fixed water contents.	51
3.4 Plots of vapor pressure (equation (1)) for silt (top), loam (middle), and sand (bottom).	55
3.5a Plots for silt: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (11)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8).	56
3.5b Plots for loam: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (11)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8).	57

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.5c Plots for sand: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (11)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8).	58
3.6 Liquid pressure as a function of molality for a loam at three fixed water contents	60
3.7 Plot of the error for silt induced by neglecting the volume correction term (worked example equation (12)).	61
3.8a Plots for silt: (a) Plot of equation (2) in units of MPa. Plots (b) through (d) are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) only the surface tension correction term ($\sigma^{LG} / \sigma_o^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).	62
3.8b Plots for loam: (a) Plot of equation (2) in units of MPa. Plots (b) through (d) are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) only the surface tension correction term ($\sigma^{LG} / \sigma_o^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).	63
3.8c Plots for sand: (a) Plot of equation (2) in units of MPa. Plots (b) through (d) are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) only the surface tension correction term ($\sigma^{LG} / \sigma_o^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).	64
3.9 Plots for silt: (a) Plot of equation (5a); (b) plot of equation (5a), but neglecting the volume correction terms; (c) error (eqn (11)) induced by neglecting volume correction terms; (d) error induced by approximating equation (5a) with the constant -0.124.	65

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.10 Plots for silt: (a) plot of equation (5b); (b) plot of equation (5b) but neglecting the volume correction terms in both the vapor pressure and the differential; (c) error (eqn (11)) resulting from the approximation described in (b).	66
3.11 Plots for equation (7a) for silt: (a) plot of equation (7a); (b) ratio of the magnitudes of the pressure differential term to the surface tension differential term; (c) error (eqn (11)) induced by assuming \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content); (d) error induced by assuming the \tilde{P}^L derivative term is negligible compared to the surface tension derivative term (but still allowing \tilde{P}^L to be a function of m)..	67
3.12 Plots of equation (7b) for silt: (a) plot of the entire equation; (b) error induced by neglecting the volume correction in the derivative; (c) error induced by neglecting the surface tension.....	68
3.13 Gravimetric water and NaCl content from Scotter (1974).	70
3.14 Fit of the van Genuchten relationship to the experimental data of Scotter.	71
3.15 Scotter's data: Plot of the error (equation (11)) induced by neglecting the volume correction term.	72
3.16a Scotter data: Pure water saturation and saline liquid saturation as a function of position.....	73
3.16b Scotter data: Computed liquid pressures using equation (2) and the data in Figure 13.....	73
3.17 Computed vapor pressure (equation (1)) as a function of position.....	74
3.18 Computed vapor pressure (equation (1)) from experiment 1 for four cases: 1) the full equation, 2) neglecting only the volume correction term (equation (4) or more specifically equation (11)), 3) neglecting the activity term (activity = 1), and 4) neglecting the entire exponential term (curved interface correction).....	75
3.19 Plots for Scotter's soil: (a) Plot of equation (5a); (b) plot of equation (5a), but neglecting the volume correction terms; (c) error (eqn (11)) induced by neglecting volume correction terms; (d) error (eqn (11)) induced by approximating equation (5a) with the constant -0.123.....	76

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
4.1 Data from Scotter (1974) converted from gravimetric water content to volumetric water content.	85
4.2 Scotter's raw data converted to volumetric water content.	86
4.3 The observed shift when plotting the volumetric liquid content vs. the liquid diffusivity.	87
4.4 This figure is identical to figure 3 except $\lambda=0.4$	93
4.5 Best fit to Scotter's data using the Brooks and Corey model with $\lambda=0.4$	93

DEDICATION

For David McLaughlin...who loved to know how things work,
who was an excellent teacher, and who is missed greatly.

Thermodynamics of Non-Dilute Saline Solutions **in Variably Saturated Porous Media.**

Chapter 1 - Introduction

For many geophysical systems, it is necessary to understand the flow of saline fluids in non-isothermal, unsaturated porous media. Understanding the effects of salt in such systems is required in soil science, in the design of hazardous waste storage, and in drying science (e.g., manufacturing and processing of materials). It has long been known that vapor density is reduced above both curved interfaces and above saline fluids. Relationships describing this vapor pressure reduction have been derived for the curved interface and the salt effect separately (see for example Edlefsen and Anderson, 1943), but to the authors' knowledge, no general derivation from first principles of the synergistic effects of salt and the curved interface has been accomplished prior to this work. However, relationships have been defined for various purposes (Olivella et al. 1996; Bear and Gilman 1995; and Nassar and Horton 1989), but the detail and method of determination of these relationships has been dictated by the level of detail necessary to accomplish specific tasks.

The goal of this work is to further the understanding of the physics of flow of saline solutions in variably saturated porous media. To accomplish this task, various relationships have been derived from first principles, and whenever possible, examples have been worked to demonstrate the use and to check the validity of the new relationships. In chapters 2 through 4, the principles of closed system, isothermal thermodynamics are used to derive general relationships. Chapter 2 provides a general derivation. Chapter 3 provides an example of use of the relations in chapter 2 for sodium chloride (NaCl). Chapter 4 provides a derivation of the necessary thermodynamic corrections for Darcy-type laws for saline solutions in isothermal unsaturated porous media. An example is again worked for NaCl for the data of

Scotter (1974). Chapter 5 develops the notions necessary to extend the above derivations to continuous non-isothermal systems. Two classical assumptions of the continuous theory are examined, and proposed corrections to the theory are made. Examples of use of the new theory are worked for the ideal gas and for a Navier-Stokes type fluid with results that are consistent with physical understanding of the systems.

Chapter 2 - Thermodynamic Correction for Salts in Variably Saturated Porous Media

Erick R. Burns¹, Jean-Yves Parlange², John S. Selker¹, and Ronald B. Guenther³

1: Department of Bioengineering; Oregon State University; Corvallis, OR

2: Department of Biological and Environmental Engineering; Cornell University; Ithaca, NY

3: Department of Mathematics; Oregon State University, Corvallis, OR

Submitted to:

Transport in Porous Media

Kluwer Academic Publishers

P.O. Box 990

3300 AZ DORDRECHT

The Netherlands

Status: Under Review

Abstract

Using thermodynamic principles, the general relationship describing the equilibrium vapor content in the gas phase above a saline liquid and across a curved liquid-gas interface is developed. Since high salt concentration affects the intensive and extensive liquid properties, it is also necessary to account for these effects in liquid water content/liquid water pressure relationship curves so that experimentally derived curves for pure water may be useful for elevated salt concentrations. The appropriate thermodynamic relationship is derived to describe the salt effects on liquid and vapor properties. The resulting equations are valid for salt concentrations between zero and saturation, and for any temperatures that nominally occur in near-surface geologic materials.

Introduction

It is important to understand the behavior of the flow of saline fluids in non-isothermal, unsaturated porous media. Understanding the effects of salt in such systems is required in soil science, in the design of hazardous waste storage, and in drying science (e.g., manufacturing and processing of materials). It has long been known that vapor density is reduced above both curved interfaces and above saline fluids. Relationships describing this vapor pressure reduction have been derived for the curved interface and the salt effect separately (see for example Edlefsen and Anderson, 1943), but to the authors' knowledge, no general derivation from first principles of the synergistic effects of salt and the curved interface has been accomplished prior to this work. However, relationships have been defined for various purposes (Olivella et al. 1996; Bear and Gilman 1995; and Nassar and Horton 1989), but the detail and method of determination of these relationships has been dictated by the level of detail necessary to accomplish specific tasks. A brief comparison of the results of this paper to those listed above is accomplished in the "Discussion" section below. The goal of this work is to define a general analytic

relationship that aids in the conceptual understanding of the underlying physics, as well as allowing the use of numerical approximation for computation.

Derivation of Constitutive Relationships

Preliminaries and Assumptions

In this section, the equilibrium relation between a saline solution and the overlying air water vapor mixture is derived for a curved gas-liquid interface. First, the general relations are developed; then, the often used dilute solution approximation is derived. Finally, derivation of a method to compute non-dilute salt concentration effects is completed.

During the derivation, several assumptions will be used. These assumptions are not overly restrictive, so the results are quite general. The assumptions are stated explicitly in an attempt to remove ambiguity over the applicability of the results. As a generalization, the assumptions may be grouped naturally into three sets.

Assumptions 1 through 5 give sufficient (though not necessary) conditions to use equilibrium thermodynamics.

Assumption 1: The total system is closed to mass transfer.

Assumption 2: The liquid-gas interface is thin and may be well-approximated by a surface.

Assumption 3: The total system is bounded by rigid walls (i.e., the total system, composed of one or more fluids, is constant volume).

Assumption 4: Equilibrium between the phases is reached much faster than changes driven by external forcing.

Assumption 5: The system is adiabatically connected to an isothermal heat reservoir, but is otherwise closed.

The equations resulting from application of the first five assumptions are very general. In fact they are so general that it is necessary to define the system of interest further before computations may be made. Assumptions 6 through 12 describe some general conditions that hold for saline fluids in an isothermal two-phase system.

Assumption 6: The mixture in each phase may be well described as a mixture of water (w), dry air (a), and pure salt (h).

Assumption 7: The salt (h) is either a single salt species or may be well-represented with effective parameters such that all salt chemical potentials (e.g., μ^{hL}) and mole numbers (e.g., N^{hL}) are well-defined as single-valued variables.

Assumption 8: The gas (G) is made up of air (aG; read as air in gas) and water vapor (wG; water in gas).

Assumption 9: The liquid (L) is made up of water (wL) and salt (hL). Explicitly, the air is considered to be negligibly-reactive with the liquid (i.e., negligible when considering the thermodynamics of electrolyte solutions).

Assumption 10: All phase changes occur under isothermal conditions. This condition may be relaxed later, but provides clarity during the derivation.

Assumption 11: The gas phase behaves like an ideal gas.

Assumption 12: There exists a unique single-valued function $V^L = V^L(N^{wL}, N^{hL})$ such that if any two of the values (V^L, N^{wL}, N^{hL}) are known, then the third variable may be computed.

Assumptions 6 through 12 narrow the scope of our relations further, and some very nice results may be derived. Lastly, assumptions 13 and 14 narrow the scope of the relations to a porous media. It is noted that while assumption 12 is grouped above, it is not used until porous media are considered.

Assumption 13: Assume that the gas phase inside the porous media is connected with

$$\text{a sufficiently large gas volume such that } \left| \int_{\infty}^B \frac{V^L}{N^{wL}} dP^L \right| \gg \left| \int_{\infty}^B \frac{V^L}{N^{wL}} dP^G \right|.$$

Assumption 14: Assume that σ^{LG} is a function of salt content and temperature only,

$$\text{and } \frac{dA^{LG}}{dV^L} \text{ is only a function of saturation.}$$

Admittedly, assumptions 13 and 14 appear somewhat cryptic at this point, but during the course of derivation, the relations arise naturally. They are listed at this point for the sake of completeness. In the following derivations, the assumptions are

implemented sequentially, so that it is easy to see what limitations exist for use of the resulting equations.

Derivations

Consider the super-system in the schematic diagram, Figure 1. The system is composed of the liquid (L), the gas (G), and the liquid-gas interface (LG). This super-system may be well approximated by two adjacent homogeneous sub-systems (i.e., a liquid phase and a gas phase) with a thin transition zone between the phases. In order to accurately describe the system thermodynamics it is necessary to account for the liquid-gas interface explicitly. If assumptions 1 through 5 are satisfied, then the tools provided by standard reversible thermodynamics may be used to provide a precise formulation of the energy relations for each phase. For a reversible process in a homogeneous system, the differential form of the conservation of energy equation is given by the Gibbs relation (Callen, 1960):

$$(1) \quad dU = TdS - PdV + \sum_i \mu^i dN^i$$

Where the index i includes every chemical constituent in the homogeneous mixture, and the symbols are defined in the “Notation” section below.

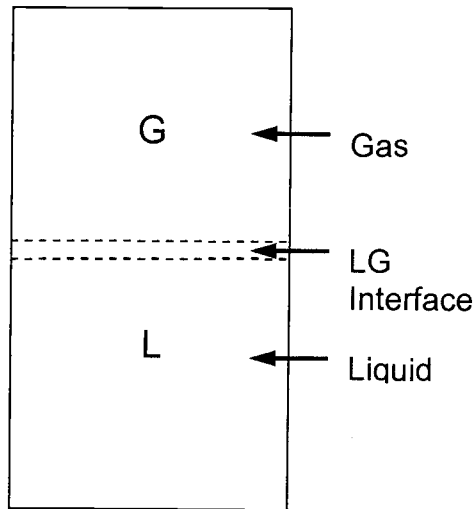


Figure 1: Schematic representation of a system composed of both a liquid and a gas.

Another well-known fact that may be used is that under the above conditions, the Gibbs-Duhem relation also holds (Callen, 1960):

$$(2) \quad 0 = SdT - VdP + \sum_i N^i d\mu^i$$

Equations (1) and (2) are the standard starting place for the use of equilibrium thermodynamics. Equation (1) relates the differentials of the extensive variables. Equation (2) relates the differentials of the intensive variables. Defining surface tension in the usual way (i.e. $\sigma^{LG} = \frac{\partial U^{LG}}{\partial A^{LG}}$), and writing the appropriate versions of equation (1) for each phase and the interface yields:

$$(3a) \quad dU^L = T^L dS^L - P^L dV^L + \sum_i \mu^{iL} dN^{iL}$$

$$(3b) \quad dU^G = T^G dS^G - P^G dV^G + \sum_i \mu^{iG} dN^{iG}$$

$$(3c) \quad dU^{LG} = T^{LG} dS^{LG} - \sigma^{LG} dA^{LG} + \sum_i \mu^{iLG} dN^{iLG}$$

Here, it is worthwhile to note that the sign convention for the pressure and surface tension terms varies from author to author and discipline to discipline. Care must be taken to use a consistent sign convention throughout application of the thermodynamic results. The corresponding Gibbs-Duhem relations are:

$$(4a) \quad 0 = S^L dT^L - V^L dP^L + \sum_i N^{iL} d\mu^{iL}$$

$$(4b) \quad 0 = S^G dT^G - V^G dP^G + \sum_i N^{iG} d\mu^{iG}$$

$$(4c) \quad 0 = S^{LG} dT^{LG} - A^{LG} d\sigma^{LG} + \sum_i N^{iLG} d\mu^{iLG}$$

Since the eventual goal is to use conservation equations to simplify the relations, it is convenient to note here that:

$$(5) \quad U^{sys} = U^L + U^G + U^{LG}$$

$$(6) \quad S^{sys} = S^L + S^G + S^{LG}$$

$$(7) \quad V^{sys} = V^L + V^G + V^{LG}$$

$$(8) \quad N^{i,sys} = N^{iL} + N^{iG} + N^{iLG} \quad \text{for all } i$$

Recall that assumptions 1 through 5 are sufficient conditions to ensure equations (1) through (8) describe the system in question, but they are not necessary. In fact, the assumptions above are more restrictive than necessary, so re-iterating the assumptions in mathematical form gives additional restrictions on the set of equations.

Assumption 1 ensures equation (8) is equal to a constant, which implies:

$$(9) \quad dN^{iL} + dN^{iG} + dN^{iLG} = 0 \quad \text{for all } i$$

Assumption 2 allowed the use of surface tension in equations (3c) and (4c), and it also implies that the volume of the interface is negligibly small. Equation (7) becomes:

$$(10) \quad V^{sys} = V^L + V^G$$

Assumption 3 ensures equations (7) and (10) are equal to constants. This implies:

$$(11) \quad dV^L + dV^G = 0$$

Assumption 4 implies that thermal and chemical equilibrium exists between the phases, giving:

$$(12) \quad T^L = T^G = T^{LG} \equiv T$$

$$(13) \quad \mu^{iL} = \mu^{iG} = \mu^{iLG} \equiv \mu^i \quad \text{for all } i$$

Assumption 5 implies that the only energy flux into or out of the system is heat flux. The heat flux is described by the imperfect differential, δQ . From Callen (1960), $\delta Q = TdS$. Combining this with equation (12) gives:

$$(14) \quad dU^{sys} = TdS^{sys}$$

Adding equations (3a), (3b), and (3c), and using relations described by equations (9) and (11) through (14) yields the commonly accepted form of the mechanical equilibrium condition across an interface:

$$(15) P^G - P^L = \sigma^{LG} \frac{dA^{LG}}{dV^L}$$

As a quick check of the validity of equation (15), Laplace's Equation may be derived.

For a meniscus with zero contact angle in a capillary tube, it is known that

$A^{LG} = \frac{1}{2} 4\pi r^2$ and $V^L = \frac{1}{2} \frac{4}{3} \pi r^3$ (r = radius of tube) from which it follows immediately that:

$$\frac{dA^{LG}}{dV^L} = \frac{2}{r} \quad \text{which results in Laplace's Equation: } P^G - P^L = \sigma^{LG} \frac{2}{r}$$

Since the Gibbs-Duhem relations relate the differentials of the intensive variables, the conservation conditions do not lead to immediate simplification. Instead, it is necessary to make additional assumptions that adequately describe the real physical system of interest. For this reason, assumptions 6 through 12 are used to describe exactly what is assumed to be true for a saline liquid.

Assumption 6 implies:

$$(16) \quad \sum_i N^{i\alpha} = N^{w\alpha} + N^{a\alpha} + N^{h\alpha} \equiv N^\alpha \quad \text{for all } \alpha$$

Assumption 7 is used in this derivation to greatly simplify notation and to show the utility of the results. The theory developed here extends naturally to multiple salts (e.g., $N_1^{hL}, N_2^{hL}, N_3^{hL}, \dots$), but appropriate definitions of chemical affinities must be made (c.f., DeHoff, 1993).

Assumptions 8 and 9 give:

$$(17) \quad N^{hG} = 0$$

$$(18) \quad N^{aL} \cong 0$$

Assumptions 8 and 9 are consistent with the notion that the change in chemical potential of air in water (and salt in air) between any two thermodynamic states has a negligible impact on the system. In a system where pH is important, it would become necessary to further subdivide the air into constituents that affect equilibrium values of pH, though this is not considered here.

Assumption 10 is used to simplify the relations, and to preclude the need for defining entropy. It is beyond the scope of this paper to show sufficient conditions for this assumption to be valid, but instead, it is noted that isothermal conditions are expected under many laboratory conditions. Also, during the drying of porous media, isothermal conditions have been documented to persist for extended periods of time (c.f., Luikov, 1975). This is true because the process of evaporation at a constant atmospheric pressure implies that the process is occurring at the saturation temperature. Assumption 10 implies:

$$(19) \quad dT = 0$$

Assumption 11 allows the use of the ideal gas law and Dalton's law of partial pressures. This assumption is deemed valid for low gas pressures (e.g., atmospheric pressure). By assumption 8, Dalton's Law gives:

$$(20) \quad P^G = P^{wG} + P^{aG}$$

Dividing equation (4b) by the total number of moles in the gas (N^G), then substituting in equations (16), (17), (19), and (20), and solving for the chemical potential of water yields:

$$(21) \quad d\mu^{wG} = \frac{1}{X^{wG}} \left(\frac{V^G}{N^G} dP^G - X^{aG} d\mu^{aG} \right) \quad \text{where } X^{iG} = \frac{N^{iG}}{N^G} \text{ is the mole fraction.}$$

Using the ideal gas law as it applies to the total and partial pressures yields the following relation:

$$(22) \quad X^{iG} P^G = \frac{N^{iG}}{N^G} P^G = \frac{N^{iG} RT}{V^G} = P^{iG} \quad \text{for all } i$$

Equation (22) allows equation (21) to be written:

$$(23) \quad d\mu^{wG} = \frac{1}{P^{wG}} (RT dP^G - P^{aG} d\mu^{aG})$$

For gases at low pressure, the following relation holds:

$$(24) \quad \mu^{iG} = \mu_0^{iG} + RT \ln \left(\frac{P^{iG}}{P_o^{iG}} \right) \quad \text{for all } i$$

It is more convenient here to write equation (24) in its differential form:

$$(25) \quad d\mu^{iG} = RT d(\ln P^{iG}) = RT \frac{dP^{iG}}{P^{iG}} \quad \text{for all } i$$

Substituting equation (25) for the air constituent into equation (23), and using equation (20) yields:

$$(26) \quad d\mu^{wG} = \frac{RT}{P^{wG}} (dP^G - dP^{aG}) = RT \frac{dP^{wG}}{P^{wG}}$$

The result of this derivation is not surprising since it is the expected result of just writing down equation (25) for the water vapor. What has been shown, however, is that the chemical potential of the water vapor is independent of the air pressure (and vice versa) when total gas pressures are sufficiently low such that the ideal gas law and Dalton's law are obeyed.

Applying equations (18) and (19) to equation (4a) yields:

$$(27) \quad d\mu^{wL} = \frac{V^L}{N^{wL}} dP^L - \frac{X^{hL}}{X^{wL}} d\mu^{hL}$$

By definition, the appropriate version of equation (25) for aqueous solutions is:

$$(28) \quad d\mu^{iL} = RT d(\ln a^{iL}) \quad \text{where } a^{iL} \text{ is the activity of constituent } i \text{ for all } i$$

Now, all of the groundwork has been laid to derive some constitutive relations. This is accomplished by using equation (13) for the water constituent. This yields the following relation:

$$(29) \quad \int_{\mu_0^{wL}}^{\mu^{wL}} d\mu^{wL} = \mu^{wL} - \mu_0^{wL} = \mu^{wG} - \mu_0^{wG} = \int_{\mu_0^{wG}}^{\mu^{wG}} d\mu^{wG}$$

Note that it is critical that the limits of integration correspond to the same equilibrium states, and that the integration path between the states must also be such that equilibrium holds at all points along the path (also known as a quasi-static process). In a more general sense, the integrals should be thought of as from one state to another. The choice of integration limits shown here is possible because the integrand may be written as functions of the variable of integration. In this case, it is the constant function = 1, and this condition is trivially satisfied.

Using equations (26) through (29), the form of the equation to be used to derive constitutive relations can be written:

$$(30) \quad \int RT \frac{dP^{wG}}{P^{wG}} = \int \left(\frac{V^L}{N^{wL}} dP^L - \frac{X^{hL}}{X^{wL}} RT d(\ln a^{hL}) \right)$$

Where the limits of integration are from some reference state to some final state. Now, by imposing physical constraints, equation (30) may be used to develop constitutive relations. In the following sub-sections, this is accomplished for several physical constraints, starting with the simplest forms. First, the psychometric equation is derived, followed by the dilute approximation for saline fluids. Since the thickness of the interface is small with respect to the curvature, thermodynamic relations derived for flat interfaces may be extended to the curved interface case (Guggenheim, 1977). For this reason, the thermodynamic relation for non-dilute salt content over a flat interface is derived. This may then be extended to the general case of brine strength saline solutions in porous media.

Vapor pressure for zero-salt condition with a curved interface:

If there is no salt in the liquid, then the second term on the right hand side of equation (30) is identically zero. If there is no salt, all of the volume of the liquid is made up of water molecules. In this case, the integrand of the liquid pressure integral is

effectively the reciprocal of the density (it is exactly the reciprocal of the *molar* density) of pure water. Assuming the liquid is virtually incompressible, the integrand is essentially a constant. Noting that we are considering isothermal conditions, equation (30) becomes:

$$(31) \quad RT \int \frac{dP^{wG}}{P^{wG}} = \int \frac{V^L}{N^{wL}} dP^L = \int \frac{V_0^L}{N_0^{wL}} dP^L = \frac{V_0^L}{N_0^{wL}} \int dP^L$$

Now, it is apparent that the limits of integration are just the initial and final pressures of water vapor and water, respectively. Evaluating the integral gives the well-known psychrometric equation:

$$(32) \quad P^L = P_{0\infty}^L + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) \quad \underline{\text{or}} \quad P^{wG} = P_{0\infty}^{wG} \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P_{0\infty}^L) \right)$$

Vapor pressure for dilute solution approximation with a curved interface:

Now, assume there is some amount of salt in the solution. If the solution is sufficiently dilute, the density change of the solution will be negligible; so again, the integrand of the liquid pressure term is essentially constant, and it necessarily must be the inverse of the pure water molar density. The left hand side of equation (30) is unchanged, so the immediate result is:

$$(33) \quad RT \int \frac{dP^{wG}}{P^{wG}} = \frac{V_0^L}{N_0^{wL}} \int dP^L - \int \frac{X^{hL}}{X^{wL}} RT d(\ln a^{hL})$$

For dilute strength solutions, $a^{hL} = X^{hL}$; and it is helpful to observe that:

$$(34) \quad X^{wL} + X^{hL} = 1 \Rightarrow dX^{wL} = -dX^{hL}$$

Substituting these facts into equation (33) yields:

$$(35) \quad RT \int \frac{dP^{wG}}{P^{wG}} = \frac{V_0^L}{N_0^{wL}} \int dP^L + RT \int \frac{dX^{wL}}{X^{wL}}$$

Where again the limits of integration become obvious. Noting that $a_0^{wL} = X_0^{wL} = 1$, (35) may be evaluated to give:

$$(36) \quad P^L = P_{0\infty}^L + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{X^{wL} P_{0\infty}^{wG}} \right) \quad \text{or} \quad P^{wG} = P_{0\infty}^{wG} X^{wL} \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P_{0\infty}^L) \right)$$

By the second relation in (36), it is apparent that increased salt concentration has the effect of lowering the vapor pressure. This is a well-documented fact, and Bear and Gilman (1995) correctly note that, under some circumstances, the salt activity term (or mole fraction in this case) may dominate the vapor depression resulting in a negligible effect of interface curvature.

According to Guggenheim (1977, pp. 50-52), as long as the thickness of the liquid-gas interface is much smaller than the radius of curvature (assumption 2), "formulae strictly derived for plane interfaces may be applied to curved interfaces with an accuracy sufficient for experimental purposes." Therefore, an alternative formulation of the activity for dilute systems ($X^{wL} = P_{\infty}^{wG} / P_{0\infty}^{wG}$) may be used yielding an alternative form of equations (36):

$$(37) \quad P^L = P_{0\infty}^L + \frac{N_0^{wL} RT}{V_0^L} \ln \left(\frac{P^{wG}}{\left(\frac{P_{\infty}^{wG}}{P_{0\infty}^{wG}} \right) P_{0\infty}^{wG}} \right) \quad \underline{\text{or}}$$

$$P^{wG} = P_{0\infty}^{wG} \left(\frac{P_{\infty}^{wG}}{P_{0\infty}^{wG}} \right) \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P_{0\infty}^L) \right)$$

Now, it becomes clear that the approximation is computed by taking the reference condition, and correcting for salt and for interface curvature. The reason that these corrections may occur independently is that the corrections are only weakly coupled for dilute concentrations.

One notes that $P_{0\infty}^L \cong P^G$, and since it is more convenient to measure the gas pressure, it becomes instructive to see under what conditions this approximation is valid.

Defining the specific volume ($v_0^{wL} = V_0^L / N_0^{wL}$), the first relation in equation (37) may be written:

$$(38) \quad P^L - P_{0\infty}^L = \frac{RT}{v_0^{wL}} \ln \left(\frac{P^{wG}}{P_{\infty}^{wG}} \right)$$

Or equivalently

$$(39) \quad \frac{P^{wG}}{P_{\infty}^{wG}} = \exp \left(\frac{(P^L - P_{0\infty}^L) v_0^{wL}}{RT} \right) = \exp \left(\frac{(P^L - P^G) v_0^{wL}}{RT} \right) \exp \left(\frac{(P^{wG} - P_{0\infty}^{wG}) v_0^{wL}}{RT} \right)$$

Where the facts that $P^G = P_{0\infty}^G + P^{wG} - P_{0\infty}^{wG}$ and $P_{0\infty}^G = P_{0\infty}^L$ have been used.

Equivalently, (39) may be written:

$$(40) \quad P^L - P^G = \frac{RT}{v_0^{wL}} \ln\left(\frac{P^{wG}}{P_\infty^{wG}}\right) - (P^{wG} - P_{0\infty}^{wG}) = \frac{v_0^{wG}}{v_0^{wL}} P^{wG} \ln\left(\frac{P^{wG}}{P_\infty^{wG}}\right) - (P^{wG} - P_{0\infty}^{wG})$$

For a curved interface, it is known that for the vapor pressure $0 < P^{wG} \leq P_\infty^{wG}$. For this condition, it is a mathematical fact that:

$$(41) \quad \left| \ln\left(\frac{P^{wG}}{P_\infty^{wG}}\right) \right| \geq \left| \left(\frac{P^{wG}}{P_\infty^{wG}} - 1\right) \right|$$

This is true, because the two functions intersect only at the point $P^{wG} / P_\infty^{wG} = 1$, and the natural log function is concave down. Equation (41) implies that:

$$(42) \quad \left| \frac{RT}{v_0^{wL}} \ln\left(\frac{P^{wG}}{P_\infty^{wG}}\right) \right| \geq \left| \frac{v_0^{wG} P^{wG}}{v_0^{wL} P_\infty^{wG}} \frac{(P^{wG} - P_\infty^{wG})}{(P^{wG} - P_{0\infty}^{wG})} (P^{wG} - P_{0\infty}^{wG}) \right| \gg |(P^{wG} - P_{0\infty}^{wG})|$$

Because $P^{wG} / P_\infty^{wG} \sim 1$, $\left| \frac{(P^{wG} - P_\infty^{wG})}{(P^{wG} - P_{0\infty}^{wG})} \right| \sim 1$, and $v_0^{wG} \gg v_0^{wL}$. This implies that the last

term in equation (40) is dominated by the natural log term. So, to a very good approximation, (37) may be rewritten:

$$(43) \quad P^L = P^G + \frac{N_0^{wL} RT}{V_0^L} \ln\left(\frac{P^{wG}}{\left(\frac{P_\infty^{wG}}{P_{0\infty}^{wG}}\right) P_{0\infty}^{wG}}\right) \quad \underline{\text{or}}$$

$$P^{wG} = P_{0\infty}^{wG} \left(\frac{P_\infty^{wG}}{P_{0\infty}^{wG}}\right) \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P^L - P^G)\right)$$

When desired, this same general procedure may be followed to substitute P^G for $P_{0\infty}^L$ in other relationships developed in this document. Considering the case above, it becomes instructive to examine the case where there is little or no curvature (i.e., the pressure term in equation (30) is negligible), but the salt effect may be considerable.

Vapor pressure for non-dilute solution with negligible interface curvature:

Using equations (27), (28), and (34), it is possible to write:

$$(44) \quad RT \int \frac{dP^{wG}}{P^{wG}} = RT \int d(\ln a^{wL}) = -RT \int \frac{X^{hL}}{1 - X^{hL}} d(\ln a^{hL})$$

The result of equation (44) is that vapor pressure may be expressed in terms of the activity of water (second integral) or in terms of the mole fraction of salt plus the activity of the salt (last integral). Clearly, the activity of a constituent is a function of its concentration, which in this case is uniquely defined by the mole fraction. It remains to define this relationship to evaluate the last integral. Since the activity of water in the presence of an electrolyte is a commonly measured value, it will often be easier to use this value for computation. Using the appropriate limits, equation (44) becomes:

$$(45) \quad P^{wG} = P_{0\infty}^{wG} a^{wL}(X^{wL}) = P_{0\infty}^{wG} \exp \left(- \int \frac{X^{hL}}{1 - X^{hL}} d(\ln(a^{hL}(X^{hL}))) \right)$$

Here it becomes apparent how chemists measure the water activity in the presence of a salt. They simply measure vapor pressures at two different salt concentrations. It is also obvious by equation (34) that either one of the activities and the integrand of the integral above may be written in terms of either mole fraction.

Vapor pressure for non-dilute solution with non-negligible interface curvature in an unsaturated porous media:

In order to determine a constitutive relationship for this more general case, it becomes necessary to account for the effects of salt concentration on the integrand of the liquid pressure integral in equation (30). To do this, it must be understood how a non-negligible change in salt concentration (intensive property) affects the volume (extensive property) and the density (intensive property) of the liquid, plus any other relevant changes to the physics of the problem. For this reason, the response to changes in volume, density, and other relevant parameters must be known for both the integrand and the variable of integration. This allows the appropriate choice of integration limits. For this exercise, the physics imposed by porous media geometry are used.

It is reasonable to suppose that for a homogenous water-salt mixture that the specific volume (analogously, density) is uniquely defined by the salt to water ratio (Motivation for the approach to be taken is developed here, but these statements will be made precise below). In a porous media, it is also reasonable to suppose that when the volume of liquid per volume of porous media is known, then the relationship between liquid volume and liquid pressure is well-defined (e.g., pressure-saturation curves). If the above two conditions are satisfied, then the moles of water and the moles of salt in a fixed volume (larger than the representative elementary volume) may act as state variables. It is known that integration over state variables is path-independent. For this reason, any convenient integration path may be selected.

Invoking the proposition of Guggenheim (stated above immediately before equation (37)), equation (30) is immediately reduced to:

$$(46) \quad RT \ln \left(\frac{P^{wG}}{a^{wL} P_{0\infty}^{wG}} \right) = \int_{\infty}^B \frac{V^L}{N^{wL}} dP^L \quad \text{where } B \text{ is the final state.}$$

Notice here that if the integrand is sufficiently close to constant, then the integrand may be replaced by the zero salt value and moved outside the integral as before. The integral is then trivial to solve. However, for the case of NaCl at 25 C, Heyrovska (1996) documents the fact that between zero and saturation (6.144 m [molal]), the integrand changes by about 15%. This implies that there exist cases where high salt concentrations may result in non-negligible effects.

In general, the integration must occur from an initial state A to a final state B. Invoking the fact that integration is path-independent, it is convenient to integrate along the path ACB (see Figure 2). Notice that path AC is a constant salt content path, and the path CB is a constant water content path. Since A for equation (46) is the zero salt, flat interface condition (i.e., 0∞), the integrand is again the zero salt case, which may be assumed to be constant. Equation (46) may be rewritten as:

$$(47) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + \int_C^B \frac{V^L}{N^{wL}} dP^L$$

Hereafter, the integral in equation (47) will be referred to as the **volume correction term**, and the zero-salt liquid pressure term will be called the **dilute approximation term** (since only considering this term is the dilute approximation). The **activity term** is self explanatory, and the term on the left-hand side of the equality is the desired resulting **vapor depression term** for which the constitutive relation is being developed. This constitutive relation provides the vapor pressure used to compute vapor flow (diffusion) resulting from vapor pressure gradients, and by use of the ideal gas law, may also be used to compute mass density of water in the gas phase.

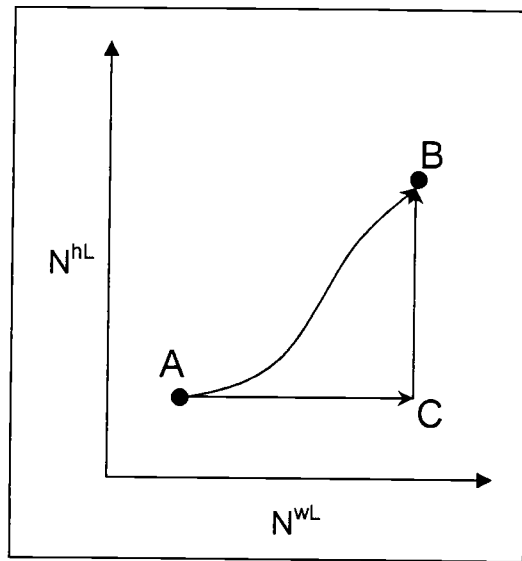


Figure 2: Diagram showing the change in state between two arbitrary states A and B, and another path AC followed by CB.

When considering the volume correction term, notice that it is a function of only liquid variables. Further, it is observed that the liquid is a function of only salt content (N^{hL}), water content (N^{wL}), liquid volume (V^L), and liquid pressure (P^L). Volume and pressure are already intimately related (classical thermodynamics gives $P^L = \frac{\partial U^L}{\partial V^L}$), and water content is a constant for this term. This implies that if a one-to-one relationship between salt content and volume or pressure can be developed, then the integral may be written as a function of salt content only, and the limits of integration are obviously from zero to the final salt concentration. This provides the motivation for computations in subsequent sections.

Liquid pressure correction for high strength salt solutions

In order to evaluate the volume correction term, it is necessary to estimate the effects of salt on the liquid pressure. It is known that surface tension is affected by salt concentration (c.f. Belton, 1935), and the condition of mechanical equilibrium

(Equation 15) shows that for relatively constant gas pressure, that the liquid pressure must necessarily be a function of salt concentration. Taking the differential of the mechanical equilibrium equation yields:

$$(48) \quad dP^G - dP^L = d\left(\sigma^{LG} \frac{dA^{LG}}{dV^L}\right)$$

Recall that assumption 13 is precisely:

$$(49) \quad \left| \int_{\infty}^B \frac{V^L}{N^{wL}} dP^L \right| \gg \left| \int_{\infty}^B \frac{V^L}{N^{wL}} dP^G \right|$$

This assumption is just a formalization of the notion that gas pressure changes negligibly in a porous media compared to the liquid pressure. To ensure the assumption is satisfied, it is sufficient to consider the system shown in Figure 3 where there is a unit volume of porous media in a closed container with a gas-filled head-space. If there was no head-space, then since it has been assumed that air is insoluble in water, any air in the system would be trapped air and the incompressibility of water would require the gas pressure to fluctuate strongly. If the head space is sufficiently large, then changes in air pressure will be small compared to changes in water pressure. Since the partial pressure of water vapor is small compared to the pressure of the total gas, changes in vapor pressure do not cause a violation of the condition (49). In a natural system, it is not necessary to assume that the system is closed. It is sufficient that that vapor pressure at the soil surface is near equilibrium with the porous media, and there is no significant gas pressure built up within the porous media. Since it is beyond the scope of this paper to describe all conditions under which this assumption is valid, this condition shall just be stated here, and it is noted that this assumption is valid for a wide range of natural conditions occurring within

soils and sediments. For the derivations in this paper, application of assumption 13 coupled with equation (48), allows use of the following for evaluation of integrals:

$$(50) \quad dP^L \cong -d\left(\sigma^{LG} \frac{dA^{LG}}{dV^L}\right)$$

To use this relation, apply assumption 14. When considering the validity of this assumption, it is convenient to note that surface tension is a microscopic property that can be shown to vary with temperature and salt concentration (c.f. Belton (1935) and Matubayasi et al. (1999)). Also, the ratio of the change in liquid-gas surface area to a change in liquid volume is clearly a function of liquid saturation. If assumption 14 is valid, then it is possible to account for the effects of salt, temperature, and saturation explicitly. In practice, it is only necessary that these functions are weakly coupled. This result should be experimentally verified for the salts of interest.

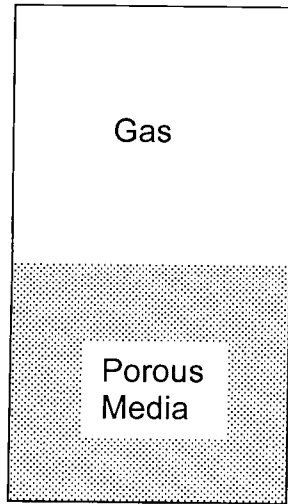


Figure 3: Schematic representation of a partially saturated porous media overlain by a gas filled space.

Applying assumption 14, and considering the case of constant temperature and zero or negligible salt concentration, it is known that P^L is a hysteretic function of saturation. This can be written:

$$(51) \quad P^L(S_0^L) = -\sigma_0^{LG} \frac{dA^{LG}}{dV^L}(S_0^L)$$

Notice that for porous media, equation (51) is simply the water content/pressure relationship that is often experimentally determined. Define $\tilde{P}^L \equiv P^L(S_0^L)$. It is clear that the functional form of \tilde{P}^L depends only on geometric constraints. If the salt does not strongly affect contact angles for a given liquid content, then the relation in equation (51) is independent of salt concentration except for its effects on the volume of the liquid. This implies that $\tilde{P}^L = P^L(S^L)$. Notice that \tilde{P}^L is not a true pressure, but rather, it represents the pressure corresponding to an equivalent saturation of fresh water. Changes to liquid pressure resulting from changes in surface tension are accounted for separately. Since the relation in Equation (51) will be experimentally determined, it is convenient to write Equation (50) as:

$$(52) \quad P^L(T, N^{hL}, S^L) = \frac{\sigma^{LG}(T, N^{hL})}{\sigma_0^{LG}} \tilde{P}^L(S^L) = -\frac{\sigma^{LG}(T, N^{hL})}{\sigma_0^{LG}} \left(\sigma_0^{LG} \frac{dA^{LG}}{dV^L}(S^L) \right)$$

Notice that the decomposition above makes clear the assumption that the pressure-saturation curve is not strongly coupled with the surface tension, and the surface tension is not affected by curvature of the interface. Again, such a decoupling should be experimentally verified.

Noting that the integrand in the volume correction term in equation (47) is in fact an intensive variable and that pressure is an intensive variable, it is recognized that total

pore volume of the porous media is arbitrary for this derivation. So, define $V^{pore} \equiv 1$ (units to be chosen based on available empirical relationships). The saturation may be defined as:

$$(53) \quad S^L \equiv \frac{V^L}{V^{pore}}$$

Since V^{pore} is a constant, this relation allows the application of assumption 12 to the saturation. Since it is possible to write V^L as a function of salt concentration, it is also possible to do the same for saturation, and in general: $S^L = S^L(N^{wL}, N^{hL})$. As a result, for isothermal conditions it is possible to write the constant water content volume correction term in terms of the function of the single variable, salt concentration.

$$(54) \quad \int_c^B \frac{V^L}{N^{wL}} dP^L = \int^{N^{hL}} \frac{S^L(N^{hL}) V^{pore}}{N^{wL}} d\left(\frac{\sigma^{LG}(N^{hL})}{\sigma_0^{LG}} \tilde{P}^L(S^L(N^{hL}))\right)$$

Where the appropriate limits of integration are obviously from zero salt to the desired final salt concentration. In order to clarify the meaning of all of the terms in equation (54), an example calculation for NaCl is accomplished in Burns et al. (2004).

Now, recognizing that equation (52) is a constitutive relation for P^L , leads to the conclusion that equation (47) may be written as the constitutive relation for P^{wG} . Suppressing the functional dependence of the variables, the constitutive relations may be summarized as follows:

$$(55a) \quad P^{wG} = P_{0\infty}^{wG} a^{wL} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \exp\left(\frac{1}{RT} \int^{N^{hL}} \frac{S^L V^{pore}}{N^{wL}} d\left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \tilde{P}^L\right)\right)$$

$$(55b) \quad P^L = \frac{\sigma^{LG}}{\sigma_0^{LG}} \tilde{P}^L \quad \text{where: } \tilde{P}^L = -\sigma_0^{LG} \frac{dA^{LG}}{dV^L}$$

Notice that since \tilde{P}^L is the equivalent pressure (equivalent to pure water) as a function of liquid saturation, it is an implicit function of salt content because saturation may be a function of salt concentration.

Derivatives

The constitutive relations (55a) and (55b) are used to couple differential equations of flow, and in particular, they provide a constraint on the mass and momentum conservation equations for water flow. For such governing equations, not only the liquid and vapor pressures are important, but so are the gradients of the liquid and vapor pressures (∇P^L and ∇P^{wG} respectively). The gradient in liquid pressure arises naturally enough, though the gradient in vapor pressure may look unfamiliar. Recognizing that the ideal gas law holds and that temperature is a constant here, it is easy to see that $\nabla P^{wG} = RT \nabla \rho^{wG}$ with ρ^{wG} defined as the molar density. Now ∇P^{wG} is recognized as the familiar diffusion of water vapor in air. For ease of notation, the gradient of vapor pressure is used here instead of gradient in molar density (or some other measure of water vapor concentration). Since liquid and water vapor pressure may also change in time, it is advantageous to consider the general derivative, $\equiv d/d \cdot$, where the “dot” may be replaced with any primary variable of interest.

Differential of water vapor pressure

The general derivative of equation (55a) is:

$$(56) \quad \frac{dP^{wG}}{d\cdot} = \frac{d}{d\cdot} \left(P_{0\infty}^{wG} a^{wL} \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) \exp \left(\frac{1}{RT} \int_{\infty}^P \frac{V^L}{N^{wL}} dP^L \right) \right)$$

Where the notation of equation (47) is used for simplicity. Notice that $P_{0\infty}^{wG}$ is a constant, a^{wL} is only a function of salt concentration (i.e., salt density), the dilute approximation term is only a function of S_0^L (water saturation), and the volume correction term is a function of both salt concentration and S_0^L . For convenience when applying the following to the NaCl example, the measure of salt concentration shall be in terms of molality (moles of salt per kg of pure water), and the variable is defined as m . Equation (56) may be rewritten:

$$(57) \quad \frac{dP^{wG}}{d\cdot} = \left(\frac{\partial P^{wG}}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^{wG}}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot}$$

With

$$(58a) \quad \frac{\partial P^{wG}}{\partial m} = P_{0\infty}^{wG} \exp \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) \left(\frac{\partial \left(a^{wL} \exp \left(\frac{1}{RT} \int_{\infty}^P \frac{V^L}{N^{wL}} dP^L \right) \right)}{\partial m} \right)$$

$$(58b) \quad \frac{\partial P^{wG}}{\partial S_0^L} = P_{0\infty}^{wG} a^{wL} \left(\frac{\partial \left(\exp \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) \exp \left(\frac{1}{RT} \int^P \frac{V^L}{N^{wL}} dP^L \right) \right)}{\partial S_0^L} \right)$$

Recognizing that $a^{wL} = \exp(\ln(a^{wL}))$ and differentiating (58a) and (58b) yields:

$$(59a) \quad \frac{\partial P^{wG}}{\partial m} = P^{wG} \left(\frac{\partial(\ln a^{wL})}{\partial m} + \frac{\partial}{\partial m} \left(\frac{1}{RT} \int^P \frac{V^L}{N^{wL}} dP^L \right) \right)$$

$$(59b) \quad \frac{\partial P^{wG}}{\partial S_0^L} = P^{wG} \left(\frac{\partial}{\partial S_0^L} \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) + \frac{\partial}{\partial S_0^L} \left(\frac{1}{RT} \int^P \frac{V^L}{N^{wL}} dP^L \right) \right)$$

Differential of liquid pressure

The general derivative of equation (55b) is:

$$(60) \quad \frac{dP^L}{d \cdot} = \frac{d}{d \cdot} \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \tilde{P}^L \right)$$

Recall that \tilde{P}^L is a function of liquid saturation which is a function of salt concentration. In Equation (55a), this term is only in the fixed water content integral.

In general, water content can also vary, implying \tilde{P}^L is a function of both m and S_0^L .

Equation (60) may be written:

$$(61) \quad \frac{dP^L}{d \cdot} = \left(\frac{\partial P^L}{\partial m} \right) \frac{dm}{d \cdot} + \left(\frac{\partial P^L}{\partial S_0^L} \right) \frac{dS_0^L}{d \cdot}$$

With

$$(62a) \quad \frac{\partial P^L}{\partial m} = \frac{1}{\sigma_0^{LG}} \left(\tilde{P}^L \frac{\partial \sigma^{LG}}{\partial m} + \sigma^{LG} \frac{\partial \tilde{P}^L}{\partial m} \right)$$

$$(62b) \quad \frac{\partial P^L}{\partial S_0^L} = \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S_0^L}$$

It is noted here that equations (62a) and (62b) are the corrections to the coefficient of conductivity that occur in Darcy's Law if the law is written in terms of a gradient in salt and water concentrations as opposed to pressure. The use of Darcy's Law and these corrections will allow estimation of the coefficients that arise naturally in the linearized theory of non-equilibrium or process thermodynamics (c.f. Luikov, 1975).

Discussion

Constitutive relationships have been defined for various purposes by Olivella et al. (1996), Bear and Gilman (1995), and Nassar and Horton (1989), but the detail and method of determination of these relationships was dictated by the level of detail necessary to accomplish specific tasks. None of the relationships presented in the aforementioned papers were completely derived from first principles, but there are many similarities to certain results from this paper.

Olivella et al. (1996) use a very similar functional form to the dilute solution approximation equations derived in this paper (equation (43)). In the references they cite, the relationships for salt and for curvature are derived separately, so it seems likely that Olivella et al. combined the functional forms in a reasonable way, getting the form they use in their model CODE_BRIGHT. To show when the approximation (equation (43)) is valid, it is necessary to compute the value of the integral in equation

(47) and to compare the magnitude of the integral with the magnitude of the other terms.

Bear and Gilman (1995) state that for their problem, the effects of a curved interface is negligible, and so write down a functional form of the vapor pressure relationship using Raoult's Law and the Clausius-Clapeyron equation. Certainly such an approximation is likely reasonable for cases where salt gradients dominate in the region of interest. The resulting equation is similar to the one derived here for dilute solutions in that it takes a reference vapor pressure and multiplies it by correction terms. Their salt correction term uses the mole fraction of water in the liquid as an approximation for the activity of the water, and so is comparable to the salt correction in equation (36). There is also a temperature correction term that includes the latent heat of vaporization. Olivella et al. and Nassar and Horton both compensate for temperature with empirical relations, but energy conservation equations are used to account for latent heats and other energy transfers.

Nassar and Horton (1989) find that the total relative humidity is equal to the relative humidity due to the matric potential multiplied by the osmotic relative humidity. Functional forms of these humidities are taken from the literature. The osmotic term has the expected exponential form, but Nassar and Horton also use an exponential approximation for the osmotic relative humidity.

None of the papers reviewed presented a methodology for handling non-dilute effects on the integrand in equation (46). The methodology developed herein results in the general relations equations (55a) (equivalently (47)) and (55b). These results are very general, and the fourteen assumptions leading to their derivation are broadly satisfied in natural unsaturated porous media. To show when various approximations to equations (55a), (55b), (59a), (59b), (62a), and (62b) are valid; experimentally determined constitutive relations must be used to compute the relative effects of each

of the terms. For an example of such computations for sodium chloride (NaCl) salt, the reader is referred to (Burns et al., 2004).

The relations developed herein are applicable for high-strength contaminants that may be well-represented by a single concentration parameter. When it becomes necessary to use multiple concentration parameters (i.e., for multiple independent salts), the above derivations will yield results in terms of affinities (c.f. DeHoff (1993)). Since the goal of this paper was to describe the theory necessary to show when non-dilute effects are appreciable, the single concentration derivation was used for clarity.

As a final note, one becomes interested in the extension of the above derivation to an-isothermal conditions (where changes in temperature occur via a quasi-static path). Obviously, it is possible to conduct the experiments necessary to repeat the above for other temperatures. If sufficient other temperatures are used, an empirical functional form for the temperature dependence may be derived. This is analogous to the temperature correction used by Olivella et al. The net result is a constitutive relation for mass exchange between the phases for an-isothermal conditions.

Conclusion

A very general relationship describing the equilibrium vapor content in the gas phase above a saline liquid and across a curved interface has been developed. Also, a method to compute the appropriate salt corrections to the constitutive relations is derived. This method requires that the changes in specific volume and surface tension with salt concentration are known. Also, the water content/water pressure relationship must be known for some fixed ionic strength water (usually done for dilute strength water). The resulting equations are valid for salt concentrations between zero and saturation, and for any temperatures that nominally occur in near surface geologic materials.

Acknowledgements

The author thanks Professor Don Solmon of the Oregon State University Department of Mathematics for several helpful discussions. This research was funded under a U.S. EPA STAR (Science to Achieve Results) Fellowship.

Notation

Variables

U = the internal energy

S = entropy

T = absolute temperature

P = pressure

V = volume

μ^i = chemical potential of the i -th constituent

N^i = mole number of the i -th constituent

$v^{iL} \equiv \frac{V^L}{N^{iL}}$ = specific volume of the i -th constituent (ratio of liquid volume to moles of water in the liquid)

$\sigma^{LG} = \frac{\partial U^{LG}}{\partial A^{LG}}$ = surface tension at the gas-liquid interface

A^{LG} = area of the gas liquid interface

$\frac{dA^{LG}}{dV^L}$ = the gas-liquid interface area to liquid volume ratio (or the density of gas-liquid interface)

$\tilde{P}^L \equiv P^L(S^L)$ = equivalent liquid pressure neglecting changes in surface tension (see discussion following Equation (51)).

ϕ^L = volumetric liquid content (volume of liquid divided by total volume of soil, liquid, and gas in porous media).

$\eta = x/t^{1/2}$ = transformed variable for data analysis.

ρ^{wG} = molar density of water in a gas

Differentials

d = total differential

∂ = partial differential

δ = imperfect differential

Superscripts

L, G = liquid and gas phase respectively

wL, wG = water in liquid and water in gas respectively

hL = salt in liquid

aG = air in gas

LG = gas-liquid interface

sys = system total

α = an arbitrary phase or sub-system

Subscripts

∞ = reference condition of flat gas-liquid interface (i.e., infinite radius of curvature)

0 = reference condition corresponding to known salt content (generally zero or negligible amount of salt)

References

- Bear, J., and A. Gilman: 1995, Migration of Salts in the Unsaturated Zone Caused by Heating, *Letters in Mathematical Physics*, **19**, 139-156.
- Belton, J.W.: 1935, The Surface Tensions of Ternary Solutions. Part I. The Surface Tensions of Aqueous Solutions of (a) Sodium and Potassium Chlorides, (b) Sodium chloride and Hydrochloric Acid, *Transactions of the Faraday Society*, **174**, 1413-1419.
- Burns, E.R., J.S. Selker, J.-Y. Parlange, and R.B. Guenther: 2004, Effects of Sodium Chloride (NaCl) on Constitutive Relations in Variably Saturated Porous Media, *In preparation*.
- Callen, H.B.: 1960, *Thermodynamics*, John Wiley and Sons, Inc., New York, NY.
- DeHoff, R.T.: 1993, *Thermodynamics in Materials Science*, McGraw-Hill, Inc., New York, N.Y.
- Edlefsen, N.E., and A.B.C. Anderson: 1943, Thermodynamics of Soil Moisture, *Hilgardia*, **15-2**, 31-298.
- Guggenheim, E.A.: 1977, *Thermodynamics: An Advanced Treatment for Chemists and Physicists*, Sixth Edition, North-Holland Publishing Company, Amsterdam.

- Heyrovska, R.: 1996, Physical Electrochemistry of Strong Electrolytes Based on Partial Dissociation and Hydration: Quantitative Interpretation of the Thermodynamic Properties of NaCl(aq) from "Zero to Saturation", *J. Electrochem. Soc.*, **143**, 1789-1793.
- Luikov, A.V.: 1975, Systems of Differential Equations of Heat and Mass Transfer in Capillary-Porous Bodies (Review), *Int. J. Heat Mass Transfer*, **18**, 1-14.
- Matubayasi, N., H. Matsuo, K. Yamamoto, S. Yamaguchi, and A. Matazawa: 1999, Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions: I. Aqueous Solutions of NaCl, MgCl₂, and LaCl₃, *Journal of Colloid and Interface Science*, **209**, 398-402.
- Nassar, I.N., and R. Horton: 1989, Water Transport in Unsaturated Nonisothermal Salty Soil: II. Theoretical Development, *Soil Sci. Soc. Am. J.*, **53**, 1330-1337.
- Olivella, S., J. Carrera, A. Gens, and E.E. Alonso: 1996, Porosity Variations in Saline Media Caused by Temperature Gradients Coupled to Multiphase Flow and Dissolution/Precipitation, *Transport in Porous Media*, **25**, 1-25

Chapter 3 - Effects of Sodium Chloride (NaCl) on Constitutive Relations in Variably Saturated Porous Media.

Erick R. Burns¹, John S. Selker¹, Jean-Yves Parlange², and Ronald B. Guenther³

1: Department of Bioengineering; Oregon State University; Corvallis, OR

2: Department of Biological and Environmental Engineering; Cornell University; Ithaca, NY

3: Department of Mathematics; Oregon State University, Corvallis, OR

Submitted to:

Water Resources Research

American Geophysical Union

2000 Florida Avenue NW

Washington, DC 20009

Status: Under Review

Abstract

Though many arid and contaminated sites have high salinity, understanding of the effects of salinity on water movement in soils has been based on dilute-solution assumptions that neglect the changes in specific volume that occur as salt concentration changes. General thermodynamic relationships describing salt effects on liquid and vapor pressure in variably saturated porous media are computed for NaCl. Changes in the specific volume of water with salt strength are shown to be of importance under dry conditions and for finer media. We employ a 1% error threshold as acceptable. For silt textures, the dilute approximation is acceptable for water content (θ) $>5\%$, for sand $\theta >1\%$, and for loam $\theta >2\%$. However, these effects are not necessarily negligible when computing gradients in vapor and liquid pressures. When computing gradients of vapor pressure resulting from gradients in salt concentration, volume correction is necessary for silt for $\theta <10\%$. Except under dilute conditions (i.e., <0.5 molal), gradients in vapor pressure with changes in water content require volume correction. For liquid pressures, except for concentrations below 0.5 molal for silt, salt effects errors are not acceptable, nor are the effects on gradients negligible. Errors for sand and loam are only marginally better with acceptable errors generally occurring only for ionic strengths of less than 1 molal. An example of use of the constitutive relations to plot experimental results illustrates how the theory may be used to determine which thermodynamic corrections must be incorporated in the analysis. For the data set in question, the volumetric effects of the salt on vapor depression are negligible, though volumetric effects may be non-negligible for computation of gradients of both vapor and liquid pressures.

Introduction

It is important to understand the behavior of flow of saline fluids in non-isothermal, unsaturated porous media. Understanding the effects of salt in such systems is required in soil science (e.g., arid soils (Weisbrod et al., 2000)), in the design of

hazardous waste storage (e.g., the Hanford site), and in drying science (e.g., manufacturing and processing of materials). It has long been known that water vapor density is reduced above both curved interfaces and above saline fluids. Relationships describing this water vapor pressure reduction and salt effects on liquid pressure have been derived from first principles in Burns et al. (2004). An illustrative example is worked here to show how the theory may be applied and to show what information is necessary to apply theory.

First, the constitutive relations derived in Burns et al. (2004) are summarized and defined below. In addition to the constitutive relations describing the salt effects on vapor and liquid pressure inside porous media, the proper forms of the generalized derivatives are also given, since these derivatives are important for modeling flow and transport processes. General notions of relative error and sufficient conditions to show terms are negligible are defined.

Second, an example is worked out for sodium chloride (NaCl). This salt is used because there is a large body of experimental relationships available in the literature. Explicitly, knowledge of the variability of surface tension and specific volume of saline solutions is required to compute the salt effects on constitutive relations. Various plots are shown to illustrate key results of the analysis and to show a rigorous method of developing robust approximations to the constitutive relations. The analysis completed for NaCl gives an indication of the types of experiments necessary to apply the theory to other salts.

Constitutive Relationships

Under a set of very mild assumptions consistent with natural, unsaturated porous media, the constitutive relations describing liquid and vapor pressure under isothermal conditions can be shown to be (Burns et al., 2004):

$$(1) \quad P^{wG} = P_{0\infty}^{wG} a^{wL} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \exp\left(\frac{1}{RT} \int^w \frac{V^L}{N^{wL}} dP^L\right)$$

$$(2) \quad P^L = \frac{\sigma^{LG}}{\sigma_0^{LG}} \tilde{P}^L \quad \text{where: } \tilde{P}^L = -\sigma_0^{LG} \frac{dA^{LG}}{dV^L}$$

All of the variables in the above equation are defined in the “Notation” section below. In the last integral, water content is fixed (N^{wL} is constant). Any variable dependent upon salt concentration also varies inside the integral. Since surface tension varies with NaCl salt concentration (Figure 1), substitution of equation (2) into equation (1) shows that the liquid pressure is a function of salt content. Similarly, Figure 2 shows that the liquid volume must necessarily change with NaCl salt concentration. For a more complete description of the variables and how they arise, the reader is referred to Burns et al. (2004). Extension to an-isothermal conditions only requires knowledge of the appropriate relations at the various temperatures of interest. If a term can be shown to be negligible for all temperatures of interest, then the term is negligible for the particular problem to be solved. For this reason, the lack of temperature variability is not a concern for the computations and subsequent analysis conducted here.

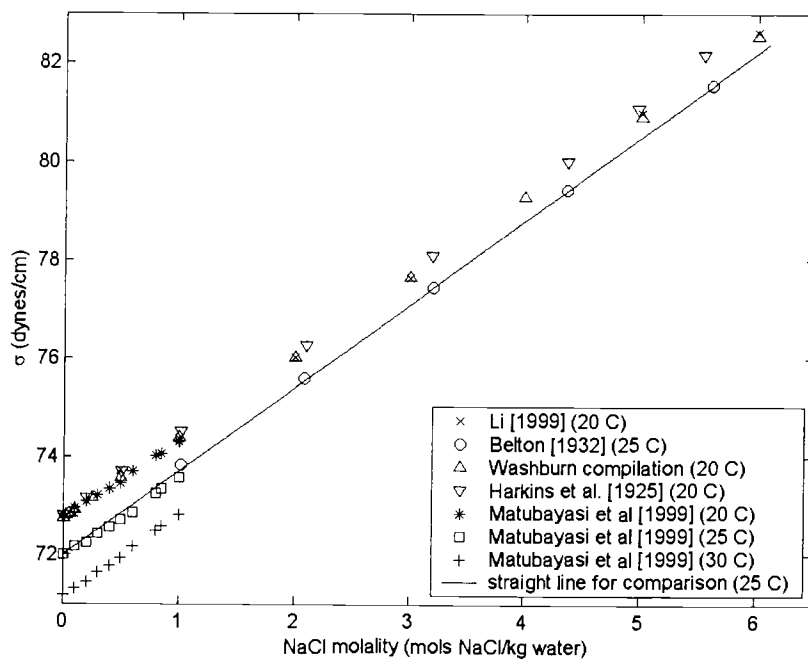


Figure 1: Surface tension as a function of NaCl(aq).

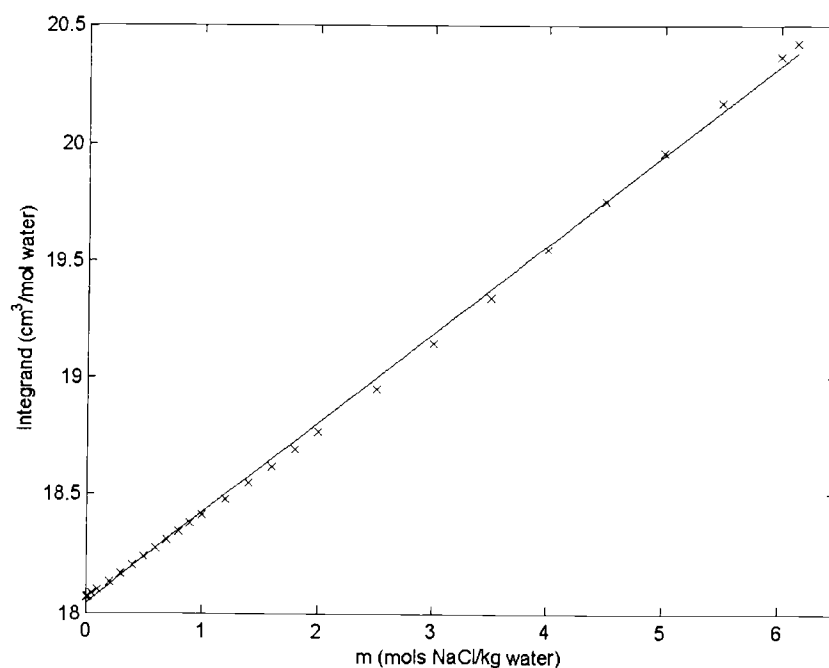


Figure 2: Integrant of the volume correction term as a function of NaCl(aq). The linear fit is to the values computed using the relations in Heyrovská (1996).

For subsequent relations, it is convenient to define the unit pore volume: $V^{pore} \equiv 1$ (units to be chosen based on available empirical relationships). Now liquid saturation may be defined as:

$$(3) \quad S^L \equiv \frac{V^L}{V^{pore}}$$

According to Burns et al. (2004), $\tilde{P}^L \equiv P^L(S^L)$. It is clear that the functional form of \tilde{P}^L depends only on geometric constraints, and S^L is an implicit function of both water and salt contents in the unit pore volume. Notice that \tilde{P}^L is not a true pressure, but rather, it represents the pressure corresponding to an equivalent saturation of fresh water. Changes to liquid pressure resulting from changes in surface tension are accounted for separately as shown in equation (2).

The constitutive relations (1) and (2) are used to couple differential equations of flow, and in particular, they provide a constraint on the mass and momentum conservation equations for water flow. For such governing equations, not only the liquid and vapor pressures are important, but so are the gradients of the liquid and vapor pressures (∇P^L and ∇P^{wG} respectively). The gradient in liquid pressure arises naturally enough, though the gradient in vapor pressure may look unfamiliar. Recognizing that the ideal gas law holds and that temperature is a constant here, it is easy to see that $\nabla P^{wG} = RT \nabla \rho^{wG}$ with ρ^{wG} defined as the molar density. Now ∇P^{wG} is recognized as the diffusion of water vapor in air, another commonly computed method of mass transfer. For ease of notation, the gradients of vapor pressure are used here instead of gradients in molar density or some other measure of concentration. In the following, consider the general derivative, $\equiv d/d \cdot$, where the “dot” may be replaced with any primary variable of interest.

The general derivative of equation (1) is:

$$(4) \quad \frac{dP^{wG}}{d\cdot} = \left(\frac{\partial P^{wG}}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^{wG}}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot}$$

With

$$(5a) \quad \frac{\partial P^{wG}}{\partial m} = P^{wG} \left(\frac{\partial (\ln a^{wL})}{\partial m} + \frac{\partial}{\partial m} \left(\frac{1}{RT} \int^P \frac{V^L}{N^{wL}} dP^L \right) \right)$$

$$(5b) \quad \frac{\partial P^{wG}}{\partial S_0^L} = P^{wG} \left(\frac{\partial}{\partial S_0^L} \left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L) \right) + \frac{\partial}{\partial S_0^L} \left(\frac{1}{RT} \int^P \frac{V^L}{N^{wL}} dP^L \right) \right)$$

Notice that to compute the derivatives it was necessary to choose two primary variables that completely describe the system via a set of constitutive relations. Such constitutive relations may be taken from any desired source. Examination of the available relations resulted in the choice of independent variables m and S_0^L . m is the salt concentration in units of molality and is therefore dependent on both salt and liquid water content in a unit volume, and S_0^L is the equivalent pure water saturation which is only a function of liquid water content in a unit volume.

The general derivative of equation (2) is:

$$(6) \quad \frac{dP^L}{d\cdot} = \left(\frac{\partial P^L}{\partial m} \right) \frac{dm}{d\cdot} + \left(\frac{\partial P^L}{\partial S_0^L} \right) \frac{dS_0^L}{d\cdot}$$

With

$$(7a) \quad \frac{\partial P^L}{\partial m} = \frac{1}{\sigma_0^{LG}} \left(\tilde{P}^L \frac{\partial \sigma^{LG}}{\partial m} + \sigma^{LG} \frac{\partial \tilde{P}^L}{\partial m} \right)$$

$$(7b) \quad \frac{\partial P^L}{\partial S_0^L} = \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S_0^L}$$

It is noted here that equations (7a) and (7b) are the corrections to the coefficient of conductivity that occur in Darcy's Law if the law is written in terms of a gradient in salt and water concentrations as opposed to pressure. The use of Darcy's Law and these corrections will allow estimation of the coefficients that arise naturally in non-equilibrium or process thermodynamics (c.f., Luikov, 1975).

Approximations to the Constitutive Relations

The ultimate goal of developing constitutive relations (1) and (2) is the solution of coupled systems of partial differential equations describing flow and transport of saline solutions in porous media. In order to solve the systems of equations, it is advantageous to make reasonable approximations. In order to rigorously show that approximations to the above constitutive relations are valid, it is necessary to show that there is a negligible impact due to neglecting one or more terms in equations (1), (2), (5a), (5b), (7a), and (7b). In principle, this can be accomplished in one of two ways: 1) it may be shown that one or more terms dominate the equation in the region (i.e., state space) of interest, or 2) it may be shown that the error introduced by the approximation is small. In general, "domination" or "small" are qualitative terms, but for the discussions herein, two orders of magnitude difference shall be considered sufficient. So, the example below will be an order of magnitude analysis of the relevant terms.

As an example of “domination”, it is convenient to consider a slightly different form of equation (1). Taking the natural log of both sides of the equation, equation (1) may be rewritten:

$$(8) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + \int_c^P \frac{V^L}{N^{wL}} dP^L$$

Hereafter, the integral in equation (8) will be referred to as the **volume correction term**, and the zero-salt liquid pressure term will be called the **dilute approximation term**. The sum of these two terms is the **curved interface correction term**. The **activity term** is self explanatory, and the term on the left-hand side of the equality is the desired resulting **vapor depression term** for which the constitutive relation is being developed. The corresponding terms in (1) will also be designated by these names, and the reason for these names becomes clear during the derivation (Burns et al., 2004).

A natural extension of the dilute solution approximation (developed in Burns et al., 2004) to equation (8) is:

$$(9) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P^L - P_{0\infty}^L)$$

This can be seen by recognizing that if the volume correction term is negligible, then $P^L \cong P_0^L$. This is a very natural extension, and a very similar constitutive relation is found in Olivella et al. (1996). Since knowledge of the vapor depression (left-hand side of (8)) is desired, the mathematically precise statement of the volume correction term being negligible is:

$$(10) \quad \frac{\left| \int^B \frac{V^L}{N^{wL}} dP^L \right|}{\left| RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) \right|} \leq 0.01$$

Additionally, since it is known that both terms in the denominator are $\neq 0$, if either term can be shown to dominate the volume correction term, then the dilute approximation is also valid.

In order to show that error is small, it is necessary to define the measure of the error. Here error will be a relative error, and will be defined as:

$$(11) \quad error = \left| \frac{[exact_eqn] - [approximation]}{[exact_eqn]} \right|$$

Using the vapor pressure as the example again, but this time solving for P^{wG} yields:

$$(12) \quad error = \left| \frac{P_{eqn.8}^{wG} - P_{eqn.9}^{wG}}{P_{eqn.8}^{wG}} \right| = \left| 1 - \exp \left(\frac{-1}{RT} \int^B \frac{V^L}{N^{wL}} dP^L \right) \right| \leq 0.01$$

Where the inequality is the condition to show the error in neglecting the volume correction term is negligible (to within an error of less than 1%). With the above notions of error and domination of terms, it is now possible to do some computations for an example for brine strength NaCl solutions.

Example: NaCl at 25°C

As will be seen, a substantial amount of experiments must be performed on the basic physical properties of the salt of interest. Since such information is readily available

for NaCl, this salt is commonly used in experiments and is used in the example below. The following development is largely restricted to analysis of the volume correction term of equation (1) (equivalently, equation (8)). For additional plots showing the magnitude of various other terms, the reader is referred to Burns (2004).

Computation of brine strength salt effects in porous media

Heyrovska (1996) provides a suitable conversion between volume and salt concentration for NaCl at 25C, though some manipulation is necessary to get consistent units. Heyrovska's empirical equations 13 and 14 (equation numbers are from Heyrovska's paper) are:

$$(13) \quad \bar{V}^L = 1002.86 + m(26.8 - 10.55\alpha)$$

$$(14) \quad \bar{V}^L = 1002.38 + 24.74\alpha m$$

Where $\alpha \leq 1$ is the experimentally determined degree of dissociation. α is a function of the molality (m), and it accounts for the incomplete dissociation of NaCl into ions in a solvent. \bar{V}^L is the molal volume of liquid (cm^3 of liquid per kg of water). The reason that there are two equations is that due to the functional form of α , the van't Hoff factor is minimum at $m \cong 2$. Heyrovska recommends that this be used as the dividing point for use of the two equations. Equation (13) holds to the left of the minimum and equation (14) to the right. For many purposes it may be sufficient to approximate the entire range as a line (see Figure 2), but for the purposes of evaluating volumetric effects on liquid pressure, this is not done here. However, it is desired that the volume function used here be continuous, so the intersection of the two curves (at $m \cong 0.1506$) is used as the transition point rather than Heyrovska's $m \cong 2$. A plot of the data (not shown) indicates that most of the departure from equation (14) occurs

below the intersection, so the formulation here still substantially captures the variation of volume with molality.

Examination of the integrand in equation (8) (equivalently (1)) reveals that the desired integrand is the volume of liquid per mole of water. Simple multiplication of \bar{V}^L by the molar weight of water ($M^{H_2O} = 0.018015 \text{ kg/mol H}_2\text{O}$) gives the integrand as a function of m only. Since it does not matter which units of salt concentration are used, the integral may be written:

$$(15) \quad \int_c^b \frac{V^L}{N^{wL}} dP^L = \int_b^m M^{H_2O} \bar{V}^L(m) d\left(\frac{\sigma^{LG}(m)}{\sigma_0^{LG}} \tilde{P}^L(S^L(m))\right)$$

For consistency of units, $V^{pore} \equiv 1 \text{ cm}^3$ is chosen. With this choice of V^{pore} , S^L is given by:

$$(16) \quad S^L(m) = \frac{N^{wL} M^{H_2O} \bar{V}^L(m)}{V^{pore}} \quad \text{for this path of integration (i.e., fixed } N^{wL} \text{).}$$

To get $S^L(S_0^L, m)$ in general, recognize that $\bar{V}^L(m)$ is only a function of m , and N^{wL} is a one-to-one function of only S_0^L . This implies that $N^{wL} = S_0^L V^{pore} / (M^{H_2O} \bar{V}_0^L)$ where \bar{V}_0^L is the zero salt molal volume. Substituting back into (16) gives the more general form:

$$(17) \quad S^L(S_0^L, m) = \frac{S_0^L \bar{V}^L(m)}{\bar{V}_0^L}$$

Examination of Figure 1 shows that a good fit to the surface tension function is given by:

$$(18) \quad \sigma^{LG}(m) = \sigma_0^{LG} + 1.7m = 72 + 1.7m \quad \text{with units of dynes/cm.}$$

For the purposes of this example, the non-hysteretic van Genuchten pressure-saturation relationship is used (as written in Carsel and Parrish, 1988) with parameter values taken from Carsel and Parrish for sand, silt, and loam. The values used are shown in Table 1, and were chosen to represent a wide range of values that may be encountered in natural porous media. The van Genuchten head was converted to pressure by multiplication by the density of fresh water and the gravitational constant yielding:

$$(19) \quad \tilde{P}^L(S^L(m)) = \frac{-\rho_0 g \left((S^L)^{\frac{N}{1-N}} - 1 \right)^{\frac{1}{N}}}{\bar{\alpha}}$$

Table 1: van Genuchten parameters (Carsel and Parrish (1988))

parameter	silt	loam	Sand
$\bar{\alpha}$	0.016	0.036	0.145
N	1.37	1.56	2.68

Equations (17) through (19) provide a complete description of the differential in equation (15) in terms of m . Now, there are two choices for computation of (15): either fit a function of m to α so that the change of variables may be completed, or plot equation (2) directly (for fixed water content) and fit a function of m to it. After evaluation of both options for NaCl, equation (2) was found to be approximately linear for most water contents, so this option was used. To plot equation (2), first compute N^{wL} using equation (16) for a given fixed pure water saturation (i.e., zero

salt); then this fixed value of N^{wL} is used in equation (16) to calculate saturation as a function of salt concentration. Lastly, equations (2) and (18) are used to compute the liquid pressure as a function of salt for a fixed water content. As an example, see Figure 3 for three different water contents. There is nothing special about these three values other than they have y-intercepts that allow them all to be plotted on the same graph. In general, for all three soil types examined, the plots are approximately linear, and the slopes vary from one water-content to another. As will be seen later, the linear approximation is good for a wide range of water contents.

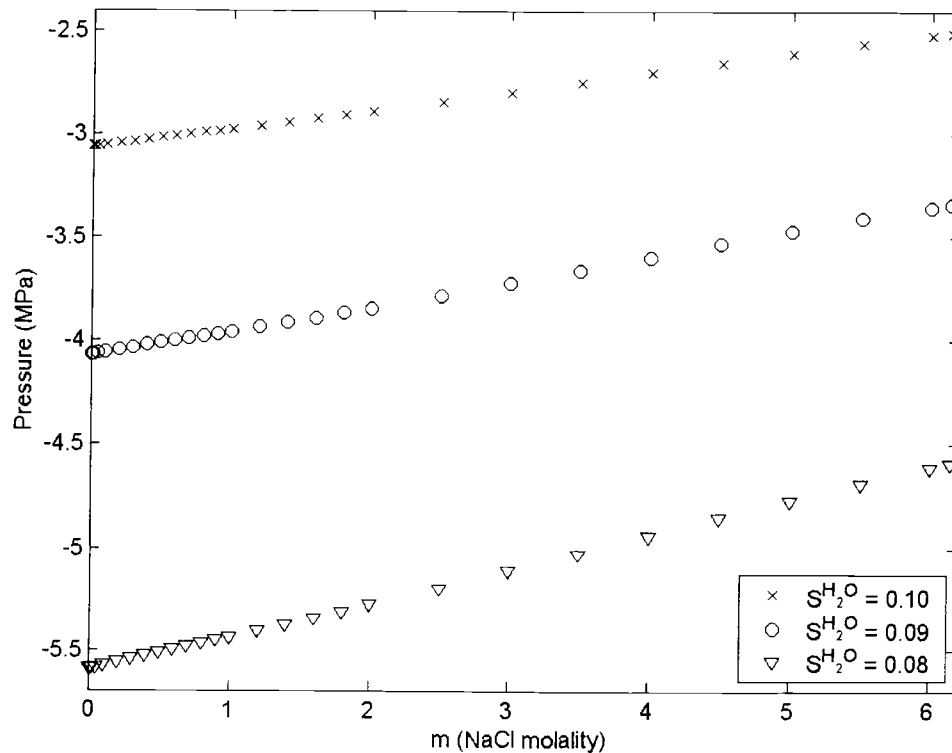


Figure 3: Liquid pressure as a function of molality for a silt for three different fixed water contents.

For fixed water content, if water pressure may be written as a linear function of m , then:

$$(20) \quad P^L(m) = bm + c \Rightarrow dP^L(m) = bdm$$

where b is a function of the water content ($b = b(S_0^L)$) which is a constant in the integral being evaluated. It is also worth noting that in general, $b(S_0^L)$ is a hysteretic function, and is in fact the sole source of hysteresis in equation (2). Since $b(S_0^L)$ is not a function of m , equation (15) may be reduced to:

$$(21) \quad \int_c^b \frac{V^L}{N^{wL}} dP^L = b(S_0^L) \int_0^m M^{H_2O} \overline{V^L}(m) dm$$

A plot of the integrand of equation (21) shows that a linear fit is a reasonable first approximation (see Figure 2). Rather than using Heyrovská's equations, if a linear fit to the integrand is utilized, the integral is easily evaluated:

$$(22) \quad \int_c^b \frac{V^L}{N^{wL}} dP^L = b(S_0^L) (0.1908m^2 + 18.04m)$$

Now, all required relations have been developed to allow an order-of-magnitude analysis of the constitutive relations. If necessary, higher order polynomial fits to the integrand are also trivial to evaluate. This is not necessary for this order of magnitude analysis.

Evaluation of approximations to the constitutive relations

In order to determine when approximations to equations (1), (2), (5a), (5b), (7a), and (7b) are valid and may be used, it is necessary to learn when the effect of various terms are negligible. To do this, equations of the form shown in (10) and (11) are used. Now that a complete set of relations have been developed for NaCl, this may be accomplished. Using the approximation given by equation (22), it is straightforward to evaluate both the vapor pressure (equation (1)) and any desired approximations. The relations described by equations (10) and (11) may then be used to evaluate the relative contribution of various terms or the error induced by any approximations.

Substitution of (22) into (8) gives:

$$(23) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL} + \frac{V_0^L}{N_0^{wL}} (P_0^L - P_{0\infty}^L) + b(S_0^L) (0.1908m^2 + 18.04m)$$

The activity is computed using relationships from Heyrovská's paper where the input parameters are tabulated values of m and α as a function of m . The density of the tabulated values is sufficient for computations here (the spacing of tabulated values is evident in Figure 2), and when necessary, a simple linear interpolation is used. Using the usual parameterization of pressure, $P_{0\infty}^L = 0$, and using pure water density at 25 °C, gives:

$$(24) \quad RT \ln \left(\frac{P^{wG}}{P_{0\infty}^{wG}} \right) = RT \ln a^{wL}(m) + \frac{M^{H_2O}}{\rho_0^{H_2O}} P^L(S_0^L) + b(S_0^L) (0.1908m^2 + 18.04m)$$

Where:

$$P^L(S_0^L) = \frac{\sigma^{LG}(m=0)}{\sigma_0^{LG}} \tilde{P}^L(S^L(0), m=0) = \tilde{P}^L(S_0^L)$$

Vapor depression resulting from interface curvature is often negligible compared to depression resulting from salt concentration (Figure 4), a fact that has been exploited in the past (e.g., Bear and Gilman, 1995). However, under drier conditions in finer porous media, the assumption of negligible effect of interface curvature is suspect.

Using equation (24) as the explicit form of equation (8), it is now possible to compare terms. Figure 5a through 5c show plots of relative magnitudes of terms and the predicted values of $b(S_0^L)$ for silt, loam, and sand, respectively. The ratio described by equation (10) is shown in plot (f) of each figure, and plots (c) through (e) show ratios of various other terms. The relative maximum error between the computed pressure (equation (2)) and the linear approximation (equation (20)) is shown in plot (b).

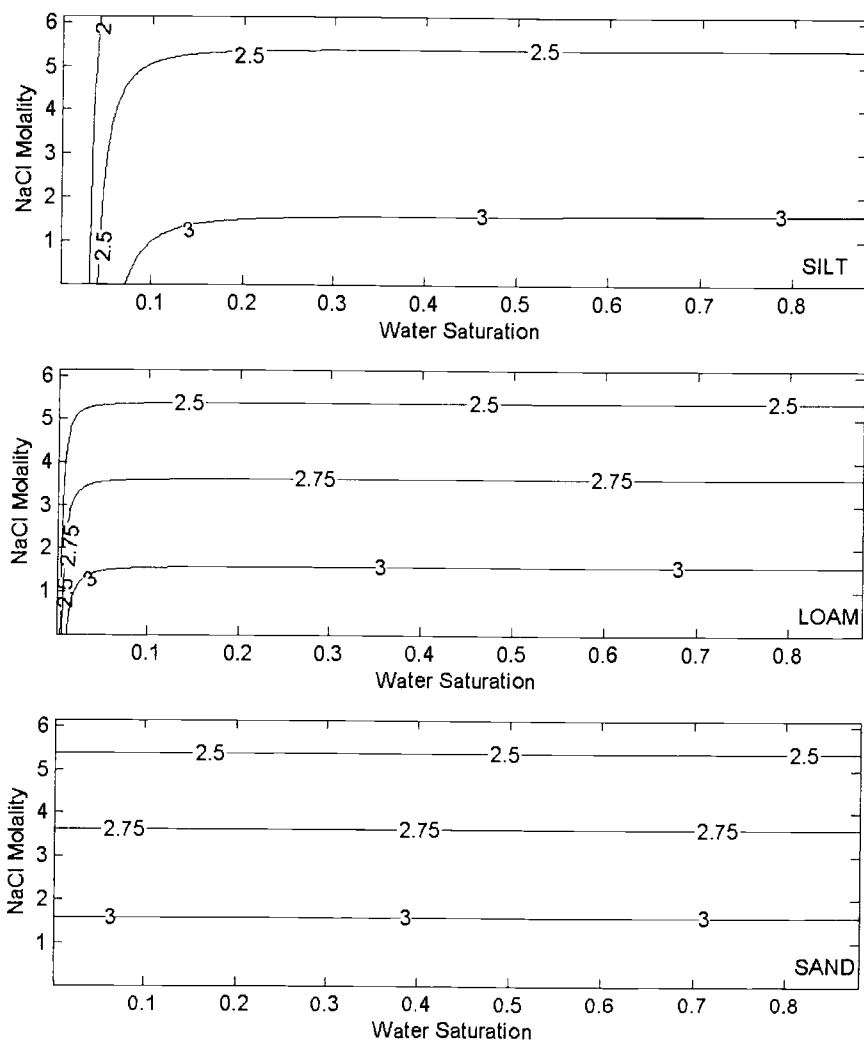


Figure 4: Plots of vapor pressure (equation (1)) for silt (top), loam (middle), and sand (bottom). Units are in kPa.

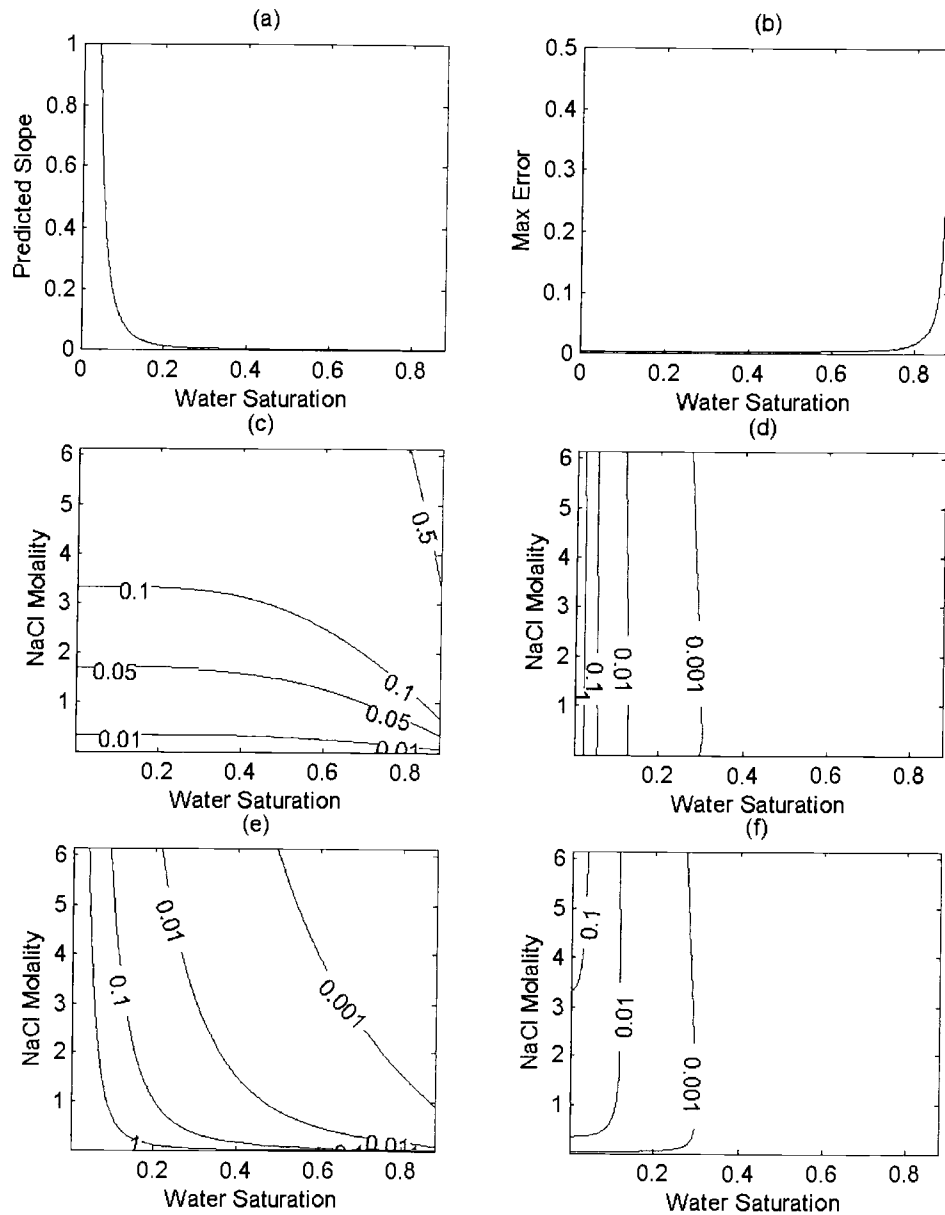


Figure 5a: Plots for **silt**: (a) The slope of the linear approximation ($b(S_0^L)$) to the pressure function. (b) The error (eqn (11)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8).

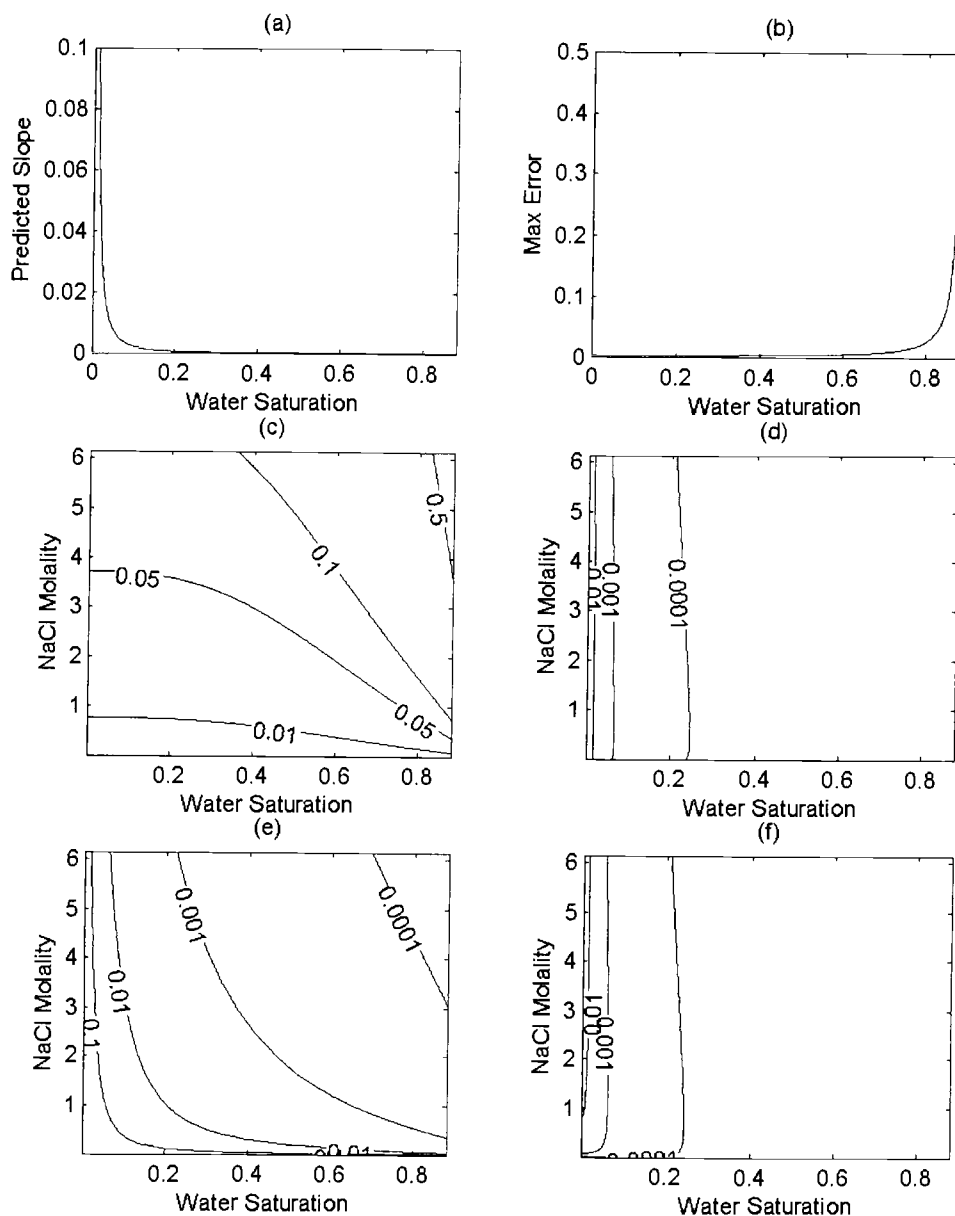


Figure 5b: Plots for **loam**: (a) The slope of the linear approximation ($b(S_o^L)$) to the pressure function. (b) The error (eqn (11)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8).

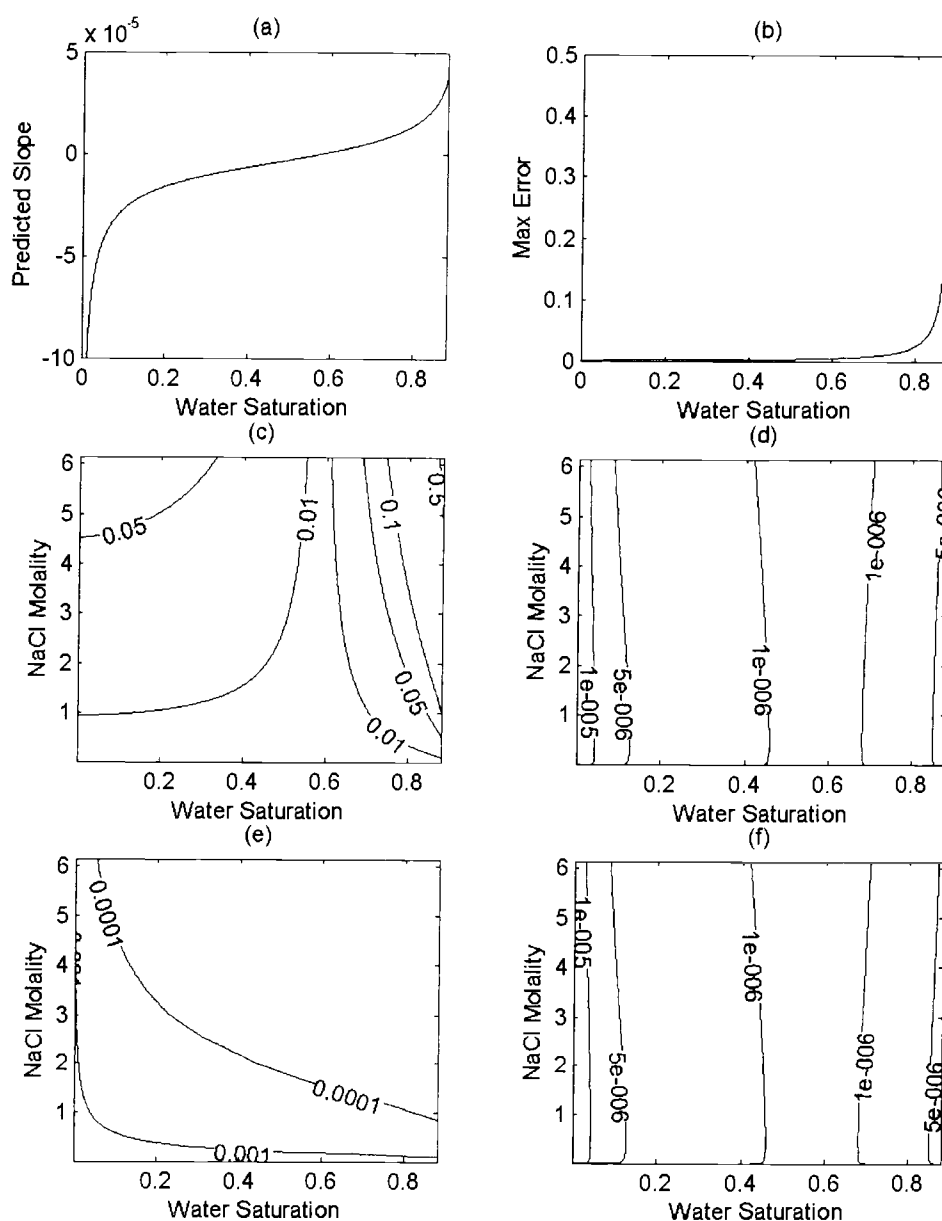


Figure 5c: Plots for **sand**: (a) The slope of the linear approximation ($b(S_0^L)$) to the pressure function. (b) The error (eqn (11)) between the linear fit and the computed pressure. (c) The absolute value of the ratio of the volume correction term to the dilute approximation term for equation (8). (d) The absolute value of the ratio of the volume correction term to the activity term for equation (8). (e) The absolute value of the ratio of the dilute approximation term to the activity term for equation (8). (f) Plot of equation (10): The absolute value of the ratio of the volume correction term to the sum of the dilute approximation and activity terms for equation (8).

The plots presented only span $0 < S_0^L \leq 0.88$ because the addition of salt necessarily implies that liquid saturation increases (because specific volume of the liquid increases). The maximum pure water content that will result in a liquid saturation of the maximum acceptable value 1 may be calculated as:

$$(25) \quad (S_0^L)_{\max} = \frac{\bar{V}_0^L}{\bar{V}_{\text{saturated}}^L} \cong 0.884$$

By considering ratios of all possible combinations of the terms on the right hand side of equation (24), it is possible to see which terms dominate for different salt concentrations and water contents. The regions with values below 0.01 on contour plots (c) through (f) of each Figure 5 describes where the approximation given by neglecting the term in the numerator in favor of the term(s) in the denominator is valid with error under 1%. As previously stated, since both the dilute approximation term and the activity term are always non-positive, there is never an instance when the effects cancel. Comparison of plots (c), (d), and (f) shows where various terms dominate the volume correction term; and plot (e) shows that while the activity often dominates, the dilute approximation term is often non-negligible.

Note that the error (plot (b) of each Figure 5) is computed per equation (11) above, and that the denominator goes to zero. This implies that even for small departures from the linear fit, the error must go to infinity. It can be shown that even at high water contents, where the linear approximation of the pressure function may be suspect, the pressure is still a well-behaved function of salt concentration and not too far from linear (see Figure 6 for an example). Since the activity term commonly dominates in this region, even a doubling or tripling of the slope to some conservative value shows that the departure from linearity is of small importance. For this reason, the high error in plot (b) of each Figure 5 is of little concern.

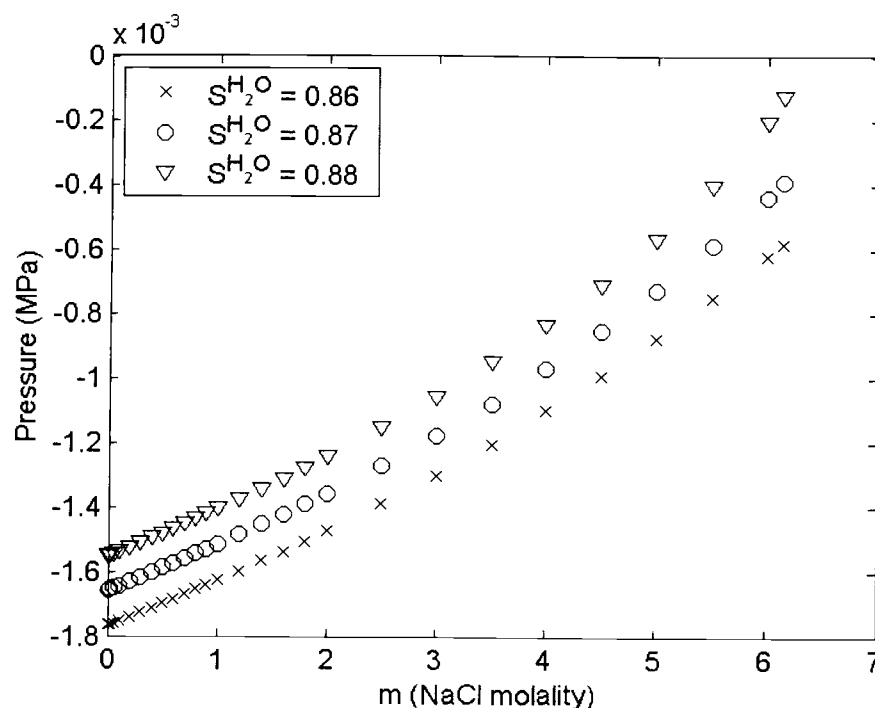


Figure 6: Liquid pressure as a function of molality for a loam at three fixed water contents. Notice this plot is at high saturation where the error function shown in Figure 5b(b) indicates the pressure may not be well-represented as a straight line.

The conclusion that may be drawn from Figures 5a through 5c is that the volume correction term is negligible except under very dry conditions. Further, the effects are more substantial for finer textured soils.

An example of the algorithm used to calculate and plot Figure 5a through 5c is given in Burns (2004). This algorithm may be used for any porous media for which the appropriate van Genuchten parameters are known. It may also be easily altered to call another pressure function (e.g., Brooks and Corey, 1964) if it is deemed that this alternative pressure function yields better results in the range of water contents of interest. Fit may especially be important in the dry region since this is the region where non-negligible effect due to the volume correction term may occur. The algorithm becomes unstable at non-physically realistic saturations (i.e., saturation greater than 1).

Figure 7 shows the error (defined by equation (11)) in computed vapor pressure (equation (1)) for silt. This is the worked example equation (12). Notice that Figure 7 and Figure 5a(f) are analogous plots. The chief difference is that when computing the error, the equation is transformed by exponentiating both sides of equation (8). This is a non-linear transform, resulting in a somewhat different shape of the plot and roughly an order of magnitude difference in values. The plot still shows that neglecting the volume correction term may yield appreciable errors for very dry conditions. Examination of plots for loam and sand (not shown, see Burns, 2004) show that the general trend of larger effects for finer textured soils still holds. In fact, since this trend is so prevalent, for the remainder of this section, only plots for silt are shown unless necessary to illustrate a point. Also, since the volume correction term is currently under investigation, many of the subsequent plots will only be concerned with examination of negligence of this term. The reader is referred to Burns (2004) for the corresponding plots for loam and sand or for additional plots examining other terms.

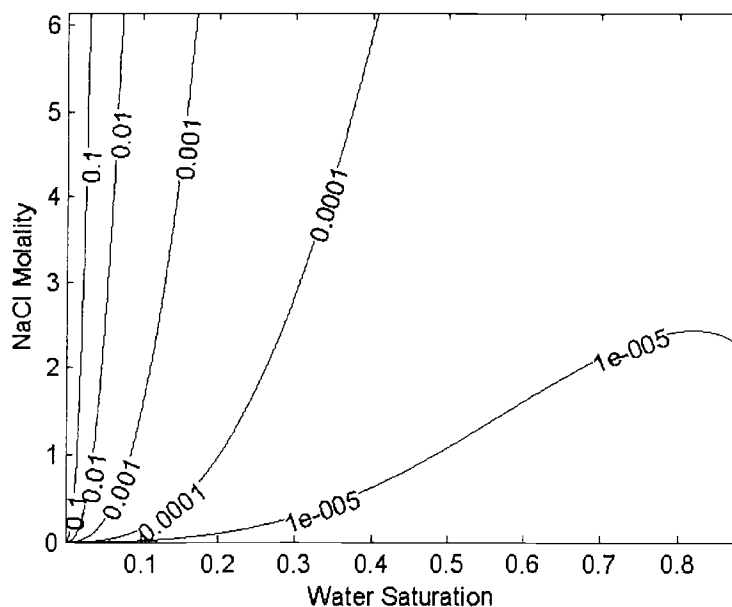


Figure 7: Plot of the error for **silt** induced by neglecting the volume correction term (worked example equation (12)).

Figures 8a through 8c show plots for liquid pressure (equation (2)) in silt, loam, and sand, respectively. Plot (a) in each figure is the liquid pressure as a function of water and salt content, and plots (b) through (d) show the error in computed liquid pressure induced by neglecting various terms or corrections. The error plots show that there may be appreciable errors induced by neglecting any corrections except under dilute conditions. Note that the error is smaller where both corrections are neglected, rather than only when the volume correction is neglected. This is because the correction to surface tension tends to increase the magnitude of the pressure, while the volume correction tends to lower the magnitude of pressure.

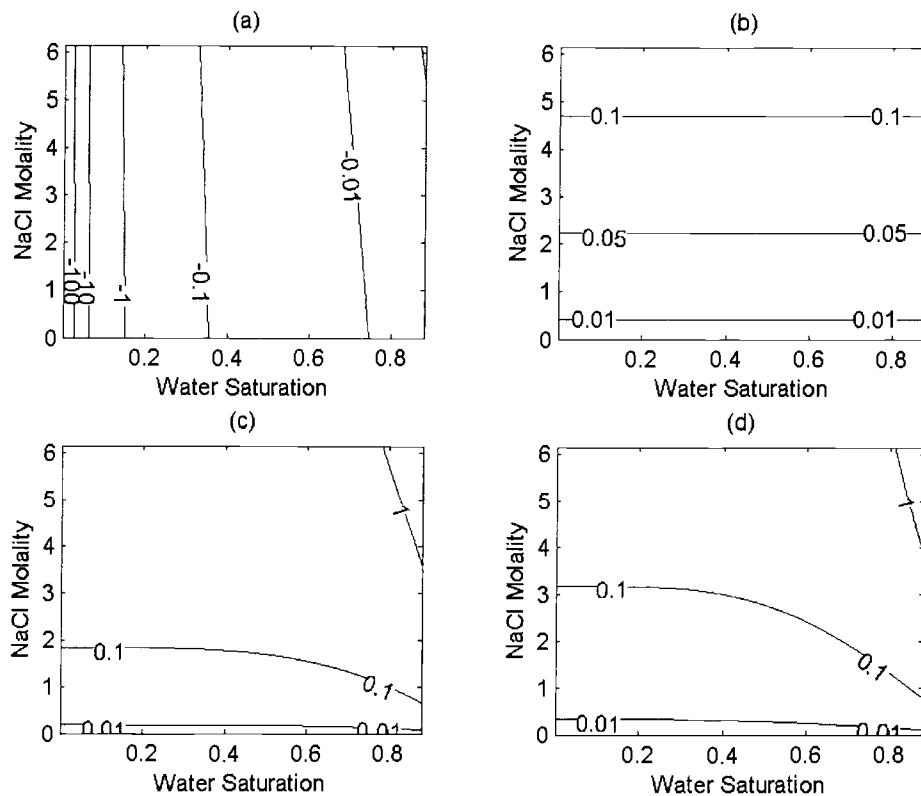


Figure 8a: Plots for **silt**: (a) Plot of equation (2) in units of MPa. Plots (b) through (d) are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) only the surface tension correction term ($\sigma^{LG} / \sigma_0^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).

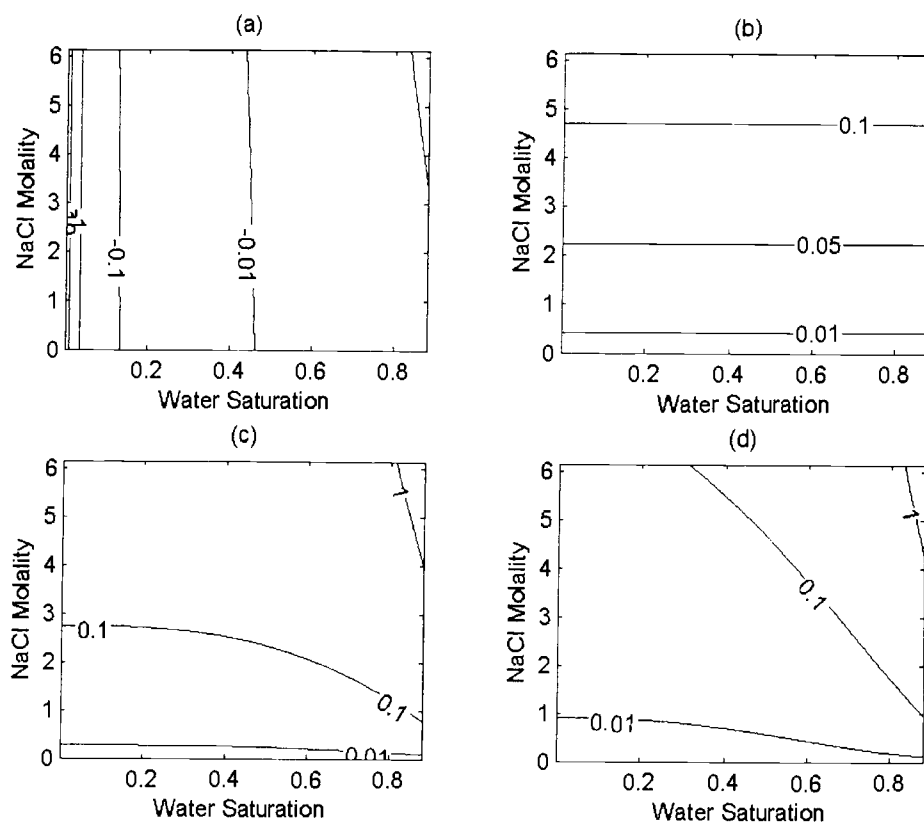


Figure 8b: Plots for **loam**: (a) Plot of equation (2) in units of MPa. Plots (b) through (d) are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) only the surface tension correction term ($\sigma^{LG} / \sigma_0^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).

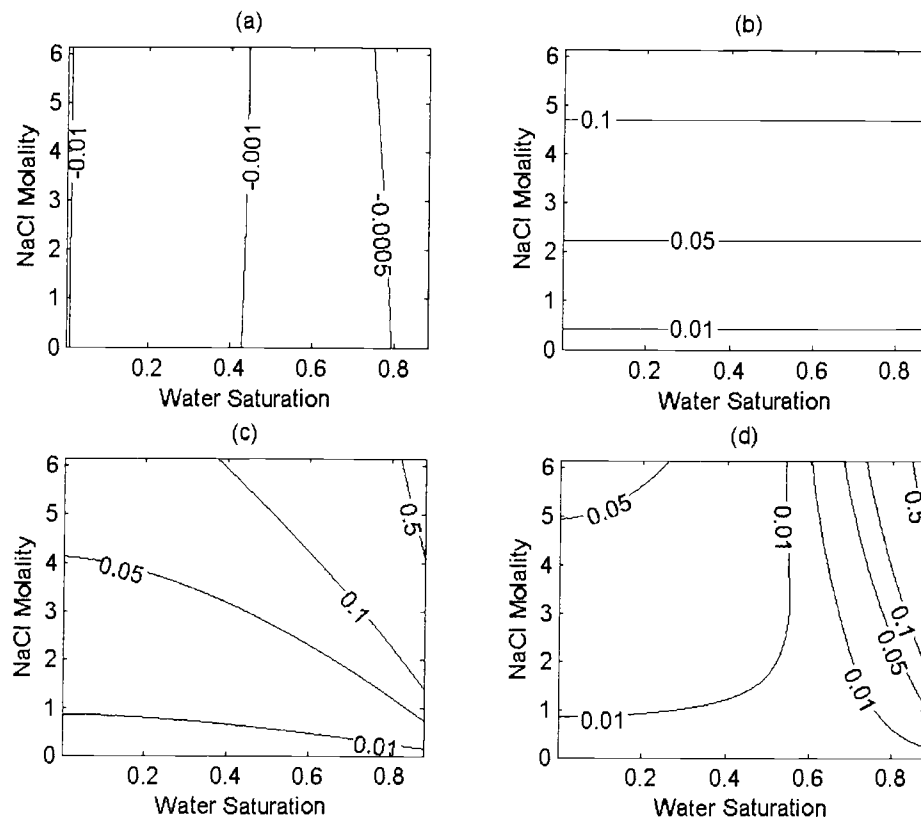


Figure 8c: Plots for **sand**: (a) Plot of equation (2) in units of MPa. Plots (b) through (d) are of the error (equation (11)) induced by neglecting one or more terms in equation (2): (b) only the surface tension correction term ($\sigma^{LG} / \sigma_0^{LG}$) is neglected; (c) only the volume correction to the saturation is neglected; and (d) both corrections are neglected (i.e., using the pressure relationship for only water content).

In order to plot equation (5a), it is necessary to take the derivative of the activity. For this order of magnitude analysis, it is sufficient to assume the activity is linear with respect to molality (see Burns (2004) for plots). With this assumption, it can be seen that the volume correction term in (5a) is largely dominated by the activity term, but that drier, finer soils are more strongly affected. Figure 9 illustrates this fact for silt. Further, it can be seen that in the wetter region, a constant value of -0.124 is a good approximation to equation (5a), and that neglecting only the volume correction terms in (5a) (in both the differential and the vapor pressure) yields only marginally better results. The domain over which this is true is even larger for loam and sand, so much

so, that the plot for sand is indistinguishable from a constant on the scale of the plots shown here.

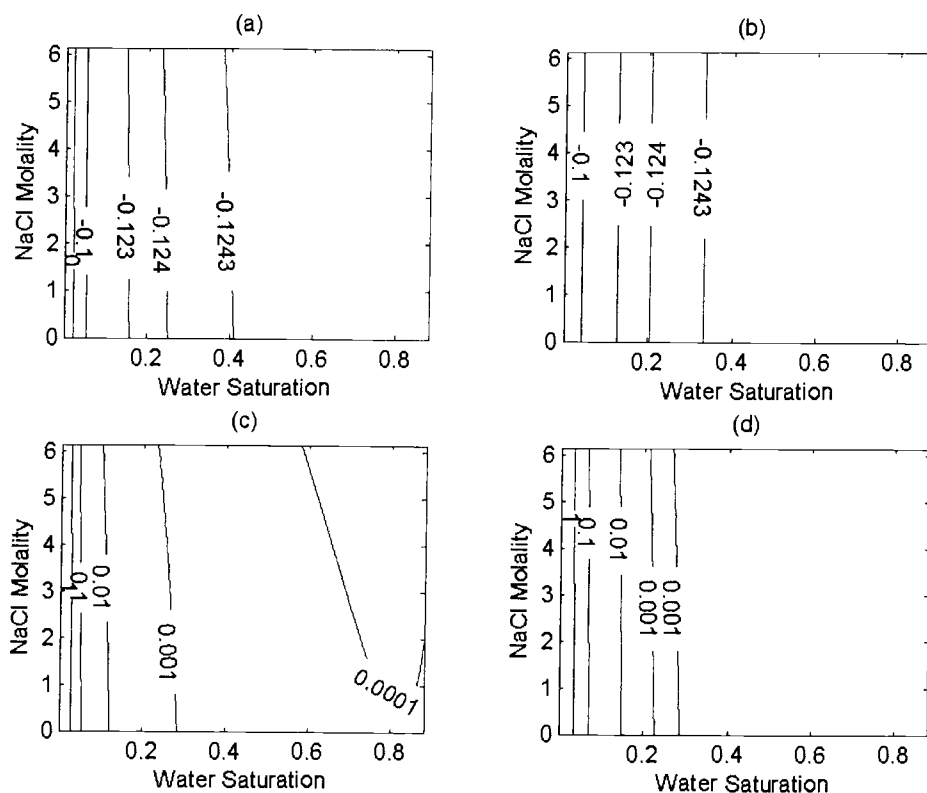


Figure 9: Plots for **silt**: (a) Plot of equation (5a); (b) plot of equation (5a), but neglecting the volume correction terms; (c) error (eqn (11)) induced by neglecting volume correction terms; (d) error induced by approximating equation (5a) with the constant -0.124.

Figure 10 shows equation (5b) for silt. For all three soil textures, neglecting the volume correction term was only acceptable for dilute solutions. The silt again showed the strongest influence, and under very dry conditions (the indistinguishable contours near zero saturation) the magnitude and sign of the differential terms in (5b) are such that they effectively cancel, resulting in a very rapid decrease to zero.

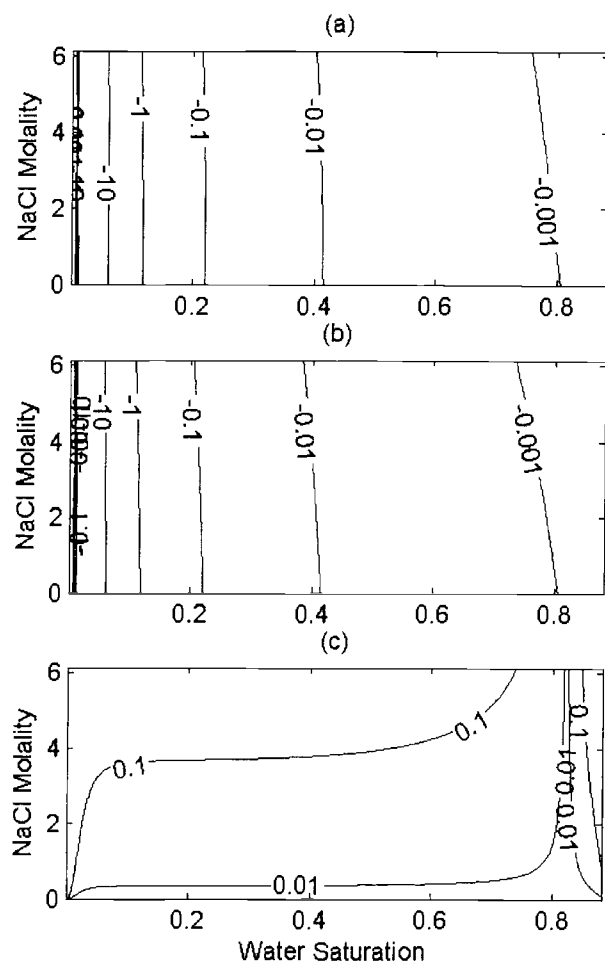


Figure 10: Plots for **silt**: (a) plot of equation (5b); (b) plot of equation (5b) but neglecting the volume correction terms in both the vapor pressure and the differential; (c) error (eqn (11)) resulting from the approximation described in (b).

Figure 11 shows analysis of equation (7a) for silt (the results for loam and sand are very similar). Plot (a) shows equation (7a) itself, and plot (b) shows that the differential in terms of pressure (\tilde{P}^L) is almost always dominated by the differential term for surface tension. Plot (c) shows that it is still necessary to account for the volumetric effect in \tilde{P}^L , except in the dilute case. Plot (d) shows that a very good approximation to equation (7a) is:

$$(26) \quad \frac{\partial P^L}{\partial m} = \frac{\tilde{P}^L}{\sigma_0^{LG}} \frac{\partial \sigma^{LG}}{\partial m} = \frac{1.7}{72} \tilde{P}^L (S_0^L, m)$$

where equation (18) was used. This is true for loam and sand also.

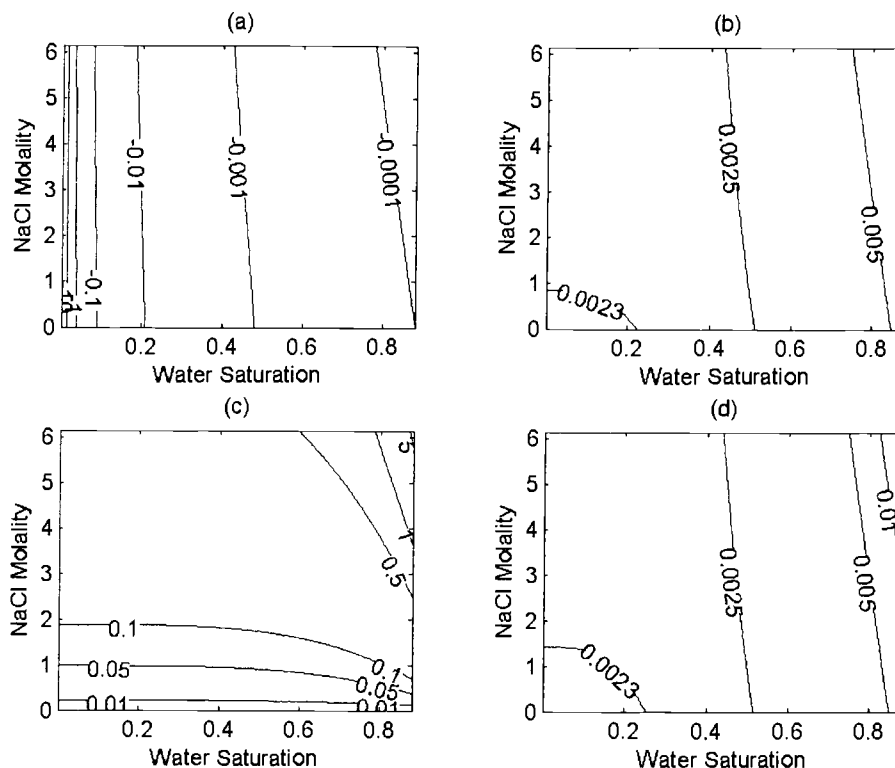


Figure 11: Plots for equation (7a) for silt: (a) plot of equation (7a); (b) ratio of the magnitudes of the pressure differential term to the surface tension differential term; (c) error (eqn (11)) induced by assuming \tilde{P}^L is not a function of salt content (i.e., there is no correction of saturation for salt content); (d) error induced by assuming the \tilde{P}^L derivative term is negligible compared to the surface tension derivative term (but still allowing \tilde{P}^L to be a function of m).

Plots of equation (7b) for silt are shown in Figure 12. Clearly, these show that neither the volume correction nor the surface tension may be neglected except in the dilute case. This is true in general for loam and sand also.

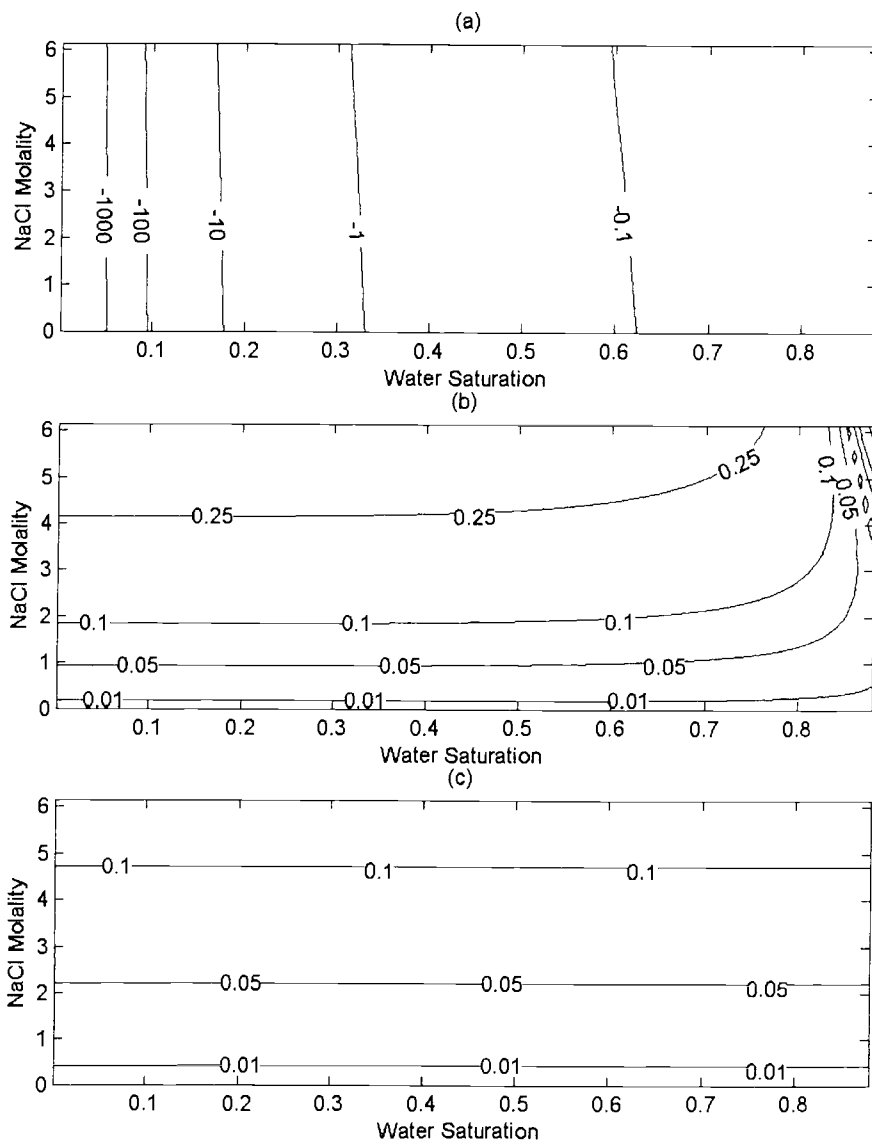


Figure 12: Plots of equation (7b) for **silt**: (a) plot of the entire equation; (b) error induced by neglecting the volume correction in the derivative; (c) error induced by neglecting the surface tension.

It is tempting to consider the magnitudes of (5a) compared to (5b) or (7a) compared to (7b), but without prior knowledge of the gradients in water and salt content to be encountered during evolution of an initial boundary value problem, it is impossible to

do this here. Instead, it is noted that (5a), (5b), (7a), and (7b) will provide the appropriate conversions from the dependent variables (pressures) to the primary variables (water and salt contents) for solution of the differential equations.

Application to the data of Scotter

In a series of papers by Scotter and Raats (1970), Parlange (1973), and Scotter (1974), the phenomenon of water condensation near salt crystals in a relatively dry porous media is experimentally and mathematically analyzed. In the experiments, a pure phase salt (in this case NaCl) was placed against an unsaturated soil at uniform unsaturated moisture content. It was found that the moisture and salt profiles are constant (for the same initial conditions) with respect to the transformed variable $\eta = x/t^{1/2}$. The reader is referred to the above papers for a more complete description of the experiments.

Figure 13 shows the results of two experiments (same initial conditions) conducted by Scotter (1974) in terms of the transformed variable and the gravimetric salt and water contents (g NaCl and g water per 100 g dry soil respectively). The salt is at $\eta = 0$.

The conceptual model is that water moves from the dry region (to the right of the dashed line) in the vapor phase to the wet region (to the left of the dashed line) where it condenses due to vapor pressure lowering associated with the salt and saline water. Once the water condenses, the moisture content is sufficiently high to allow water flow back towards the dry region. It is sufficient to think of the right-hand side as the vapor flow region (hereafter called the dry region), and the left-hand side as the combined liquid-vapor flow region (hereafter called the wet region).

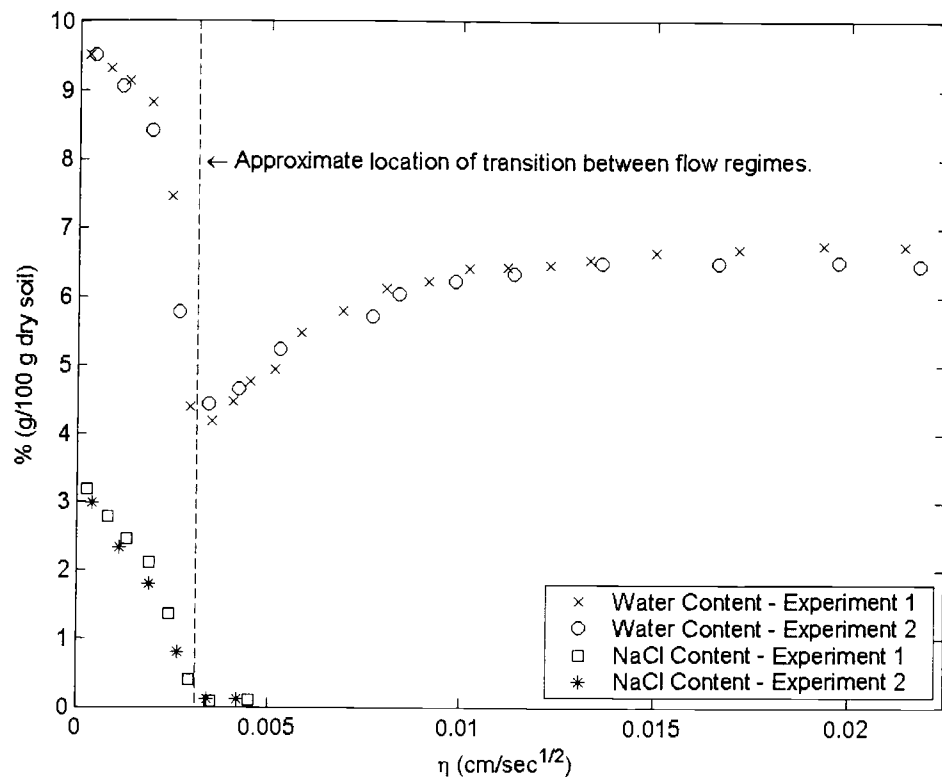


Figure 13: Gravimetric water and NaCl content from Scotter (1974). Pure phase NaCl is at $\eta = 0$.

Using the theory developed above, it is now possible to plot the vapor pressures and water potentials for the Scotter data. Since Scotter measured gravimetric values of water and salt, it is necessary to compute liquid volumes, water volumes, molal salt concentrations, etc. in order to plot the desired results. Figure 14 shows Scotter's measured values for water content versus soil water pressure for fresh water (assumed here to be zero or negligible salt), along with a fit to the data of the van Genuchten relationship (van Genuchten, 1980). The fit of the model is sufficient for the purposes of this example, and the values of the van Genuchten parameters used are $\bar{\alpha} = 0.000329573$ and $N = 1.483$. This relationship is the required functional form for equation (19) above.

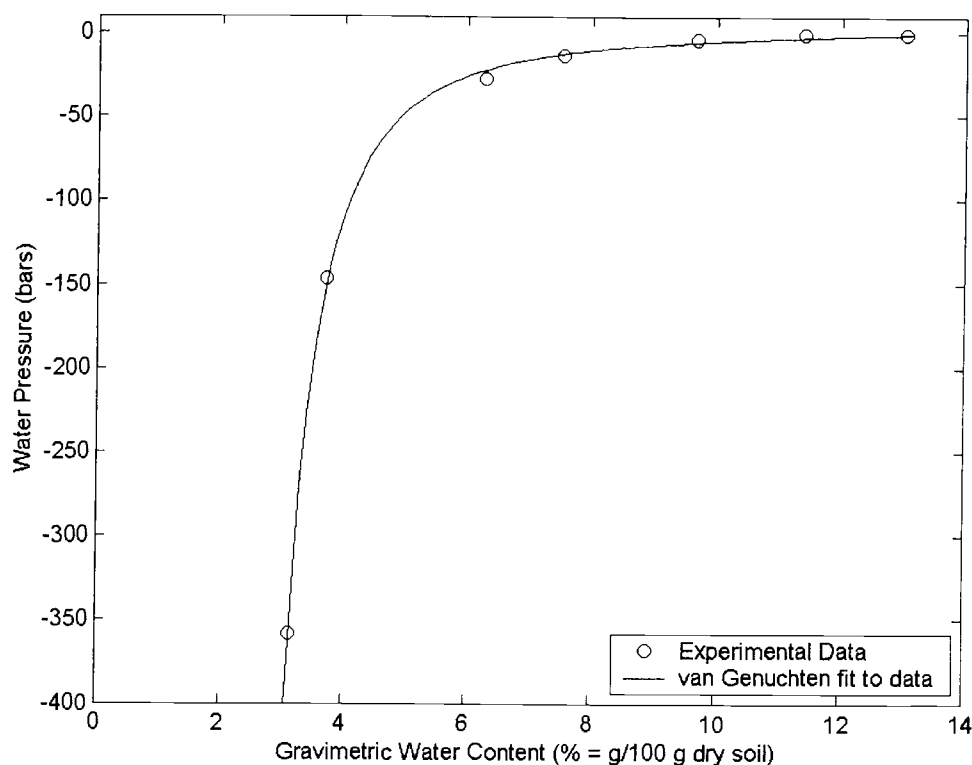


Figure 14: Fit of the van Genuchten relationship to the experimental data of Scotter. The data is for very low strength or pure water.

Since Scotter's experiments were all conducted at 25 C (298.15 K), it is assumed that the straight line in Figure 1 is sufficient for this example. For the remaining estimates and conversions from the gravimetric data of Scotter, a porosity of 0.3 and a density for the dry soil of 2.65 g/cm³ were used. Equation 6 of Heyrovská (1996) was used to compute a^{wL} (using linear interpolation of α from the closely spaced tabulated values), providing the last required information. If desired, the method of Pitzer (Pitzer and Peiper 1984) could be used to get all information computed from the Heyrovská relations. The method of Heyrovská was selected for superior full range performance at 25 C, and because the underlying physics proposed by Heyrovská appears to be more likely correct. The Pitzer theory supposes that the salts completely dissociate even at high strength, then correct for this error with an activity coefficient.

Equation (24) may again be employed to perform an order of magnitude analysis and to plot vapor pressure. Figure 15 shows the error induced in equation (1) by neglecting the volume correction term, as well as the data points from Scotter's experiment 1. Examination of this plot shows that neglecting this term will, in general, result in small errors in predicted vapor pressure.

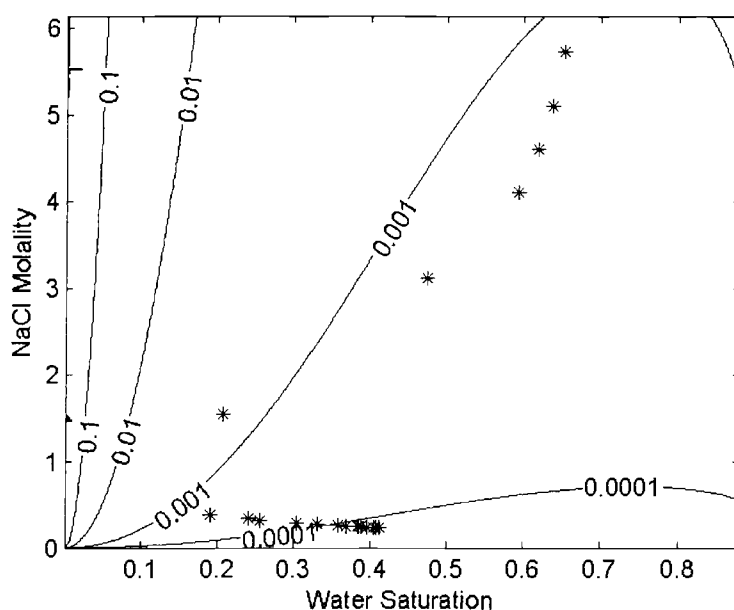


Figure 15: Scotter's data: Plot of the error (equation (11)) induced by neglecting the volume correction term. The asterisks are data from experiment 1.

Figure 16a shows that the liquid saturations and the equivalent water saturations are different in the wet region, and Figure 16b shows the resulting liquid pressure profiles (computed using equation (2)). Figure 17 shows the resulting vapor pressure profile for the Scotter data (i.e., equation (24) solved for vapor pressure). The vapor pressure of pure water over a flat interface is available in any chemistry handbook, and the vapor pressure over a saturated salt solution is an approximate value taken from the compilation of Appelblat and Korin (1998).

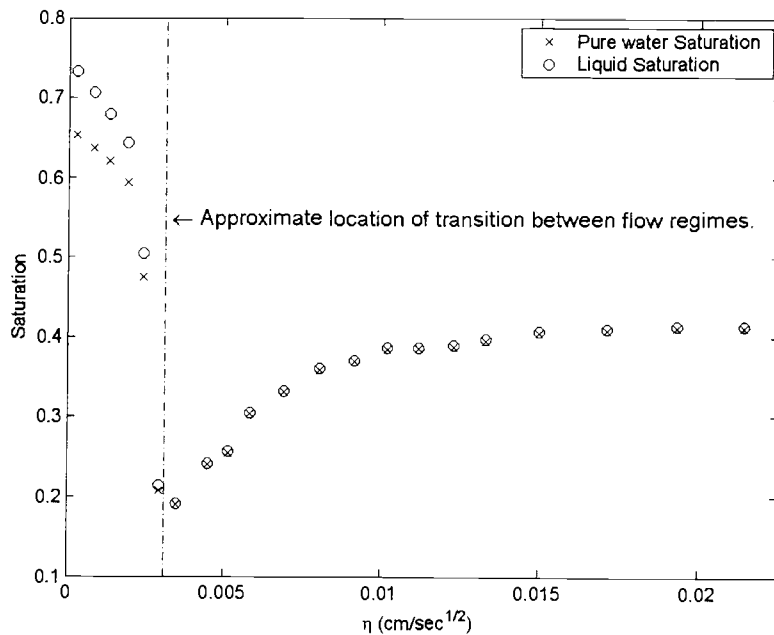


Figure 16a: Scotter data: Pure water saturation and saline liquid saturation as a function of position.

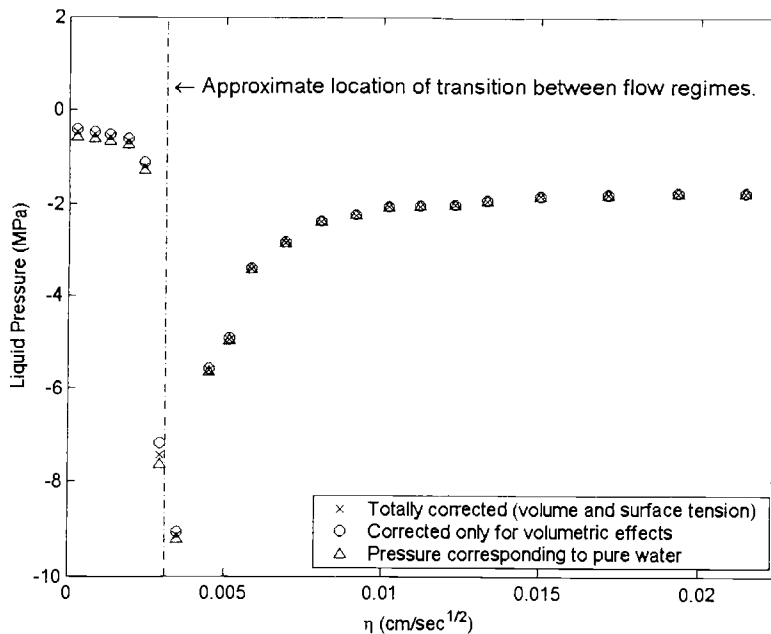


Figure 16b: Scotter data: Computed liquid pressures using equation (2) and the data in Figure 13: equation (2) is shown with x's, not correcting for salt at all shown with triangles, and correcting for changes in volume, but not surface tension shown by o's. Evidently, the volume effect is larger, but the increase in surface tension lessens the effect.

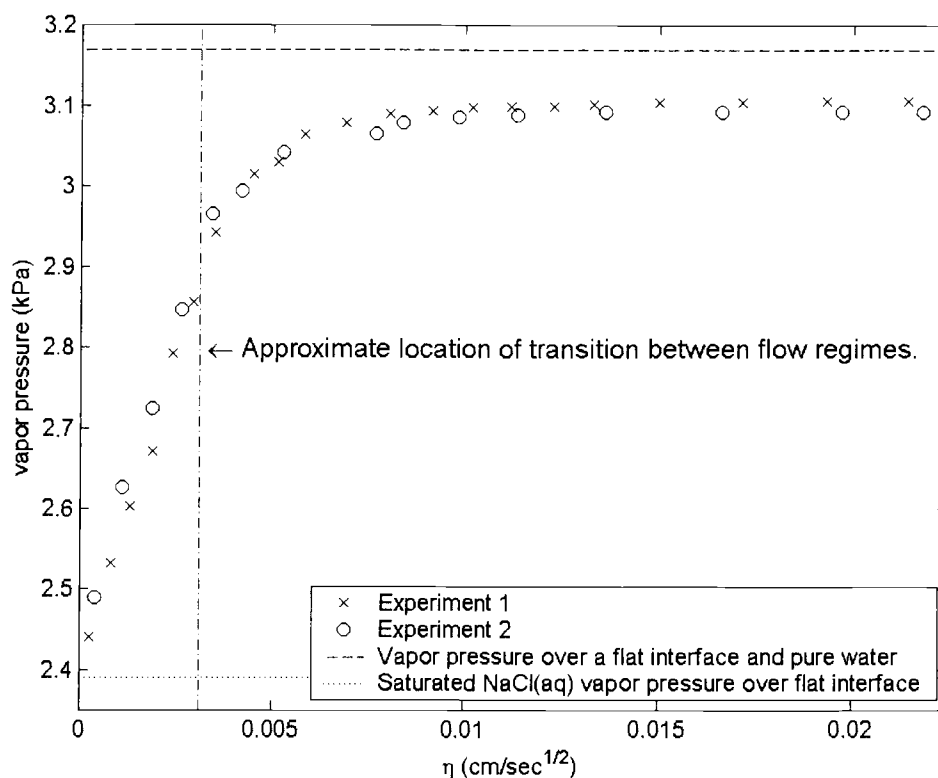


Figure 17: Computed vapor pressure (equation (1)) as a function of position.

Clearly, there is a large effect of the salt content on the vapor pressure. To emphasize this, the vapor pressure is plotted in Figure 18 with various terms assumed to be negligible. There appears to be little effect due to neglecting the volume correction term. It is likely that measurement errors are larger than errors induced by neglecting the volume correction term. In the dry region, Scotter's data showed detectable salt concentrations, resulting in the non-negligible salt effects seen in Figure 18. In most of the wet region, high salt concentrations result in the interface curvature effects being relatively small. A plot analogous to Figure 5a(e) (Burns, 2004) shows these competing effects clearly.

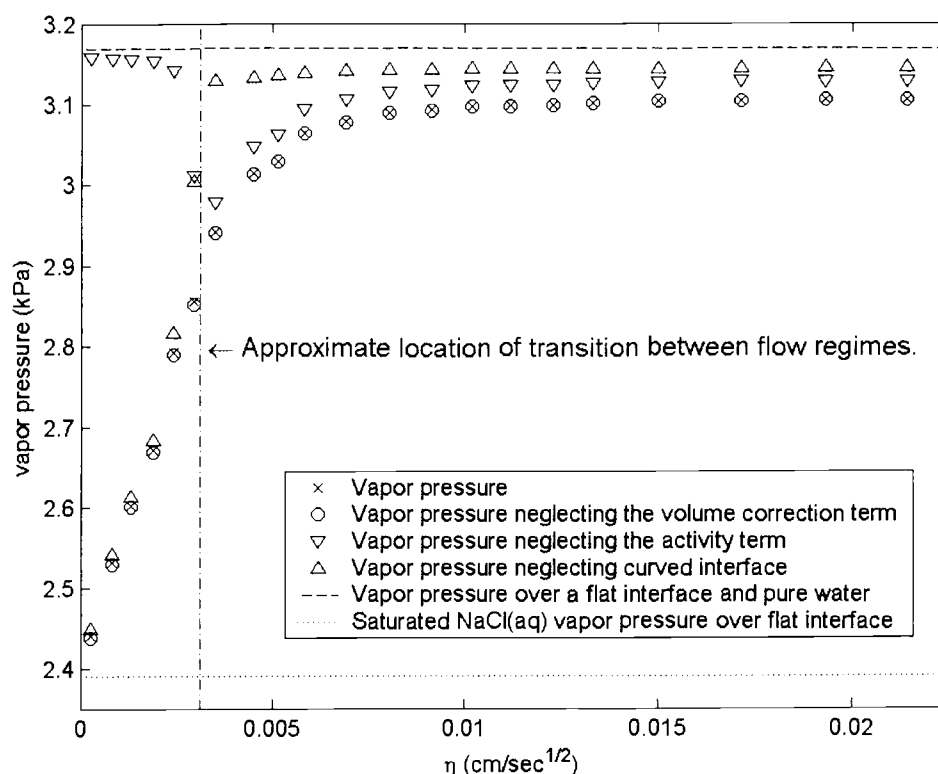


Figure 18: Computed vapor pressure (equation (1)) from experiment 1 for four cases: 1) the full equation, 2) neglecting only the volume correction term (equation (4) or more specifically equation (11)), 3) neglecting the activity term (activity = 1), and 4) neglecting the entire exponential term (curved interface correction).

Figure 19 (analogous to Figure 9) shows that the volume correction term needs to be accounted for when computing equation (5a) for Scotter's soil. This implies that accounting for the volume correction term is necessary when computing the conversions between gradients in vapor pressure and gradients in water and salt contents.

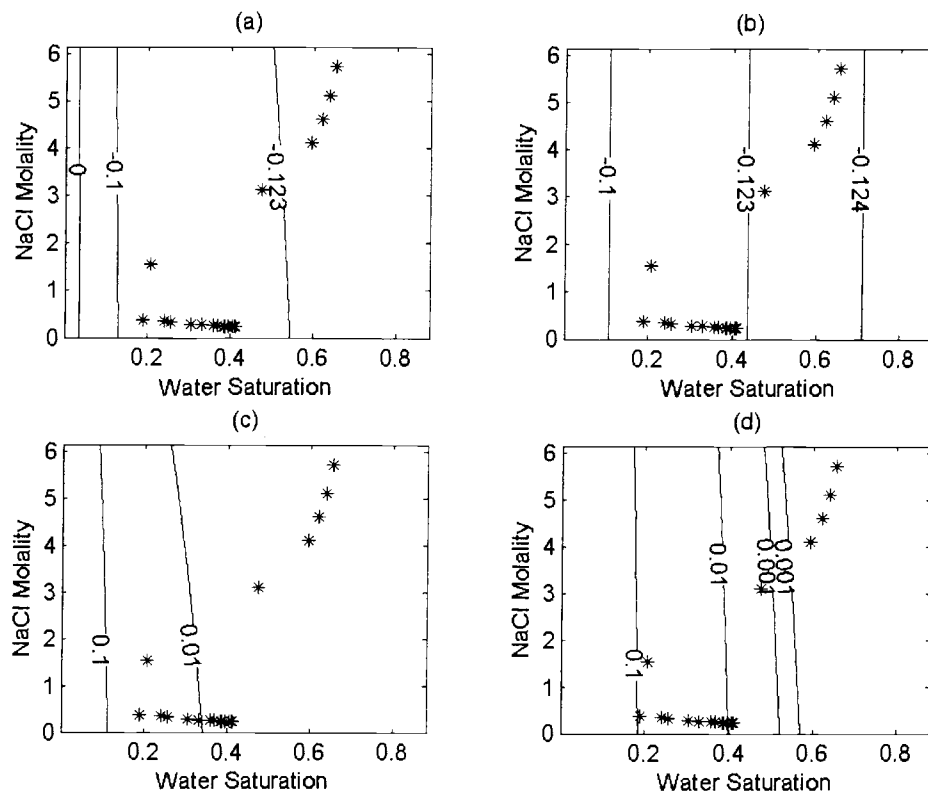


Figure 19: Plots for Scotter's soil: (a) Plot of equation (5a); (b) plot of equation (5a), but neglecting the volume correction terms; (c) error (eqn (11)) induced by neglecting volume correction terms; (d) error (eqn (11)) induced by approximating equation (5a) with the constant -0.123. Asterisks are data from experiment 1.

As expected, equation (26) is also a good approximation for equation (7a) for the Scotter data. Examination of Figures 10 and 12 make it fairly obvious that no terms may be neglected for equations (5b) and (7b). The reader is referred to Burns (2004) for additional plots that directly support the aforementioned conclusions for Scotter's soil.

Conclusion

For NaCl, it has been shown that the volume correction term is potentially important to account for under various conditions. The importance increases under drier conditions and for finer textured sediments. Such sediments are prevalent in many of

the world's hazardous waste storage sites. The Scotter example shows that while the volume correction term may not be important for computation of vapor pressure, it may be important to account for when computing the coefficients of gradients in the primary variables. The above methodology can be used to estimate the importance of various terms for any particular problem of interest.

For dryer soils, the linear approximation to pressure as a function of NaCl salt concentration (yielding $b(S_0^L)$) can be shown to be quite good (Burns et al., 2004).

Since the slope function, $b(S_0^L)$, appears to be a well-behaved function that would be easy to approximate analytically for any fixed soil type of interest; the approximation scheme, given by equation (22), provides a simple and effective first-order correction for high strength brines. Implementation of this approximation is trivial when using numerical models.

Acknowledgements

This work was funded under a U.S. EPA STAR (Science to Achieve Results) Fellowship.

Notation

Variables

U = the internal energy

T = absolute temperature

P = pressure

V = volume

R = universal gas constant

$\mu^{i\alpha}$ = chemical potential of the i -th constituent in phase α

$a^{i\alpha}$ = chemical activity of the i -th constituent in phase α

$N^{i\alpha}$ = number of moles of the i -th constituent in phase α

$v^{iL} \equiv \frac{V^L}{N^{iL}}$ = specific volume of the i -th constituent in the liquid phase (ratio of liquid volume to moles of water in the liquid)

$\sigma^{LG} = \frac{\partial U^{LG}}{\partial A^{LG}} =$ surface tension at the gas-liquid interface

$A^{LG} =$ area of the gas liquid interface

$\frac{dA^{LG}}{dV^L} =$ the gas-liquid interface area to liquid volume ratio (or the density of gas-liquid interface)

$\tilde{P}^L \equiv P^L(S^L) =$ equivalent liquid pressure neglecting changes in surface tension (see discussion following Equation (3)).

$S =$ saturation

$\phi^L =$ volumetric liquid content (volume of liquid divided by total volume of soil, liquid, and gas in porous media).

$\eta = x/t^{1/2} =$ transformed variable for data analysis.

Differentials

$d =$ total differential

$\partial =$ partial differential

$\delta =$ imperfect differential

Superscripts

$L, G =$ liquid and gas phase respectively

$wL, wG =$ water in liquid and water in gas respectively

$hL =$ salt in liquid

$aG =$ air in gas

$LG =$ gas-liquid interface

$sys =$ system total

$\alpha =$ an arbitrary phase or sub-system

Subscripts

$\infty =$ reference condition of flat gas-liquid interface (i.e., infinite radius of curvature)

$0 =$ reference condition corresponding to known salt content (generally zero or negligible amount of salt)

References

- Apelblat, A., and Korin, E., 1998. "The Vapour Pressures of Saturated Aqueous Solutions of Sodium Chloride, Sodium Bromide, Sodium Nitrate, Sodium Nitrite, Potassium Iodate, and Rubidium Chloride at Temperatures from 227 K to 323 K," J. Chem. Thermodynamics, v. 30, pp. 59-71.

- Bear, J., and A. Gilman, 1995. "Migration of Salts in the Unsaturated Zone Caused by Heating," *Letters in Mathematical Physics*, v. 19, pp. 139-156.
- Belton, J.W., 1935. "The Surface Tensions of Ternary Solutions. Part I. The Surface Tensions of Aqueous Solutions of (a) Sodium and Potassium Chlorides, (b) Sodium chloride and Hydrochloric Acid." *Transactions of the Faraday Society*, no. 174, pp. 1413-1419.
- Brooks, R.H. and A.T. Corey, 1964. "Hydraulic Properties of Porous Media." *Hydrology Papers*, Colorado State University, Ft. Collins.
- Burns, E.R., 2004. "Thermodynamic Correction for Salts in Variably Saturated Porous Media." Thesis for M.S. in mathematics. Oregon State University, Corvallis, OR.
- Burns, E.R., J.-Y. Parlange, J.S. Selker, and R.B. Guenther, 2004. "Thermodynamic Correction for Salts in Variably Saturated Porous Media." Submitted to
- Carsel, R.F., and R.S. Parrish, 1988. "Developing Joint Probability Distributions of Soil Water Retention Characteristics," *Water Resources Research*, V. 24, No. 5, pp. 755-769.
- Harkins, W.D., and H.M. McLaughlin, 1925. "The Structure of Films of Water on Salt Solutions I. Surface Tension and Adsorption for Aqueous Solutions of Sodium Chloride," *J. Amer. Chem. Soc.*, v. 47, pp. 2083-2089.
- Heyrovska, R., 1996. "Physical Electrochemistry of Strong Electrolytes Based on Partial Dissociation and Hydration: Quantitative Interpretation of the Thermodynamic Properties of NaCl(aq) from "Zero to Saturation"," *J. Electrochem. Soc.*, v. 143, no. 6, pp. 1789-1793.
- Li, Y.G., 1999. "Reply to "Comments on 'Surface Tension Model for Concentrated Electrolyte Solutions by the Pitzer Equation'"", *Ind. Eng. Chem. Res.*, v. 38, pp. 4137-4138.
- Luikov, A.V., 1975. "Systems of Differential Equations of Heat and Mass Transfer in Capillary-Porous Bodies (Review)," *Int. J. Heat Mass Transfer*, v. 18, pp. 1-14.
- Matubayasi, N., H. Matsuo, K. Yamamoto, S. Yamaguchi, and A. Matazawa, 1999. "Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions: I. Aqueous Solutions of NaCl, MgCl₂, and LaCl₃," *Journal of Colloid and Interface Science*, v. 209, pp.398-402.

- Olivella, S., J. Carrera, A. Gens, and E.E. Alonso, 1996. "Porosity Variations in Saline Media Caused by Temperature Gradients Coupled to Multiphase Flow and Dissolution/Precipitation," *Transport in Porous Media*, v. 25, pp. 1-25.
- Parlange, J.Y., 1973. "Movement of Salt and Water in Relatively Dry Soils," *Soil Science*, v. 116, no. 4, pp. 249-255.
- Pitzer, K.S., and J.C. Peiper, 1984. "Thermodynamic Properties of Aqueous Sodium Chloride Solutions," *J. Phys. Chem. Ref. Data*. V. 13, no. 1, pp.1-102.
- Scotter, D.R., 1974. "Salt and Water Movement in Relatively Dry Soil," *Aust. J. Soil Res.*, v. 12, pp. 27-35.
- Scotter, D.R., and P.A.C. Raats, 1970. "Movement of Salt and Water Near Crystalline Salt in Relatively Dry Soil," *Soil Science*, v. 109, no. 3, pp.170-178.
- van Genuchten, M.T., 1980. "A closed form equation for predicting the hydraulic conductivity of unsaturated soils," *Soil Sci. Soc. Am. J.*, v. 44, pp. 892-898.
- Washburn, E.W. (Ed.). *Numerical Data, Physics, Chemistry and Technology: First Electronic Edition*.
- Weisbrod, N., R. Nativ, E.M. Adar, and D. Ronen, 2000. "Salt Accumulation and Flushing in Unsaturated Fractures in an Arid Environment," *Groundwater*, v. 38, no. 3, pp. 452-461.

Chapter 4 - Darcy's Law for Flow of Variable Strength Salt Solutions in Variably Saturated Porous Media.

Erick R. Burns¹, Maria I. Dragila², Ronald B. Guenther³, John S. Selker¹, and Noam Weisbrod⁴

1: Department of Bioengineering; Oregon State University; Corvallis, OR

2: Department of Crop and Soil Science; Oregon State University; Corvallis, OR

3: Department of Mathematics; Oregon State University, Corvallis, OR

4: Department of Environmental Hydrology and Microbiology; Institute for Water Sciences and Technologies; Blaustein Institutes for Desert Research; Ben-Gurion University of the Negev, Beer-Sheva, Israel

Submitted to:

Not yet decided.

Status: In Preparation

Abstract

The necessary correction to Darcy's Law for non-negligible ionic strength salt solutions is derived for variably saturated porous media. An example is worked for sodium chloride (NaCl) and the results are compared to the data of Scotter (1974). The results show good agreement with the data, though there appear to be some systematic discrepancies between the data and the predicted results. These discrepancies may be the result of ionic interaction of the salt with the loamy sand used, and/or the effect of hysteresis in the water content-pressure relationship.

Introduction

It is important to understand the behavior of flow of saline fluids in non-isothermal, unsaturated porous media. Understanding the effects of salt in such systems is required in soil science (e.g., arid soils (Weisbrod et al., 2000)), in the design of hazardous waste storage (e.g., the Hanford site), and in drying science (e.g., manufacturing and processing of materials). The addition of salt to water is known to depress the overlying water vapor content (c.f., Edlefsen and Anderson, 1943), and to increase the surface tension (c.f., Belton, 1935), density, and volume of the liquid phase (c.f., Heyrovská, 1996). These fundamental changes to the physics of the fluid result in changes in how the fluid flows through porous media. For the first time, a first principles derivation of the above effects is accomplished in Burns et al. (2004) for non-dilute strength salt solutions. In order to utilize the new theory for flow problems in porous media, it may be necessary to account for the effects of non-dilute strength salts on Darcy's Law; and in order to examine the effect of salt, a general method of correction of Darcy's Law needs to be developed.

In the following, the appropriate corrections to Darcy's Law for saline fluids are derived. The corrections for both hydraulic conductivity and hydraulic diffusivity are derived from basic thermodynamic principles. Following the derivation, an example

computation is performed using the excellent dataset provided by Scotter (1974). The resulting thermodynamic corrections are shown to perform well, and probable reasons for discrepancy between theory and data are discussed. Utilizing the results of this paper, researchers may now include the salt effects for comparison with the dilute approximation (i.e., zero salt).

Derivation of Corrections to Darcy's Law

Salinity Correction to Hydraulic Conductivity

Suppose that Darcy's Law may be written:

$$(1) \quad \bar{q}^L = \phi^L \bar{v}^L = -K^L \nabla P^L = -\frac{k^L}{\mu^L} \nabla P^L$$

where the variables are all defined in the "Notation" section. k is a function of the porous media and the volumetric liquid content only. It is implicitly a function of salt concentration, only in that the specific volume of the liquid is altered by addition of salt. The viscosity μ^L is a sub-pore scale property, dependent upon solute concentration. In equation (1) the gravitational term has been assumed to be negligible, though this is unnecessary for determination of the correction to the hydraulic conductivity. Notice that the pressure is the liquid pressure which may also be a function of variables other than the water content (e.g., salt concentration).

In order to compute the appropriate corrections, it is necessary to assume functional relationships between water content and pressure, and also between water content and unsaturated hydraulic conductivity. For the following derivation, the functional forms provided by Brooks and Corey (1964) are particularly useful. With minor manipulation, the Brooks and Corey relationships (Eqs. 2 and 3) may be written:

$$(2) \quad S^L = \left(\frac{P_{cr}^L}{P^L} \right)^\lambda$$

$$(3) \quad K^L = K_s^L \cdot (S^L)^\eta$$

where P_{cr}^L and λ are fitting parameters, and where μ^L is implicitly fixed at the pure water value and $\eta = \frac{2}{\lambda} + 3$. The viscosity condition is relaxed in the derivation below, by recognizing that:

$$(4) \quad k^L = k_s^L (S^L)^\eta \quad \text{for any viscosity.}$$

Using the above, it is easily shown that the corrected hydraulic conductivity is:

$$(5) \quad K^L = K_0^L \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{S^L}{S_0^L} \right)^\eta$$

Salinity Correction to Hydraulic Diffusivity

Scotter (1974) performed a series of laboratory experiments investigating unsaturated flow and transport of water and salt in a variety of soils at a constant 25° C.

Supplemental experiments were run for a loamy-sand, allowing the following analysis. Hydraulic diffusivity experiments were performed for three different initial pure water contents and one initial NaCl saturated solution content. A soil moisture characteristic curve was generated (water-content versus pressure). The results of these experiments are reproduced in Figures 1 and 2, where the data have been converted to volumetric water contents instead of the gravimetric water contents reported by Scotter. Since Scotter was only concerned with measuring water diffusivity, Figure 2 represents both vapor and liquid water flow (i.e., a total water diffusivity). It is assumed that vapor

flow dominates below ~8% volumetric content, and above this, liquid flow dominates (Scotter, 1974).

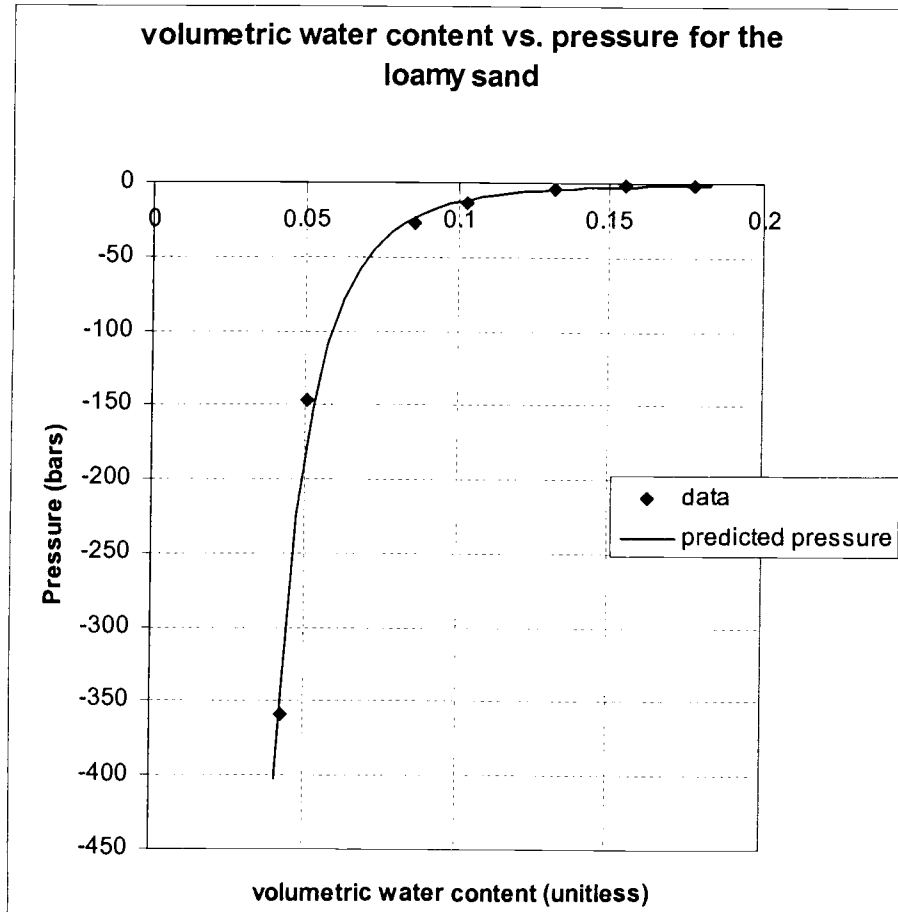


Figure 1: Data from Scotter (1974) converted from gravimetric water content to volumetric water content. The predicted pressure is computed using the Brooks and Corey model (equation 2) with $P_{cr}^L = 0.90684$ and $\lambda = 0.26$.

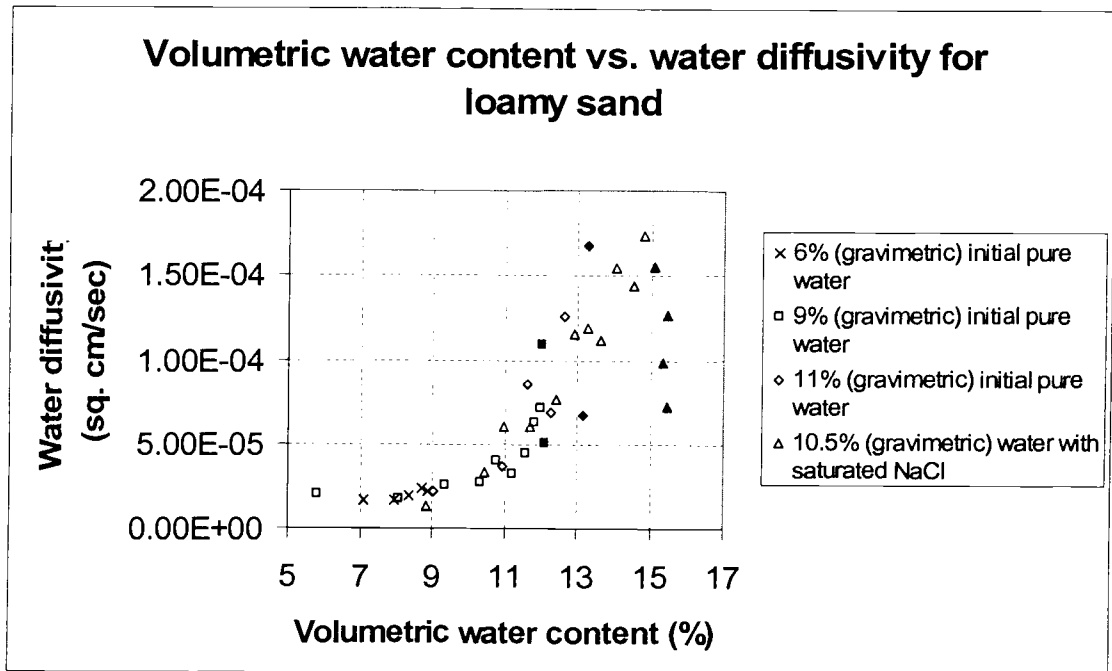


Figure 2: Scotter's raw data converted to volumetric water content. The gravimetric labels have been retained to facilitate comparison of the results with Scotter's work. The solid symbols are the data points collected near the start of the experiment (i.e., near the initial water contents), and these points are emphasized here to show that anomalous behavior occurs at these times.

In Figure 3, the axes have been changed to liquid content and liquid diffusivity. The changes only affect the saturated salt solution dataset. This is because the volume occupied by a saturated salt solution is not the same as the volume occupied by the water in the salt solution. Correction of the data is accomplished by multiplying both the x and the y coordinate by a volume correction factor (described below). Also in Figure 3, the pure water diffusivity data are fit by a curve of the form:

$$(6) \quad D_0^L = a \cdot (\phi_0^L - \phi_{\min}^L)^b$$

where a and b are fitting parameters.

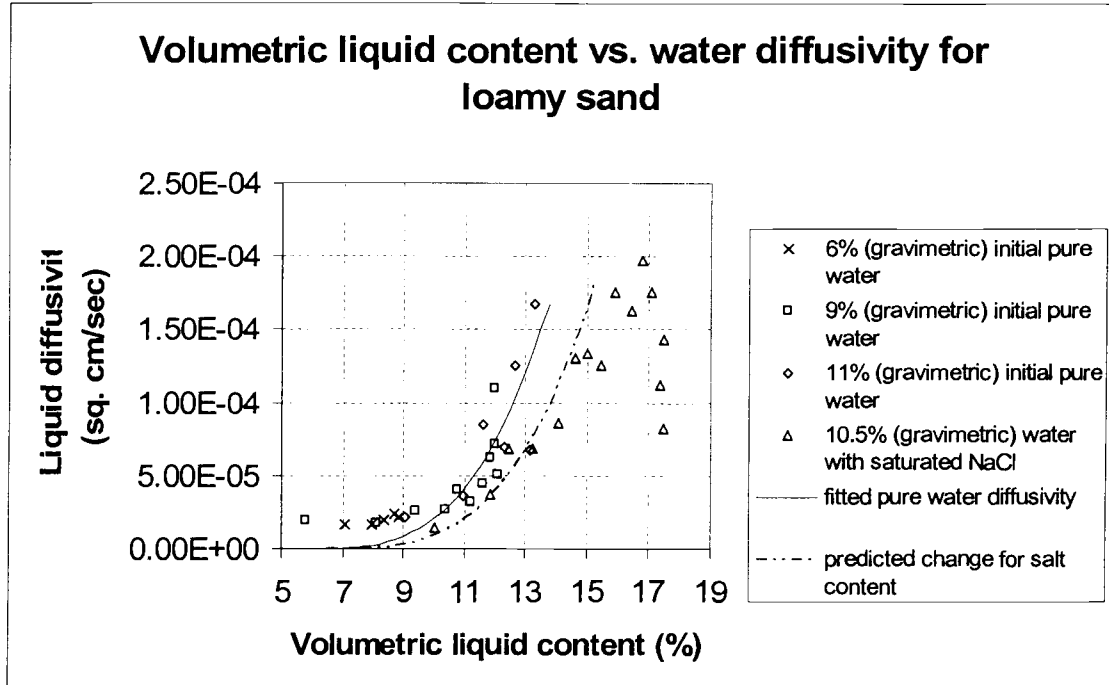


Figure 3: The observed shift when plotting the volumetric liquid content vs. the liquid diffusivity. Also, the original water diffusivity curve and the computed shift of this curve (Equation (14)) are shown.

For Scotter's data, the following holds:

$$(7) \quad \rho^L \phi^L \bar{v}^L = -D^L \nabla (\rho^L \phi^L)$$

The left-hand side of (7) is merely the Darcy flux, and the right-hand side is the diffusion law that Scotter is using to estimate the diffusivity. Since, for each of the experiments, the salt concentration was constant, which implies the density is also constant. Therefore, Equation (7) reduces to:

$$(8) \quad \phi^L \bar{v}^L = -D^L \nabla \phi^L = -K^L \nabla P^L$$

which implies

$$(9) \quad D^L = K^L \frac{\partial P^L}{\partial \phi^L}$$

So, to compare the theory above with Scotter's data, and in general, to be able to provide the proper thermodynamic correction of salt to the liquid diffusion coefficient (as defined here), it remains to evaluate the differential term in (9). Assuming that porosity is constant, and recognizing that a constant density implies a constant saturation ratio (S^L / S_0^L), it is true that:

$$(10) \quad \frac{\partial P^L}{\partial \phi^L} = \frac{S_0^L}{n S^L} \frac{\partial P^L}{\partial S_0^L}$$

But, in Burns et al. (2004), it is shown that:

$$(11) \quad \frac{\partial P^L}{\partial S_0^L} = \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S_0^L}$$

where $\tilde{P}^L = P^L(S^L)$. The functional form of \tilde{P}^L depends only on geometric constraints (Burns et al., 2004), and S^L is an implicit function of both water and salt contents. Notice that \tilde{P}^L is not a true pressure, but rather, it represents the pressure corresponding to an equivalent saturation of fresh water, and it is in fact given by the functional relationship of equation (2). So, equation (10) may be rewritten:

$$(12) \quad \frac{\partial P^L}{\partial \phi^L} = \frac{1}{n} \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S^L}$$

And the above may be used to write:

$$(13) \quad D = D_0 \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \right) \left(\frac{S^L}{S_0^L} \right)^\eta \left(\frac{\left(\frac{\partial \tilde{P}^L}{\partial S^L} \right)}{\left(\frac{\partial \tilde{P}_0^L}{\partial S_0^L} \right)} \right)$$

Where the terms on the right hand side are the pure water diffusivity, a viscosity correction, a surface tension correction, and the last two terms are volume corrections. Using equation (2) to evaluate the derivative, many terms cancel in the ratio, leaving:

$$(14) \quad D = D_0 \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \right) \left(\frac{S^L}{S_0^L} \right)^\eta \left(\frac{S^L}{S_0^L} \right)^{-\frac{1}{\lambda}-1} = D_0 \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \right) \left(\frac{S^L}{S_0^L} \right)^{\frac{1}{\lambda}+2}$$

Equation (14) is the general correction to the diffusivity for saline fluids moving through variably saturated porous media assuming the soil is described well by Equations (2) and (3). The above method of estimation may be accomplished for any functional relationships for hydraulic conductivity and pressure. The Brooks and Corey relationships were selected only for convenience and to allow a comparison with real data.

Comparison with the experimental data of Scotter

In a series of papers by Scotter and Raats (1970), Parlange (1973), and Scotter (1974), the phenomenon of water condensation near salt (NaCl) crystals in a relatively dry porous media is experimentally and mathematically analyzed. All of Scotter's experiments published in 1974, were conducted at 25 C. Among these experiments, were the experiments summarized in Figure 2. Most of these experiments were conducted using dilute salt-strength water, but one experiment was performed using a saturated salt solution. A diffusivity curve may be fit to the dilute experiments (see Figure 3), and using the above relations, the predicted shift (resulting from salt effects)

of the “pure” water curve to the saturated curve may be computed and compared to the high salt-strength data. In order to compute the effects of salt on Scotter’s diffusion coefficient data (Figure 2), Equation (14) may be used. In order to use equation (14) it is necessary to estimate each of three ratios and the exponent of the volumetric term. Estimated values for λ are obtained by fitting Equation (2) to only the pure water data of Scotter (Figure 1). The volumetric correction can be estimated using the definition of saturation to obtain:

$$(15) \quad \frac{S^L}{S_0^L} = \frac{V^L}{V_0^L}$$

The method of Heyrovska (1996) provides functional forms for computation of the non-idealities associated with density, volume, and activity for non-dilute strength NaCl solutions; and therefore may be used to compute the volumetric term for any salt concentration. Diffusion data compiled by Scotter is only for pure water and a saturated salt solution. For this reason, it is only necessary to estimate the terms in Equation (14) for saturated salt conditions. Here a volume correction term of 1.131 is used (Heyrovska, 1996). The experimental surface tension data of Belton (1935) may be used to estimate the surface tension correction term as 1.15. Kestin et al. (1981) provides a table of tabulated viscosities using correlations established from experimental data. Kestin et al. estimate an overall accuracy of within 0.5%. Using the tabulated values, the viscosity ratio is estimated as 0.5123.

Using these parameters, and a density correction of 1.201 (Heyrovska, 1996) for the saturated salt solution, it is possible to compute the correction to the pure water curve shown in Figure 3. The results are shown as the “predicted change” curve, also in Figure 3. This new curve is computed using Equation (14).

Discussion

Figure 3 shows the computed diffusivity coefficient curve for saturated salt concentration. This computed “shift” of the curve is in the correct direction and is close to the correct magnitude as indicated by close correlation of the curve with the data, though the data is noisy, especially at higher water contents. Several factors may affect the data, and therefore the correlation between the data and the curve. These include hysteresis, chemical interaction of soil with the salt, the variability of the samples, and use of equation (3) with no validation.

Since Scotter conducted all experiments from a specific initial water content (i.e., a soil prepared at some uniform water content), it was necessary that as the soil drained, the soil moisture must move first from the initial state to the state described by the primary drainage curve. It is observed that consistently, the estimated soil water diffusivity for water contents very close to the initial water content shows anomalous behavior (see the solid data points in Figure 2), and further, that it consistently gives lower values of diffusivity than would be expected by projecting the drainage data back to higher water contents. For the one saturated salt experiment, there are approximately three data points that behave most strongly anomalously, but they are all very close to the initial water content.

The reason for the anomalous behavior near the start of the experiments may be explained by examining the experimental setup. Scotter likely prepared a well mixed soil at a known homogeneous water content, then subsequently filled the sample chamber with this mixture. Initially, the water is suspended in the porous media in a random fashion. The diffusivity determination would be performed by imposing a gradient on the sample chamber, then measuring the resulting water flux. But, in order for the water to move through the porous media, it is first necessary to establish connections between the isolated and disordered suspended water. Once the water is connected, hydraulic conductivity will be higher, even though the total water content

in the media is lower. This is the pattern seen for high water contents, and for this reason, it is postulated that the hysteretic component only affects diffusivity values at high water content (i.e., it only has effect until the system water moves into the drainage configuration).

It is also noted that Scotter used a loamy sand for his experiments. It is likely that there is an appreciable fine fraction of in this soil. This fine fraction, having higher surface areas with surface charges, may affect the flow of the liquid due to electrostatic interactions with the dissociated (or partially dissociated) salts. It is unclear from the theory developed here how significant an effect this may be, but it may be one reason for the larger scatter of the data for the high salt strength experiment.

Scotter's experiments are all performed on different preparations of the same soil. For this reason, dry bulk densities range from 1.24 to 1.48 g/cm³, with no reported value for the soil sample used to generate the water release curve (Figure 1). Unfortunately, the high density soils are the 6% and the saturated salt solution experiments. Since the 6% experiment had no appreciable liquid water diffusion, it is impossible to see if the shift is more consistent based on bulk density.

If water release curves are plotted for "typical" loam or sand (not shown), as described by coefficients given by Carsel and Parish (1988), then it is discovered that the curvature of the data in Figure 1 is more extreme than would be expected. If it is assumed that the soil used for Figure 1 has a stronger curvature compared to the norm for this loamy sand, then the value of λ for most of the experiments should be a bit higher. Figures 4 and 5 show the results of allowing λ to be slightly higher. As evidenced by Figure 4, a larger λ does shift the curve more towards the bulk of the data. Notice that equation (3) was used with no experimental validation. Since λ is used in a functional form, this may also be a source of discrepancy between theory and the data.

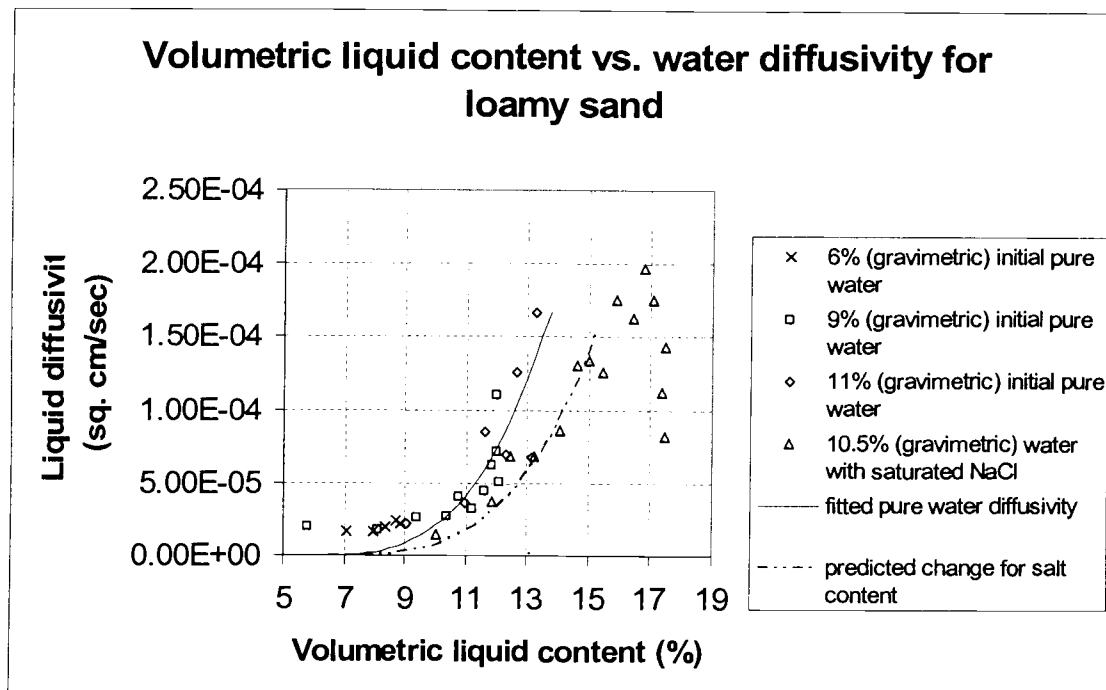


Figure 4: This figure is identical to figure 3 except $\lambda=0.4$.

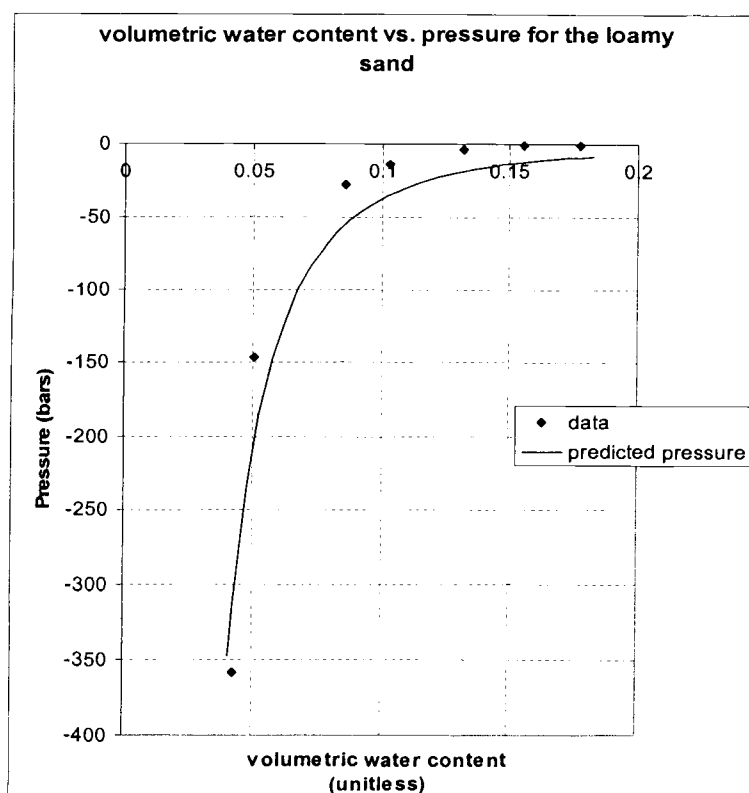


Figure 5: Best fit to Scotter's data using the Brooks and Corey model with $\lambda=0.4$.

As a result of the above observations, it is recommended that future experiments be conducted with a porous media that is not likely to interact with the salt being studied. Multiple experiments performed on the same soil samples over a range of salt concentrations would permit further analysis of the theoretical results. Experimental validation of equation (3) is also important.

Examination of Figure 2 shows that a volumetric water content to water diffusivity curve might be generated to describe both the dilute and saturated salt solutions for this soil. It is unclear whether or not this is just fortuitous for this particular soil. Figure 3 shows that liquid flow properties may be non-negligibly affected by the addition of a solute. Since a first-principles derivation of a flow model for a saline solution would arise naturally by conserving momentum of the center of mass of a unit of liquid, it is necessary to formulate the problem in terms of liquid movement, and not movement of water in the liquid. For this reason, it is desirable that experimental parameters that are measured for pure water may be extended to the case where the water is not pure. This results in savings of time and effort that would otherwise be spent characterizing a particular porous media for the appropriate flow properties. The approach described above provides this method of correction, where the viscosity, surface tension, and saturation (volumetric) ratios are all functions of only the effect of the solute on the solution; and λ depends only on the soil texture.

Conclusion

A correction of hydraulic conductivity and hydraulic diffusivity coefficients for high salt concentrations in variably saturated porous media is derived. The resulting relations are given in equations (5) and (14). Comparison of the predicted results to the data of Scotter (1974) shows that the computed corrections substantially predict the effect of salt on the diffusion coefficient, permitting a correction to Darcy's Law. However, there appear to be some systematic discrepancies that may be explained by considering a few additional factors. These factors may include hysteretic behavior of

the porous media, possible complications in flow due to ionic interaction of the salt with fine sediments carrying substantial surface charges, a lack of sufficient experiments to show that the discrepancies between predicted and observed behavior are not the result of data scatter (especially for the single experiment for elevated salt concentration), and use of the relation in equation (3) with no experimental validation for the soil being tested. Future experiments should be performed to address these issues, and if the model performs well in porous media with low electrostatic forces, then it may be assumed that equations (5) and (14) are accurate. If (5) and (14) are shown to be accurate, investigations should be performed to evaluate the need to formulate corrections for natural porous media with appreciable silt and clay content.

Acknowledgements

This work was funded under a U.S. EPA STAR (Science to Achieve Results) Fellowship.

Notation

Variables

\vec{v} = phase velocity

\vec{q} = Darcy (volumetric) flux

K = hydraulic conductivity

k = intrinsic permeability

D = hydraulic diffusivity

P = pressure

V = volume

μ = viscosity

S = saturation (volume of liquid divided by pore volume)

n = porosity (pore volume divided by total volume)

ϕ = volumetric liquid content (volume of liquid divided by total volume of soil, liquid, and gas in porous media).

σ^{LG} = surface tension at the gas-liquid interface

$\tilde{P}^L \equiv P^L(S^L)$ = equivalent liquid pressure neglecting changes in surface tension (see discussion in Burns et al. (2004)).

ϕ_{nan}^L , a , b , λ , P_{cr}^L = fitting parameters

Superscripts and Subscripts (Note: The superscript may seem unnecessary for this derivation, but the eventual use of this work is for multi-phase flow processes.)

L = liquid phase

0 = reference condition corresponding to zero salt content

s = saturated condition

References

- Belton, J.W., 1935. "The Surface Tensions of Ternary Solutions. Part I. The Surface Tensions of Aqueous Solutions of (a) Sodium and Potassium Chlorides, (b) Sodium chloride and Hydrochloric Acid." Transactions of the Faraday Society, no. 174, pp. 1413-1419.
- Brooks, R.H. and A.T. Corey, 1964. "Hydraulic Properties of Porous Media." Hydrology Papers, Colorado State University, Ft. Collins.
- Burns, E.R., J.-Y. Parlange, J.S. Selker, and R.B. Guenther, 2004. "Thermodynamic Correction for Salts in Variably Saturated Porous Media." Submitted to Transport in Porous Media.
- Carsel, R.F., and R.S. Parrish, 1988. "Developing Joint Probability Distributions of Soil Water Retention Characteristics," Water Resources Research, V. 24, No. 5, pp. 755-769.
- Edlefsen, N.E., and A.B.C. Anderson: 1943, Thermodynamics of Soil Moisture, *Hilgardia*, **15-2**, 31-298.
- Heyrovska, R., 1996. "Physical Electrochemistry of Strong Electrolytes Based on Partial Dissociation and Hydration: Quantitative Interpretation of the Thermodynamic Properties of NaCl(aq) from "Zero to Saturation"," J. Electrochem. Soc., v. 143, no. 6, pp. 1789-1793.
- Kestin, J., H.E. Khalifa, and R.J. Correia, 1981. "Tables of the Dynamic and Kinematic Viscosity of Aqueous NaCl Solutions in the Temperature Range 20-150° C and the Pressure Range 0.1-35 MPa," J. Phys. Chem. Ref. Data, v. 10, no. 1, pp. 71-87.
- Parlange, J.Y., 1973. "Movement of Salt and Water in Relatively Dry Soils," Soil Science, v. 116, no. 4, pp. 249-255.

- Scotter, D.R., 1974. "Salt and Water Movement in Relatively Dry Soil," *Aust. J. Soil Res.*, v. 12, pp. 27-35.
- Scotter, D.R., and P.A.C. Raats, 1970. "Movement of Salt and Water Near Crystalline Salt in Relatively Dry Soil," *Soil Science*, v. 109, no. 3, pp.170-178.
- Weisbrod, N., R. Nativ, E.M. Adar, and D. Ronen, 2000. "Salt Accumulation and Flushing in Unsaturated Fractures in an Arid Environment," *Groundwater*, v. 38, no. 3, pp. 452-461.

Chapter 5 - Developing an Axiomatic Method for Derivation of the Thermodynamic Relations of Irreversible Processes: Assumptions Reexamined

Erick R. Burns¹, Maria I. Dragila², Ronald B. Guenther³, John S. Selker¹, and Jean-Yves Parlange⁴

1: Department of Bioengineering; Oregon State University; Corvallis, OR

2: Department of Crop and Soil Science; Oregon State University; Corvallis, OR

3: Department of Mathematics; Oregon State University, Corvallis, OR

4: Department of Biological and Environmental Engineering; Cornell University;
Ithaca, NY

Submitted to:

Not yet decided.

Status: In Preparation

Abstract

Utilizing the assumptions of mixture theory and continuum mechanics, a thermodynamic description of irreversible equilibrium continuous processes are derived. Classic assumptions are re-examined, and two new ideas are introduced. The first idea is that temperature is not the generalized intensive variable associated with entropy. The second idea is a generalized notion of how to select extensive variables for a given system. It is possible that in general, these notions may be used to define a sufficient number of dissipation variables so that the entropy term may be considered negligible. Examples comparing the “usual” and new theories are accomplished for ideal gases and for isotropic Newtonian liquids. The results of the new theory are consistent with the physics of the problems, while a contradiction is found in the Gibbs-Duhem Relation of the isotropic Newtonian liquid for the “usual” theory. The new theory is general enough to be used in all instances, and the “usual” theory is still sufficient for use under some conditions. It is necessary to use the new theory when existing theory is insufficient to describe conditions without encountering a contradiction.

Introduction

The use of irreversible, or process, thermodynamics to describe continuous media is widespread through the literature of a variety of disciplines. The application of these principles to energy and fluid flows is prevalent in the heat and mass transfer literature, and to a lesser extent, in the hydrology literature. Commonly, in both of these fields, the development of many ideas may be traced back to the theory as recorded by deGroot and Mazur in their classic 1962 text. Certainly the excellent the collective works of deGroot, Mazur, and their colleagues (e.g., Prigogine, 1967) are cited and relied upon by many of the most eminent names in the field of drying theory (c.f. Whitaker, 1999, and Luikov, 1966), where it is necessary to account for mass and energy fluxes of multiple phases.

During attempts to derive the governing equations for the transport of variable strength (non-dilute) salt solutions in variably saturated porous media under non-isothermal conditions, it was discovered that various overly-restrictive assumptions were made in the theory of deGroot and Mazur. When the assumptions are relaxed to include more general cases, it is discovered that a-priori assumptions of functional forms were used to facilitate formulation of various problems. While these assumptions do not affect the resulting equations for many important examples, it became of interest to examine the ramifications of taking a slightly more general approach to equation development. In this paper, the notions that temperature is the general intensive variable associated with entropy and the a-priori assumption of a particular form of the specific energy (see equation (33b)) are examined.

First, basic conservation laws for mass, momentum, and kinetic energy for a mixture are developed. Next, the usual notions of internal and total system energy are developed, and the standard assumptions are introduced. The standard assumptions are analyzed, and a more “naïve,” axiomatic approach to equation development is then proposed and implemented. The “usual” equations are then compared to the new equations both in an abstract form and by application of the theories to simple examples of single phase fluids described by the ideal gas law and by the Navier-Stokes stress tensor. Finally, a discussion of the results is completed, conclusions are drawn, and suggestions for use of the new theory are proposed.

Basic Conservation Laws

Preliminary Notions

The proper use of thermodynamics requires that the practitioner have a good understanding of the time-scales of interest (Woods, 1975). The timescale of the process controls what physics needs to be incorporated into a problem in order to properly model the system of interest. For timescales and processes of interest to

engineers and physical scientists studying fluid flows, it is often necessary to model the processes as spatially continuous processes using the theories of continuum mechanics and process (or irreversible) thermodynamics (Woods, 1975; and DeGroot and Mazur, 1962). An irreversible thermodynamic process may occur as an equilibrium or non-equilibrium process (Woods, 1975). The derivations in most books or papers are completed for equilibrium irreversible processes. This is true also for all derivations accomplished here.

The concept of entropy is central to the use of process thermodynamics. For all natural processes entropy either remains constant or increases unless entropy is transferred across a system boundary (via the transfer of heat, work, chemical diffusions, etc.). Here, use of the term, system, is quite cavalier, though it will be made precise in the following derivations. Processes are considered irreversible if there is a net entropy increase other than entropy that is conservatively transferred across system boundaries. A useful concept of entropy is that it is a “coordinate” that tracks dissipation in a system. It describes the dissipative losses to variables that are otherwise unaccounted for in the equations, and therefore, entropy as a function of one set of variables is not necessarily equal to entropy when defined by a second set of variables. See Woods (1975) for a more complete development of this idea.

The continuum approach and mixture theory are used to derive a set of equations that describe multi-phase flow in porous media. The continuum approach assumes that super-REV (i.e., at a scale larger than the REV, or “representative elementary volume,” Bear, 1972) parameters such as mass density (ρ^α) and volume fraction (ϕ^α) are well-defined mathematically. Mixture theory assumes that each component of a mixture is well-defined in terms of the above parameters, and that the sum of all of the components represents the total material in an arbitrary volume (V). Mixture theory assumes that the phases and constituents co-exist at all points in space. This assumption of co-existence allows the definition of a density in the mathematical

sense, which in turn allows the use of differential and integral calculus in problem solving. However, by “smearing” the properties into well-defined densities (e.g., mass density, energy density, etc.), knowledge of microscopic (sub-REV) interactions is lost. Therefore, it is necessary to develop meso-scale (super-REV, but smaller than the process to be modeled) constitutive relations that operate on the time-scale of concern. One approach to this is through the use of the Onsager Relations (1931¹, 1931²).

A *component* is a general term defined in this document as any sub-part of a mixture for which the previous notions holds. *Constituents* are defined as the simplest components that it is necessary to divide a mixture into (e.g., H₂O and a homogeneous mixture of dry air might be a typical choice of constituents used to describe moist air for a given problem). *Phases* are defined as components of the mixture that may be delineated from other phases by a distinct (i.e., sudden) change in one or more of the densities (e.g., liquid water containing dissolved air and moist gaseous air, or oil and water). Each phase is made up of one or more constituents. Normally, different phases have different equations of motion and/or energy, though sometimes, energy equations for the entire mixture of phases may be written to simplify the mathematics of the system. An example of the latter case is when heat conduction is the dominant form of energy transfer.

Derivation of Equations

Using the previous ideas, flow in a porous media may easily be divided into immiscible flows (describing the relation between the phases) and miscible flow (describing flow within a phase). Variables and other notation used for the following derivations are defined in the “Notation” section.

When considering the volume fractions of the phases and the mass fractions of the constituents in each phase, by definition,

$$(1a) \quad \sum_{\alpha} \phi^{\alpha} = 1 \quad \text{for } \alpha = 1, \dots, N$$

$$(1b) \quad \sum_{\beta} X^{\beta\alpha} = 1 \quad \text{for } \beta = 1, \dots, \tilde{N} \text{ and } \alpha = 1, \dots, N$$

where N is the total number of consistent phases into which a substance may be divided, and \tilde{N} is the total number of consistent constituents in an arbitrary phase α . Consistency of the components means that no component is a sub-component of another component. This ensures that there is no double-counting any components.

In order to provide clarity to the derivation and to allow the reader to use their intuition, it may be assumed that $\alpha = S, L, G$ (i.e., solid, liquid, and gas phases) and $\beta = ss, h, w, a$ (i.e., non-reactive solid, salt, pure water, and dry air constituents) are consistent sets of components for the same system. Notice that the number of components in each set does not need to be equal between the sets. The choice of these indices is explained in the “Notation” section, and they are representative of a large class of flow problems (subject to re-definition of the component designators). Implicitly, it is assumed that for the set $\beta = ss, h, w, a$ each constituent is chemically pure (i.e., they respond as if they are homogeneous) but that they may mix in the phases. It will become evident that an arbitrary number of phases and constituents may be considered, while the aforementioned assumption of discrete well-defined sets is employed to assist the reader’s intuition.

Define the bulk density of α -phase as $\rho^{\alpha B} = \phi^{\alpha} \rho^{\alpha}$, and the bulk density of the β -constituent in the α -phase as $\rho^{\beta\alpha B} = \phi^{\alpha} \rho^{\beta\alpha} = \phi^{\alpha} X^{\beta\alpha} \rho^{\alpha}$. Clearly, the bulk density is the density of the component in the entire mixture of all the phases. This results in the usual notion of bulk density for the mixture:

$$(2) \quad \rho^B = \sum_{\alpha} \rho^{\alpha B} = \sum_{\alpha} \phi^{\alpha} \rho^{\alpha} = \sum_{\alpha} \sum_{\beta} \phi^{\alpha} X^{\beta \alpha} \rho^{\alpha}$$

The Gauss Divergence Theorem (Equation 3) and the Reynolds Transport Theorem (Equation 4) are used during the following derivation, so they are stated here for completeness. The Gauss Divergence Theorem allows conversion of surface integrals to volume integrals. When taking the time derivative of an integral, the Reynolds Transport Theorem allows for the fact that the volume of integration may be a function of time. Let f be an arbitrary function, and let \vec{z} be an arbitrary vector of sufficient smoothness (different sufficient conditions are given by Kellogg (1929), but most commonly, the condition of continuous differentiability is used).

$$(3) \quad \int_V (\nabla \cdot \vec{z}) dV = \oint_B (\vec{z} \cdot \vec{n}) dB$$

$$(4) \quad \frac{d}{dt} \int_{V(t)} f(\vec{x}, t) dV = \int_{V(t)} f_t(\vec{x}, t) dV + \oint_{B(t)} f(\vec{x}, t) \vec{w} \cdot \vec{n} dB = \int_{V(t)} [f_t(\vec{x}, t) + \nabla \cdot (f(\vec{x}, t) \vec{w})] dV$$

The vector \vec{w} arises naturally as the velocity of the boundary during the derivation of (4), but use of the Gauss Divergence Theorem converts this velocity to the localized velocity at each point. Note that both theorems also apply to higher order tensors, but that some adjustments in notation become necessary (e.g., the cross product between a vector and a second order tensor must be specially defined). Also, the so-called material derivative or substantial derivative of an arbitrary function f is given by:

$$(5) \quad \frac{Df}{Dt} \equiv f_t + \vec{w}^{\alpha} \cdot \nabla f$$

The notation $f_t \equiv \frac{\partial f}{\partial t}$ will be used interchangeably in the following in whichever form seems clearer at the time.

Conservation of Mass

In words, mass conservation states that the rate of change of mass in a volume is equal to the net rate at which mass is added or taken away from the volume. It is possible to conduct a mass balance on the mixture, the phase, the constituent in a phase, or any combination of identifiable quantities. Define the mass of constituent β in phase α as:

$$(6) \quad [\text{mass of constituent } \beta \text{ in phase } \alpha] = \int_V \rho^{\beta\alpha} dV = \int_V \phi^\alpha \rho^{\beta\alpha} dV = \int_V \phi^\alpha X^{\beta\alpha} \rho^\alpha dV$$

Before the time-dependent mass conservation equation can be derived, it is advantageous to choose a volume, $V(t)$, such that the results of our derivation results in a convenient form. Denote $V(t=0) = V_0$, an arbitrary initial volume. Using the methods of continuum mechanics, it is postulated that every particle of constituent β is well-defined by an initial location \bar{x}_0 , and that at some later time, the location of this particle is described by a variable \bar{x} , where $\bar{x} = \chi(\bar{x}_0, t)$. χ is a well-defined function describing the path of motion, for which an inverse function exists. It is also assumed that at some arbitrarily small time after $t=0$, all particles initially inside V_0 will be arbitrarily close to their initial positions. This means that it is possible to define a new volume, $V(t)$, such that only particles of β initially inside V_0 are still in $V(t)$ (minus any particles lost to sources or sinks). At the molecular level, certainly this is false, but since only the macroscopic level is considered, this is unimportant as long as the same net amount of mass of β remains inside the volume (minus

sources/sinks) and that the deformation of the volume corresponds to the effective motion of β .

As a result of the above choice of volumes, it is clear that there is no movement of constituent β (in phase α) across the surface $B(t)$ of $V(t)$. Movement of constituent β between phases looks like a source/sink term because all phases coexist by the mixture theory assumptions. The resulting mathematical description of the mass conservation law is:

$$(7) \quad \frac{d}{dt} \int_{V(t)} \rho^{\beta\alpha B} dV = \int_{V(t)} \hat{M}^{\beta\alpha} dV$$

Since the volume possibly encompasses other phases of the mixture, sources/sinks include exchange between the phases as well as any other possible sources. Possible internal (to the phase) sources/sinks are exchanges between the constituents in a phase (e.g., chemical uptake by organic colloids suspended in the liquid phase). Application of the Reynolds Transport Theorem to equation (7), and subsequent rearranging yields:

$$(8) \quad \int_{V(t)} [\rho_t^{\beta\alpha B} + \nabla \cdot (\rho^{\beta\alpha B} \vec{w}^{\beta\alpha}) - \hat{M}^{\beta\alpha}] dV = 0$$

Since $V(t)$ is arbitrary in size and location, the integrand must be identically zero, giving us the local form of the conservation of mass equation.

$$(9) \quad \rho_t^{\beta\alpha B} + \nabla \cdot (\rho^{\beta\alpha B} \vec{w}^{\beta\alpha}) - \hat{M}^{\beta\alpha} = 0$$

Summing equation (9) over the constituents yields:

$$(10) \quad \rho_i^{\alpha B} + \nabla \cdot \left(\sum_{\beta} \rho^{\beta \alpha B} \vec{w}^{\beta \alpha} \right) - \hat{M}^{\alpha} = 0$$

where the term \hat{M}^{α} is the source/sink term that describes exchange between the phases (i.e., all intra-phase exchanges must sum to zero by mass conservation principles). Defining the term in the parentheses as $\rho^{\alpha B} \vec{w}^{\alpha}$ implies that

$$(11) \quad \vec{w}^{\alpha} = \frac{\sum_{\beta} \rho^{\beta \alpha B} \vec{w}^{\beta \alpha}}{\sum_{\beta} \rho^{\beta \alpha B}}$$

Noticing that

$$(12) \quad \sum_{\beta} \rho^{\beta \alpha B} \vec{w}^{\beta \alpha D} \equiv \sum_{\beta} \rho^{\beta \alpha B} (\vec{w}^{\beta \alpha} - \vec{w}^{\alpha}) = 0$$

From (12), it is clear that \vec{v}^{α} is the barycentric (center of mass) velocity of the phase, and $\vec{v}^{\beta \alpha D}$ is the diffusion/dispersion velocity (i.e., the velocity relative to the phase velocity). This barycentric velocity is particularly useful because the proper formulation of the momentum equation is concerned with the velocity of the center of mass. As a result of the above, the mass conservation equation for the phase is

$$(13) \quad \rho_i^{\alpha B} + \nabla \cdot (\rho^{\alpha B} \vec{w}^{\alpha}) - \hat{M}^{\alpha} = 0$$

and the mass conservation for the constituent is

$$(14) \quad \rho_i^{\alpha\beta} + \nabla \cdot (\rho^{\beta\alpha\beta} \vec{w}^\alpha) + \nabla \cdot (\rho^{\beta\alpha\beta} \vec{w}^{\beta\alpha D}) - \hat{M}^{\beta\alpha} = 0$$

where the second term represents advection of the constituent along with the phase, and the third term represents diffusion/dispersion of the constituent within the phase. Notice that $\rho^{\beta\alpha\beta}$ is the volumetric concentration of β in phase α , so (14) is the transport equation associated with the flow equation (13).

Conservation of Linear Momentum

The conservation of momentum equations are often called the equations of motion. They are based on Newton's Second Law that states that the rate of change of momentum of a body (or more precisely, its center of mass) is equal to the net force acting on the body. The continuum mechanics formulation of this law considers a body that is allowed to deform as a result of applied forces.

Conservation of momentum may be performed for any constituent, but describing the interaction of a disperse constituent within a phase is problematic. Normally, the description of motion is undertaken for a phase rather than a constituent. Define:

$$(15) \quad [\text{momentum of phase } \alpha] = \int_V \rho^{\alpha\beta} \vec{w}^\alpha dV = \int_V \phi^\alpha \rho^\alpha \vec{w}^\alpha dV$$

The momentum conservation equation may be written as:

$$(16) \quad \frac{d}{dt} \int_{V(t)} \rho^{\alpha\beta} \vec{w}^\alpha dV + \oint_{B(t)} (\vec{T}^\alpha \vec{n}) dB + \int_{V(t)} (\sum_\beta \rho^{\beta\alpha\beta} \vec{b}^{\beta\alpha}) dV = \int_{V(t)} \hat{Q}^\alpha dV$$

From left to right, the terms are the time rate of change of the momentum plus the stress felt across the boundary plus the body forces is equal to the sources/sinks of

momentum. Notice that the stress tensor is strongly related to the traction vector (of classical continuum mechanics), and it describes how stress is transmitted intra-phase. In order to apply the Gauss Divergence Theorem easily, it is convenient to write the i -th component of the vector only. Applying the Reynolds Transport Theorem yields.

$$(17) \quad \int_{V(t)} \left[\frac{\partial}{\partial t} (\rho^{aB} w_i^a) + \nabla \cdot (\rho^{aB} w_i^a \tilde{w}^a) \right] dV + \oint_{B(t)} (\bar{T}^a \bar{n})_i dB \\ + \int_{V(t)} \left(\sum_B \rho^{\beta aB} b_i^{\beta a} \right) dV = \int_{V(t)} \left(\hat{\hat{Q}}^a \right)_i dV$$

Utilizing the Gauss Divergence Theorem, assuming that gravity is the only body force, and localizing the equation yields the vector form of the equation:

$$(18) \quad \rho^{aB} \frac{D\tilde{w}^a}{Dt} + \tilde{w}^a \left(\rho_i^{aB} + \nabla \cdot (\rho^{aB} \tilde{w}^a) \right) = -\nabla \cdot \bar{T}^a - \bar{g} \sum_B \rho^{\beta aB} + \hat{\hat{Q}}^a \\ = -\nabla \cdot \bar{T}^a - \rho^{aB} \bar{g} + \hat{\hat{Q}}^a$$

Notice that $\hat{\hat{Q}}^a$ contains the momentum exchange associated with mass exchange between the phases, and it also contains the momentum lost to normal and shear forces associated with flow of one phase past another. Essentially, the forces associated with flow are the boundary conditions associated with the stress tensor \bar{T}^a . Assuming that $\hat{\hat{Q}}^a$ may be separated into these two parts, where \hat{Q}^a only contains the mass exchange terms, the boundary conditions for the stress tensor may be lumped in with the tensor to give the following final form of the momentum equation:

$$(19) \quad \rho^{aB} \frac{D\tilde{w}^a}{Dt} + \tilde{w}^a \left(\rho_i^{aB} + \nabla \cdot (\rho^{aB} \tilde{w}^a) \right) = -\nabla \cdot \bar{P}^a - \rho^{aB} \bar{g} + \hat{Q}^a$$

where \bar{P}^α is called the pressure tensor, and it is the resulting tensor that contains both the intra-phase stresses plus the boundary conditions (this will be the source of such relations as Darcy's Law). Such a re-grouping of terms is necessary because the use of mixture theory results in a loss of specifics relating the relative motion of the phases. In a single phase system, $\bar{P}^\alpha = \bar{T}^\alpha$ and $\hat{Q}^\alpha = 0$, which provides classic results such as recovery of the Navier-Stokes equations. If desired, (19) may be re-written as:

$$(20) \quad \frac{\partial}{\partial t}(\rho^{ab} \bar{w}^\alpha) + \nabla \cdot (\rho^{ab} \bar{w}^\alpha \otimes \bar{w}^\alpha) = -\nabla \cdot \bar{P}^\alpha - \rho^{ab} \bar{g} + \hat{Q}^\alpha$$

where $\bar{w}^\alpha \otimes \bar{w}^\alpha$ is a dyadic tensor defined as $\bar{w}^\alpha \otimes \bar{w}^\alpha \equiv w_i w_j$. For further questions regarding this or other notation, the reader is referred to Appendix I of deGroot and Mazur (1962).

Conservation of angular momentum, also called the moment of momentum, for a mixture normally allows the partial stress for each phase to have a skew part (Bowen, 1976). In classical continuum mechanics the conservation of angular momentum puts a symmetry condition on \bar{T}^α . Here it is noted that in the case of creeping flow in porous media, that the anti-symmetric part of \bar{P}^α is small. For the derivation herein, it is assumed that \bar{P}^α is symmetric, which implies there is zero energy associated with rotational flows. In actuality, for the following, it is only necessary that the rotational energy is very small compared to the other energy terms. So, in order to simplify the discussion here, angular momentum is neglected.

Kinetic Energy Equation

In order to evaluate the energy equations, it will be useful to have a kinetic energy equation that describes the loss of kinetic energy with the loss of momentum. To get this, the scalar product of the phase velocity with equation (19) may be computed as:

$$(21) \quad \rho^{\alpha B} \bar{w}^\alpha \cdot \frac{D\bar{w}^\alpha}{Dt} + (\bar{w}^\alpha \cdot \bar{w}^\alpha) \left(\rho_i^{\alpha B} + \nabla \cdot (\rho^{\alpha B} \bar{w}^\alpha) \right) = \bar{w}^\alpha \cdot \left(-\nabla \cdot \bar{P}^\alpha - \rho^{\alpha B} \bar{g} + \hat{Q}^\alpha \right)$$

Which may be re-written as:

$$(22) \quad \rho^{\alpha B} \frac{D \frac{1}{2} (\bar{w}^\alpha \cdot \bar{w}^\alpha)}{Dt} + (\bar{w}^\alpha \cdot \bar{w}^\alpha) \left(\rho_i^{\alpha B} + \nabla \cdot (\rho^{\alpha B} \bar{w}^\alpha) \right) = \bar{w}^\alpha \cdot \left(-\nabla \cdot \bar{P}^\alpha - \rho^{\alpha B} \bar{g} + \hat{Q}^\alpha \right)$$

Conservation of Energy

Historically, it has been taken a-priori that the specific energy (energy per unit mass) of phase α may be written:

$$(23) \quad e^\alpha = u^\alpha + \frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha + \psi \quad \text{where } \nabla \psi = \bar{g} \text{ which implies } \psi = \bar{g} \cdot \bar{x}.$$

Assuming a single phase, constant density, constant velocity rigid body, multiplication of (23) by the phase density and integration over a volume yields the expected result for the macroscopic energy equation (i.e., $E = U + \frac{1}{2} m \bar{w} \cdot \bar{w} + m \bar{g} \cdot \bar{x}$). In the following sections, the usual use of (23) is examined, and the validity of the relations is examined by generalizing the derivation procedure and examining the results. First, the classical (or “usual”) results are derived so that the reader may see where the results come from and so that differences between the usual results and any other results derived will be clear.

The Usual Results

Internal Energy

When performing thermodynamic derivations, it is important to specify the volume of interest. All other parameters are then referred to this volume. For this reason, all specific variables (quantity per unit mass) must be converted to densities (quantity per unit volume). This is accomplished easily by multiplying specific variables by the mass density. Hereafter, the density of a parameter is designated by a tilda (e.g., $\tilde{u}^\alpha = \rho^{\alpha B} u^\alpha$) unless a convenient variable already exists (e.g., $\tilde{X}^{\beta\alpha} = \rho^{\beta\alpha B}$).

In closed homogeneous system steady-state thermodynamics, the internal energy U is assumed to be a function of the extensive variables: entropy (S^α), volume (V^α), and the moles of each constituent ($N^{\beta\alpha}$). The corresponding specific variables are given by the corresponding lower case letters. Consequently, $\tilde{u}^\alpha = \tilde{u}^\alpha(\tilde{s}^\alpha, \tilde{v}^\alpha, \{\rho^{\beta\alpha B}\})$ where $\{\rho^{\beta\alpha B}\} = \{\rho^{\beta_1\alpha B}, \rho^{\beta_2\alpha B}, \dots, \rho^{\beta_N\alpha B}\}$ and N is the total number of constituents in phase α . Notice that the specific volume is the volume of α per unit mass. This implies that $\tilde{v}^\alpha = \rho^{\alpha B} v^\alpha = \phi^\alpha \rho^\alpha (1 / \rho^\alpha) = \phi^\alpha$. Consider the differential of the internal energy density:

$$(24) \quad d\tilde{u}^\alpha = \left(\frac{\partial \tilde{u}^\alpha}{\partial \tilde{s}^\alpha} \right) d\tilde{s}^\alpha + \left(\frac{\partial \tilde{u}^\alpha}{\partial \phi^\alpha} \right) d\phi^\alpha + \sum_\beta \left(\frac{\partial \tilde{u}^\alpha}{\partial \rho^{\beta\alpha B}} \right) d\rho^{\beta\alpha B}$$

If the above was evaluated over a homogeneous, steady-state volume filled with a single phase, then:

$$(25) \quad \left(\frac{\partial U}{\partial S} \right) = T ; \quad \left(\frac{\partial U}{\partial V} \right) = P ; \quad \left(\frac{\partial U}{\partial N^\beta} \right) = \mu^\beta \quad \text{for all } \beta.$$

So, define the local temperature, pressure, and chemical potential as:

$$(26) \quad \left(\frac{\partial \tilde{u}^\alpha}{\partial s^\alpha} \right) \equiv T^\alpha ; \quad \left(\frac{\partial \tilde{u}^\alpha}{\partial \phi^\alpha} \right) \equiv P^\alpha ; \quad \left(\frac{\partial \tilde{u}^\alpha}{\partial \rho^{\beta\alpha B}} \right) \equiv \mu^{\beta\alpha} \quad \text{for all } \beta.$$

The relations in (26) are known as the *intensive variables* that are associated with each of the corresponding extensive variables. Notice that the chemical potential in (26) is slightly different from the chemical potential in (25). The analogous potential in (25) would be chemical potential defined by taking the differential with respect to the mass in the volume, rather than the number of moles.

Like the chemical potential, the temperature and pressure may be thought of as potentials that define a scalar field. Gradients in these variables result in corresponding fluxes of the associated extensive variables (e.g., a gradient in temperature results in a transmission of heat, and a gradient in pressure results in a volumetric flux). This provides an intuition that the name intensive variable does not convey. Substituting (26) into (24) gives the *standard* Gibbs Relation:

$$(27) \quad d\tilde{u}^\alpha = T^\alpha d\tilde{s}^\alpha + P^\alpha d\phi^\alpha + \sum_{\beta} \mu^{\beta\alpha} d\rho^{\beta\alpha B}$$

Also, it is known that the internal energy is a homogeneous function of the first degree (Callen, 1960, and Kestin, 1966). This means that an increase of each of the extensive variables by the same amount corresponds to a change in the energy by that amount.

Therefore, the following is true:

$$(28) \quad \lambda \tilde{u}^\alpha = \hat{\tilde{u}}^\alpha \left(\lambda \tilde{s}^\alpha, \lambda \tilde{v}^\alpha, \{ \lambda \rho^{\beta\alpha B} \} \right)$$

Suppose none of the extensive variables are functions of λ . Taking the derivative with respect to λ , gives:

$$(29) \quad \tilde{u}^\alpha = \frac{\partial \hat{u}^\alpha}{\partial (\lambda \tilde{s}^\alpha)} \tilde{s}^\alpha + \frac{\partial \hat{u}^\alpha}{\partial (\lambda \phi^\alpha)} \phi^\alpha + \sum_\beta \frac{\partial \hat{u}^\alpha}{\partial (\lambda \rho^{\beta\alpha B})} \rho^{\beta\alpha B}$$

Since λ is arbitrary, choose $\lambda=1$. This results in the *standard* Euler Relation:

$$(30) \quad \tilde{u}^\alpha = T^\alpha \tilde{s}^\alpha + P^\alpha \phi^\alpha + \sum_\beta \mu^{\beta\alpha} \rho^{\beta\alpha B}$$

Taking the differential of (30) and subtracting (27) yields the *standard* Gibbs-Duhem Relation:

$$(31) \quad 0 = \tilde{s}^\alpha dT^\alpha + \phi^\alpha dP^\alpha + \sum_\beta \rho^{\beta\alpha B} d\mu^{\beta\alpha}$$

Notice that the derivation of (30) relies only on the fact the internal energy is a homogeneous function of the first degree and the definitions of the intensive variables in (26). This implies that the derivation of the Euler Relation is independent of the Gibbs Relation, and that if it is known that any given energy function is a homogeneous function of the first degree, and the associated intensive variables are known, the Euler Relation for that function may immediately be written down (a fact that will be used several times below).

Total Energy

In order to use (23) it becomes necessary to multiply each side by the density of the phase to get the *general* Euler Relation for the densities:

$$(32) \quad \rho^{aB} e^\alpha = \tilde{e}^\alpha = \tilde{u}^\alpha + \frac{1}{2} \rho^{aB} \tilde{w}^\alpha \cdot \tilde{w}^\alpha + \rho^{aB} \psi = \rho^{aB} u^\alpha + \frac{1}{2} \rho^{aB} \tilde{w}^\alpha \cdot \tilde{w}^\alpha + \rho^{aB} \psi$$

This relation is used extensively throughout the literature (c.f. deGroot and Mazur (1962) and Luikov (1966)). While the method of introduction varies, the net effect of this formulation is that the differential is used as:

$$(33a) \quad d\tilde{e}^\alpha = d\tilde{u}^\alpha + d\left(\frac{1}{2} \rho^{aB} \tilde{w}^\alpha \cdot \tilde{w}^\alpha\right) + d(\rho^{aB} \psi)$$

$$(33b) \quad d\tilde{e}^\alpha = T^\alpha d\tilde{s}^\alpha + P^\alpha d\phi^\alpha + \sum_{\beta} \mu^{\beta\alpha} d\rho^{\beta aB} + d\left(\frac{1}{2} \rho^{aB} \tilde{w}^\alpha \cdot \tilde{w}^\alpha\right) + d(\rho^{aB} \psi)$$

Taking the differential of (32) and subtracting (33b) again yields the *standard* Gibbs-Duhem Relation (31). While the transition between (33a) and (33b) seems natural at first glance, it is curious to note that the Gibbs-Duhem Relation does not retain any portion of the kinetic or potential terms. If the Gibbs-Duhem Relation is viewed as the relation that describes the conversion of one intensive variable (which may be thought of as a potential to causes a thermodynamic flux) to another, it is natural to assume that gravitational potential or “kinetic potential” might be converted to heat or some other potential. This hypothesis is the subject of the following analysis.

The New Results

Examining (23) more closely, one notes that at first glance, the kinetic term and the gravitational potential are both intensive variables, while the total specific energy and the specific internal energy are both extensive variables. This is not truly the case, because the macroscopic kinetic and potential energies are associated with the center of mass of a body. In order to get the specific kinetic and potential energies, the macroscopic energies are divided by the mass giving a “1” that carries the units of mass per mass. Subsequent multiplication by the mass density yields:

$$(34) \quad \tilde{e}^\alpha = \tilde{u}^\alpha + \frac{1}{2} \rho^{\alpha B} \bar{w}^\alpha \cdot \bar{w}^\alpha + \rho^{\alpha B} \bar{g} \cdot \bar{x}$$

Now it is apparent that there is an extensive component associated with the kinetic and gravitational term. Hereafter, $\frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha$ shall be called the *kinetic potential* to distinguish it from the specific kinetic energy (i.e., the extensive units are now associated with the density). This seems a natural analog to the gravitational potential (i.e., $\psi = \bar{g} \cdot \bar{x}$), and both potentials may be viewed as potentials to perform work or to be dissipatively converted to other forms of energy (e.g., viscous losses to heat). Replacing the internal energy density in (34) with the usual representation yields:

$$(35) \quad \tilde{e}^\alpha = T^\alpha \tilde{s}^\alpha + P^\alpha \phi^\alpha + \sum_\beta \mu^{\beta\alpha} \rho^{\beta\alpha B} + \frac{1}{2} \rho^{\alpha B} \bar{w}^\alpha \cdot \bar{w}^\alpha + \rho^{\alpha B} \bar{g} \cdot \bar{x}$$

This precipitates the natural question: If the kinetic and gravitational potentials are intensive variable serving the same purpose as temperature, pressure, and chemical potential, then why isn't the differential of (35):

$$(36) \quad d\tilde{e}^\alpha = T^\alpha d\tilde{s}^\alpha + P^\alpha d\phi^\alpha + \sum_\beta \mu^{\beta\alpha} d\rho^{\beta\alpha B} + \frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha d\rho^{\alpha B} + \bar{g} \cdot \bar{x} d\rho^{\alpha B} \quad ?$$

Rather than assuming (33b) a-priori, suppose a more naïve approach to writing the total energy function is taken. Assume that the total energy density is a function of only the localized extensive variables. Since (2) is true, the energy density may be written as a function of the same variables as the internal energy (i.e.,

$\tilde{e}^\alpha = \tilde{e}^\alpha(\tilde{s}^\alpha, \phi^\alpha, \{\rho^{\beta\alpha B}\})$). Assuming (23) is true, and noticing that the only extensive variables that the kinetic and potential terms depend on are the species densities (i.e., $\{\rho^{\beta\alpha B}\}$) yields:

$$(37) \quad d\tilde{e}^\alpha = T^\alpha d\tilde{s}^\alpha + P^\alpha d\phi^\alpha + \sum_\beta \left(\frac{\partial \tilde{e}^\alpha}{\partial \rho^{\beta\alpha B}} \right) d\rho^{\beta\alpha B}$$

It remains to evaluate the partial differential. Utilizing the notion that the partial differential fixes all other variables, differentiating (23) yields:

$$(38) \quad \left(\frac{\partial \tilde{e}^\alpha}{\partial \rho^{\beta\alpha B}} \right) = \mu^{\beta\alpha} + \left(\frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha + \bar{g} \cdot \bar{x} \right) \left(\frac{\partial \rho^{\alpha B}}{\partial \rho^{\beta\alpha B}} \right)$$

Substituting (2) into (38) gives a value of one for the last differential, so substituting (38) back into (37) yields:

$$(39) \quad d\tilde{e}^\alpha = T^\alpha d\tilde{s}^\alpha + P^\alpha d\phi^\alpha + \sum_\beta \mu^{\beta\alpha} d\rho^{\beta\alpha B} + \frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha d\rho^{\alpha B} + \bar{g} \cdot \bar{x} d\rho^{\alpha B}$$

This is the new general Gibbs Relation. The total energy density is homogeneous first order in the same way as the internal energy density, so the general Euler Relation (i.e., (23)) will be recovered using the same arguments as above. Differentiating (23) and subtracting (39) yields the new Gibbs-Duhem Relation:

$$(40) \quad 0 = \tilde{s}^\alpha dT^\alpha + \phi^\alpha dP^\alpha + \sum_\beta \rho^{\beta\alpha B} d\mu^{\beta\alpha} + \rho^{\alpha B} d\left(\frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha\right) + \rho^{\alpha B} d(\bar{g} \cdot \bar{x})$$

Notice that (40) has a natural coupling between all of the intensive variables. Since nothing has been done to invalidate the standard Gibbs-Duhem Relation, (31) may be subtracted from (40). Noticing that density is non-zero and that gravity is a constant, the resulting equation is:

$$(41) \quad -d\left(\frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha\right) = \bar{g} \cdot d\bar{x}$$

(41) is a statement that the change in kinetic energy only depends on the change in position, which is false in general. This means that there is an error in the derivation. Natural places to look for this error include terms that are poorly understood or hypotheses that may not be satisfied. For this reason, the homogeneous first-order property and the entropy term shall be examined.

One of the more complete discussions on application of the homogeneous first order property to thermodynamics is given by Kestin (1966). In addition to the fact that the extensive variables have the homogeneous first-order property, Kestin states that the intensive variables should be homogeneous zero-order. Holding all of the extensive variables constant for a gas in a fixed volume, and doubling the temperature will result in corresponding changes in pressure and chemical potential. This also results in an increase in system internal energy. Therefore, the intensive variables are not homogeneous zero-order, and neglecting the functional dependence of the system energy on the intensive variables does not mean that system energy does not depend on these variables. Unfortunately, if this argument invalidates (40), then it also invalidates (31). So, supposing that there is some underlying physics that makes (31) true, it may be assumed that (40) might also be valid.

Notice that the total energy density function is an improved description of state compared to describing system energy only in terms of the internal energy. According to Woods (1975), improving the description of state results in the following inequality:

$$(42) \quad d\tilde{s}^\alpha(\tilde{u}^\alpha) \geq d\tilde{s}^\alpha(\tilde{e}^\alpha) \geq 0$$

where the functional dependence of entropy on the equation of state is made explicit. If the description is improved sufficiently (i.e., the new description includes terms that describe dissipations explicitly so that it is no longer necessary to lump the dissipations into the entropy term), then it is reasonable to believe the first inequality

in (42) is strict. In this case, $\tilde{s}^\alpha(\tilde{u}^\alpha) \neq \tilde{s}^\alpha(\tilde{e}^\alpha)$. But, this implies that the extensive variable $\tilde{s}^\alpha(\tilde{e}^\alpha)$ is not independent of the kinetic and potential terms as supposed above. Correction of this oversight implies that (39) becomes:

$$(43) \quad d\tilde{e}^\alpha = \left(T^\alpha + \frac{\partial \left(\frac{1}{2} \rho^{aB} \vec{w}^\alpha \cdot \vec{w}^\alpha + \rho^{aB} \vec{g} \cdot \vec{x} \right)}{\partial \tilde{s}^\alpha} \right) d\tilde{s}^\alpha + P^\alpha d\phi^\alpha \\ + \sum_\beta \mu^{\beta\alpha} d\rho^{\beta\alpha B} + \frac{1}{2} \vec{w}^\alpha \cdot \vec{w}^\alpha d\rho^{aB} + \vec{g} \cdot \vec{x} d\rho^{aB}$$

In (43), it has been assumed that the partial differential of the internal energy with respect to the entropy is still the temperature. If the new term is zero, then the same contradiction as before arises. If the new term is non-zero, then the intensive variable in front of the entropy term cannot be temperature. In general, if

$$\tilde{s}_u^\alpha \equiv \tilde{s}^\alpha(\tilde{u}^\alpha) \neq \tilde{s}^\alpha(\tilde{e}^\alpha) \equiv \tilde{s}_e^\alpha, \text{ then there is no reason to suspect that } \frac{\partial \tilde{u}^\alpha}{\partial \tilde{s}_u^\alpha} = \frac{\partial \tilde{e}^\alpha}{\partial \tilde{s}_e^\alpha}, \text{ so}$$

the notion that temperature is the generalized extensive variable associated with entropy is suspect. This should come as no surprise if (42) may be made strict by adding relevant information. This implies that entropy is a variable that is an accounting tool that is used to preserve the equality of (23) (or analogously (30)). It is a variable that accounts for the unknown, and hence is a function of the unknown variables. Once a variable is explicitly defined, the corresponding intensive variable need not account for this new variable.

So, it remains to define a new extensive variable whose associated intensive variable is the true temperature T^α . Let c^α be the heat energy per unit mass per unit change in temperature T^α . This implies that $\rho^{aB} c^\alpha = \tilde{c}^\alpha$ and the resulting Gibbs Relation is:

$$(44) \quad d\tilde{e}^\alpha = Z_e^\alpha d\tilde{s}_e^\alpha + T^\alpha d\tilde{c}^\alpha + P^\alpha d\phi^\alpha + \sum_\beta \mu^{\beta\alpha} d\rho^{\beta\alpha B} + \frac{1}{2} \vec{w}^\alpha \cdot \vec{w}^\alpha d\rho^{aB} + \vec{g} \cdot \vec{x} d\rho^{aB}$$

Notice that entropy must still be included as long as there are non-negligible dissipations that are unaccounted for by the other variables. A general extensive variable Z_i^a has been introduced with the subscript on both this variable and the entropy making it explicit that another choice of energy function possibly results in a different entropy and its associated intensive variable. This suggests a strategy to remove entropy from the Gibbs Relation. If it is possible to choose a sufficient number of controlling extensive variables such that the entropy term in (44) (or equivalent) is negligible (or otherwise separable by subtracting a corresponding piece from both sides of the equality), then the entropy may be dropped from the equation. This is effectively what has happened in the ideal gas law. There was only one remaining dominant extensive variable whose intensive counterpart turned out to be temperature. As shall be shown below in the examples, considering the static case of (44) (when (44) is written for the proper system) yields the ideal gas law as derived by Chapman and Cowling (1970).

System Specific Relations

The general concepts developed above may be used to develop *system specific* Gibbs, Euler, and Gibbs-Duhem Relations. This is possible because the volume of the system was well defined during the derivation of mass conservation laws. It is convenient to note here that the following may be shown to be true (for an arbitrary function f^a) using the definition of the material derivative:

$$(45) \quad (\rho^{aB} f^a)_{,i} + \nabla \cdot (\rho^{aB} f^a \vec{w}) = \rho^{aB} \frac{Df^a}{Dt} + f^a (\rho_{,i}^{aB} + \nabla \cdot (\rho^{aB} \vec{w}))$$

This is a particularly useful form for the case where mass is conserved, because the quantity in the parentheses on the left hand side of (45) is equal to zero.

The conservation of energy states that the rate of change of energy in a volume is equal to the energy fluxes across the boundary plus any sources/sinks of energy within the volume. The conservation of mass equation may then be written as:

$$(46) \quad \frac{d}{dt} \int_{V(t)} \rho^{aB} e^{\alpha} dV + \oint_{B(t)} \sum_k (\vec{j}_k^{\alpha} \cdot \vec{n}) dB = \int_{V(t)} \hat{E}^{\alpha} dV$$

Where the second term is the sum of an arbitrary number of fluxes across B(t) and the last term is the sources/sinks. Using the Gauss Divergence Theorem, Reynolds Transport Theorem, and localizing yields:

$$(47) \quad (\rho^{aB} e^{\alpha})_t + \nabla \cdot (\rho^{aB} e^{\alpha} \vec{w}^{\alpha}) = - \sum_k \nabla \cdot \vec{j}_k^{\alpha} + \hat{E}^{\alpha}$$

The first term is the accumulation of energy, and the second term is the divergence of the advected energy flux. Equation (47) holds for both the “usual” derivation of the energy equations and the new results derived above. In the following; first, the “usual” relationships will be developed, then the results using the new theory will be completed. Recall that the Euler Relation only requires definition of the intensive variables and the homogeneous first order property to be derived. Once the proper Gibbs Relation is derived, the Euler Relation may immediately be written. The Gibbs-Duhem Relation follows immediately from these two relations.

The “Usual” System Specific Relations

Recalling that $\psi = \vec{x} \cdot \vec{g} = x_3 g$, equation (27) may be used to convert (47) to:

$$\begin{aligned}
(48) \quad & T^\alpha \left[(\rho^{\alpha B} s^\alpha)_i + \nabla \cdot (\rho^{\alpha B} s^\alpha \bar{w}^\alpha) \right] + P^\alpha \left[(\phi^\alpha)_i + \nabla \cdot (\phi^\alpha \bar{w}^\alpha) \right] \\
& + \sum_\beta \mu^{\beta\alpha} \left[(\rho^{\beta\alpha B})_i + \nabla \cdot (\rho^{\beta\alpha B} \bar{w}^\alpha) \right] + \left[\left(\frac{1}{2} \rho^{\alpha B} (\bar{w}^\alpha \cdot \bar{w}^\alpha) \right)_i + \nabla \cdot \left(\frac{1}{2} \rho^{\alpha B} (\bar{w}^\alpha \cdot \bar{w}^\alpha) \bar{w}^\alpha \right) \right] \\
& + \left[(\rho^{\alpha B} (\bar{g} \cdot \bar{x}))_i + \nabla \cdot (\rho^{\alpha B} (\bar{g} \cdot \bar{x}) \bar{w}^\alpha) \right] = - \sum_k \nabla \cdot \bar{j}_k^\alpha + \hat{E}^\alpha
\end{aligned}$$

Notice that each term in square brackets is written in terms of an accumulation and an advection term. Equation (48) is the “usual” *system specific* Gibbs Relation. Since all of the intensive variables are the same, then the *system specific* Euler Relation is the same as that given in (32). Substituting (32) into (47) and differentiating, then subtracting (48), yields the “usual” *system specific* Gibbs-Duhem Relation.

$$(49) \quad 0 = \rho^{\alpha B} s^\alpha \frac{DT^\alpha}{Dt} + \phi^\alpha \frac{DP^\alpha}{Dt} + \sum_\beta \rho^{\beta\alpha B} \frac{D\mu^{\beta\alpha}}{Dt}$$

The System Specific Relations for the New Theory

Equation (44) may be used with equation (47) to develop the *system specific* Gibbs Relation for the new theory:

$$\begin{aligned}
(49) \quad & Z_\varepsilon^\alpha \left[(\rho^{\alpha B} s_\varepsilon^\alpha)_i + \nabla \cdot (\rho^{\alpha B} s_\varepsilon^\alpha \bar{w}^\alpha) \right] + T^\alpha \left[(\rho^{\alpha B} c^\alpha)_i + \nabla \cdot (\rho^{\alpha B} c^\alpha \bar{w}^\alpha) \right] \\
& + P^\alpha \left[(\phi^\alpha)_i + \nabla \cdot (\phi^\alpha \bar{w}^\alpha) \right] + \sum_\beta \mu^{\beta\alpha} \left[(\rho^{\beta\alpha B})_i + \nabla \cdot (\rho^{\beta\alpha B} \bar{w}^\alpha) \right] \\
& + \left(\frac{1}{2} \bar{w}^\alpha \cdot \bar{w}^\alpha \right) \left[(\rho^{\alpha B})_i + \nabla \cdot (\rho^{\alpha B} \bar{w}^\alpha) \right] + (\bar{g} \cdot \bar{x}) \left[(\rho^{\alpha B})_i + \nabla \cdot (\rho^{\alpha B} \bar{w}^\alpha) \right] \\
& = - \sum_k \nabla \cdot \bar{j}_k^\alpha + \hat{E}^\alpha
\end{aligned}$$

Again, each term in square brackets is written in terms of an accumulation and an advection term. The *system specific* Euler Relation is derived in the usual way, and is:

$$(50) \quad \tilde{e}^\alpha = Z_{\tilde{e}}^\alpha \tilde{s}_{\tilde{e}}^\alpha + T^\alpha \tilde{c}^\alpha + P^\alpha \phi^\alpha + \sum_{\beta} \mu^{\beta\alpha} \rho^{\beta\alpha B} + \frac{1}{2} \rho^{\alpha B} \tilde{w}^\alpha \cdot \tilde{w}^\alpha + \rho^{\alpha B} \tilde{g} \cdot \tilde{x}$$

Substituting (50) into (47) and differentiating, then subtracting (49), yields the *system specific* Gibbs-Duhem Relation.

$$(51) \quad 0 = \rho^{\alpha B} s_{\tilde{e}}^\alpha \frac{DZ_{\tilde{e}}^\alpha}{Dt} + \rho^{\alpha B} c^\alpha \frac{DT^\alpha}{Dt} + \phi^\alpha \frac{DP^\alpha}{Dt} + \sum_{\beta} \rho^{\beta\alpha B} \frac{D\mu^{\beta\alpha}}{Dt} \\ + \rho^{\alpha B} \frac{D\left(\frac{1}{2} \tilde{w}^\alpha \cdot \tilde{w}^\alpha\right)}{Dt} + \rho^{\alpha B} \frac{D(\tilde{g} \cdot \tilde{x})}{Dt}$$

Which may be rewritten as:

$$(52) \quad 0 = \rho^{\alpha B} s_{\tilde{e}}^\alpha \frac{DZ_{\tilde{e}}^\alpha}{Dt} + \rho^{\alpha B} c^\alpha \frac{DT^\alpha}{Dt} + \phi^\alpha \frac{DP^\alpha}{Dt} + \sum_{\beta} \rho^{\beta\alpha B} \frac{D\mu^{\beta\alpha}}{Dt} \\ + \rho^{\alpha B} \frac{D\left(\frac{1}{2} \tilde{w}^\alpha \cdot \tilde{w}^\alpha\right)}{Dt} + \tilde{w}^\alpha \cdot (\rho^{\alpha B} \tilde{g})$$

Examples – Comparison of the two theories.

Up to this point, the two different theories have been developed. The mathematics certainly appears to be consistent, though it is unclear which theory is correct. Ideally, some relevant examples should be worked that contrast the two theories, but that retain the appropriate physics. Applications of this sort are few. They are commonly restricted to single phase fluids that have been idealized. It is a requirement of the theory of mixtures that the theory must collapse to standard theory in the case of a

single phase. For this reason, the above may be applied to an ideal gas and to slightly compressible Newtonian fluids. Making the assumption of incompressibility will require that pressure is no longer a thermodynamic variable, so this assumption is not useful here, though very small compressibility will allow the negligence of some terms. Whenever possible, the comparisons are conducted on the Gibbs-Duhem Relations because the right hand side of (47) is poorly defined.

In all of the following examples, it is assumed that there are sufficient variables in the new theory to make the entropy terms and the gradients in entropy's corresponding intensive variable negligible. In general, this may not be true and it may be necessary to explicitly include extra extensive variables and their associated intensive variables. An example of possible extra variables is the interface terms included by Gray (1999).

The Gibbs-Duhem Relation for an Ideal Gas with Zero Advective Velocity

Assuming that the advective velocity of the single-phase fluid described by an ideal gas is zero ($\vec{w}^G = \vec{0}$), the Gibbs-Duhem Relation for the new theory is identical to the old (with $c^\alpha = s^\alpha$). For this reason, all results of the old theory apply to the new. Writing the proper form of equation (51) gives:

$$(53) \quad 0 = \rho^G c^G \frac{\partial T^G}{\partial t} + \frac{\partial P^G}{\partial t} + \rho^G \frac{\partial \mu^G}{\partial t}$$

which immediately reduces to:

$$(54) \quad \frac{\partial \mu^G}{\partial t} = -c^G \frac{\partial T^G}{\partial t} - \frac{1}{\rho^G} \frac{\partial P^G}{\partial t}$$

The ideal gas law states that:

$$(55) \quad P^G = \frac{N^G}{V^G} RT^G \quad \text{which in the limit goes to}$$

$$(56) \quad P^G = \left(\frac{\partial N^G}{\partial V^G} \right) RT^G = \rho^G \bar{R} T^G$$

where \bar{R} differs from R by the molar weight of the gas, and therefore, is a constant for any given homogeneous gas. If $\mu^G = \mu_0^G - \bar{R} T^G \ln\left(\frac{P^G}{P_0^G}\right)$ (caution must be exercised here because the chemical potential has been corrected to apply to mass densities vs. molar densities), as is said to apply to an ideal gas, then

$$(57) \quad \frac{\partial \mu^G}{\partial t} = -\bar{R} \ln(P^G) \frac{\partial T^G}{\partial t} - \frac{\bar{R} T^G}{P^G} \frac{\partial P^G}{\partial t} \quad \text{where } \frac{\bar{R} T^G}{P^G} = \frac{1}{\rho^G} \text{ by the ideal gas law.}$$

This implies that $c^G = \bar{R} \ln(P^G)$, which makes sense because the specific heat of a gas should vary with its density, and density and pressure are directly related. Substituting the ideal gas law in for pressure in equation (54) gives:

$$(58) \quad \frac{\partial \mu^G}{\partial t} = -c^G \frac{\partial T^G}{\partial t} - \frac{1}{\rho^G} \frac{\partial (\rho^G \bar{R} T^G)}{\partial t}$$

For the ideal gas law, it is permissible to assume that any one of the three free variables may be fixed. Fixing the density, which is analogous to fixing the volume in a closed system, implies:

$$(59) \quad \frac{\partial \mu^G}{\partial t} = -(\bar{R} + c_v^G) \frac{\partial T^G}{\partial t}$$

If instead, (54) were evaluated for a constant pressure system, then the result is:

$$(60) \quad \frac{\partial \mu^G}{\partial t} = -c_p^G \frac{\partial T^G}{\partial t}$$

Comparison of (59) and (60) implies:

$$(61) \quad \bar{R} + c_v^G = c_p^G$$

where (61) is the same relation derived by Chapman and Cowling (1970, pg. 40). As a result, the ideal gas derivation for the case of negligible advective velocities appears to be consistent for both theories (since the two theories are virtually identical).

The Gibbs-Duhem Relation for Single Phase Steady Flow with Mass Conserved

Assuming that flow is steady with $\vec{w}^\alpha \neq \vec{0}$, then the “usual” Gibbs-Duhem Relation may be written:

$$(62) \quad 0 = \vec{w}^\alpha \cdot (\rho^\alpha s^\alpha \nabla T^\alpha + \nabla P^\alpha + \rho^\alpha \nabla \mu^\alpha)$$

Since $\vec{w}^\alpha \neq \vec{0}$ and the velocity will not be orthogonal to the potential fields causing the velocity, the following must be true:

$$(63) \quad 0 = \rho^\alpha s^\alpha \nabla T^\alpha + \nabla P^\alpha + \rho^\alpha \nabla \mu^\alpha$$

A similar argument holds for the new theory, resulting in:

$$(64) \quad 0 = \rho^\alpha c^\alpha \nabla T^\alpha + \nabla P^\alpha + \rho^\alpha \nabla \mu^\alpha + \rho^\alpha \nabla \left(\frac{1}{2} \bar{\mathbf{w}}^\alpha \cdot \bar{\mathbf{w}}^\alpha \right) + \rho^\alpha \bar{\mathbf{g}}$$

Since mass is conserved, substitution of (22) into the Gibbs-Duhem Relation is permitted, yielding an alternate form of (64):

$$(65) \quad 0 = \rho^\alpha c^\alpha \nabla T^\alpha + \nabla P^\alpha + \rho^\alpha \nabla \mu^\alpha - \nabla \cdot \bar{\mathbf{P}}^\alpha$$

Recall that the pressure tensor and the stress tensor are identical for a single phase fluid. This means that any constitutive relation describing $\bar{\mathbf{P}}^\alpha$ must describe the transfer of stress across the surface of an arbitrary volume. Continuum mechanics commonly approaches this problem in terms of traction vectors. Traction is a very useful concept, because the traction exerted by a liquid (e.g., water) on itself is different than the traction a gas (e.g., air) exerts on itself. For this reason, the common form of the pressure tensor used to derive Navier-Stokes is amended with a coefficient (λ) as follows:

$$(66) \quad \bar{\mathbf{P}}^\alpha = \lambda^\alpha P^\alpha \bar{\mathbf{I}} + \hat{\eta}^\alpha \text{Tr}(\bar{\mathbf{D}}^\alpha) \bar{\mathbf{I}} + 2\eta^\alpha \bar{\mathbf{D}}^\alpha \equiv \lambda^\alpha P^\alpha \bar{\mathbf{I}} + \bar{\mathbf{V}}^\alpha$$

where $\bar{\mathbf{D}}^\alpha = \frac{1}{2} (\nabla \bar{\mathbf{w}}^\alpha + (\nabla \bar{\mathbf{w}}^\alpha)^T)$. $\bar{\mathbf{D}}^\alpha$ is commonly called the rate of deformation tensor; $\bar{\mathbf{V}}^\alpha$ encapsulates the compressibility and viscosity effects (for notational convenience to be used later) and is defined by (66); and the rest of the terms are the usual terms (defined in the Nomenclature section). The exception to this is λ , which shall be called the interface traction efficiency. If $\lambda=1$, then the exact form used to derive Navier-Stokes is recovered. $\lambda=1$ corresponds to the assumption that the stresses due to gradients in pressure are transmitted perfectly without loss across the interface. In other words, the interface acts like a perfect reflector of pressure. If only some particles are reflected, but many pass through the interface without being reflected, then $\lambda < 1$. This is the case for an ideal gas, where an implicit assumption of statistical

derivations of gas laws is that there are very few collisions. Notice that the same physical principle governs the magnitude of viscosity of the fluid. For this reason, it will be assumed that λ is proportional to the viscosity (η).

Steady Flow of an Ideal Gas with Mass Conserved

For an ideal gas, it is apparent that if (53) is true (with $c^\alpha = s^\alpha$), then so is (63). It remains to verify the validity of (64). Chapman and Cowling (1970) state that the ideal gas law is valid for only very small departures from a homogeneous distribution. For very small departures, one expects the gradients resulting in advective flows are small. This, coupled with the low density of a gas, implies that the kinetic term and the gravitational term in (64) will become diminishingly small. Substituting (66) into (65), and assuming the coefficients are all approximately constant over the range of consideration, yields:

$$(67) \quad 0 = \rho^G c^G \nabla T^G + (1 - \lambda^G) \nabla P^G + \rho^G \nabla \mu^G - \hat{\eta}^G \nabla (\nabla \cdot \bar{w}^G) - 2\eta^G \nabla \cdot \bar{D}^G$$

where the identity $\nabla \cdot (Tr(\bar{D}^\alpha) \bar{I}) = \nabla (\nabla \cdot \bar{w}^G)$ has been used. Since the viscosity of air is approximately two orders of magnitude smaller than the viscosity of water, and it has been assumed that λ^α is proportional to the viscosity, this implies that $\lambda^G = 0.01$ (because $\lambda^L = 1$). This implies that

$$(68) \quad |\nabla P^G| \gg |\lambda^G \nabla P^G|$$

Assuming that \bar{P}^G is symmetric positive definite and that the isotropic portion dominates (else, viscosities drive flows, not pressures), then the following is true:

$$(69) \quad |\lambda^G \nabla P^G| > |\hat{\eta}^G \nabla (\nabla \cdot \bar{w}^G) - 2\eta^G \nabla \cdot \bar{D}^G|$$

Application of (68) and (69) implies that for the range over which the ideal gas law holds, the following is true:

$$(70) \quad 0 = \rho^G c^G \nabla T^G + \nabla P^G + \rho^G \nabla \mu^G + \rho^G \nabla \left(\frac{1}{2} \vec{w}^G \cdot \vec{w}^G \right) + \rho^G \vec{g}^G$$

$$\approx \rho^G c^G \nabla T^G + \nabla P^G + \rho^G \nabla \mu$$

In other words, the kinetic and gravitational terms are negligible. The net result is that, again, the “usual” relation and the new theory reduce to the same equation (assuming $c^\alpha \approx s^\alpha$).

Steady Flow of an Idealized Liquid with Mass Conserved

Consider an isolated system (requires entropy must be strictly increasing in a dissipative system) consisting of a capillary tube through which a liquid is flowing as a result of only a pressure gradient. Assuming that flow is steady with $\vec{w}^\alpha \neq \vec{0}$, then the “usual” Gibbs-Duhem Relation may be written:

$$(71) \quad 0 = \vec{w}^L \cdot \left(\rho^L s^L \nabla T^L + \nabla P^L + \rho^L \nabla \mu^L \right)$$

Since $\vec{w}^\alpha \neq \vec{0}$ and the velocity will not be orthogonal to the potential fields causing the velocity, the following must be true:

$$(72) \quad 0 = \rho^L s^L \nabla T^L + \nabla P^L + \rho^L \nabla \mu^L$$

And a similar argument to the one above yields the Gibbs-Duhem Relation for the new theory:

$$\begin{aligned}
 (73) \quad 0 &= \rho^L c^L \nabla T^L + \nabla P^L + \rho^L \nabla \mu^L - \nabla P^L - \hat{\eta}^L \nabla (\nabla \cdot \bar{w}^L) - 2\eta^L \nabla \cdot \bar{D}^L \\
 &= \rho^L c^L \nabla T^L + \rho^L \nabla \mu^L - \hat{\eta}^L \nabla (\nabla \cdot \bar{w}^L) - 2\eta^L \nabla \cdot \bar{D}^L
 \end{aligned}$$

where it has been assumed $\lambda \approx 1$, which is consistent with Navier-Stokes derivations, and there are sufficient dissipative variables to render the entropy term negligible.

In order to interpret the above, it is necessary to understand chemical potential. Pressure is the “potential” associated with volume, and chemical potential is associated with the mass in the volume. A gradient in chemical potential between two open systems is a measure of the tendency of mass to escape from one system into another. Unlike pressure, chemical potential is not a potential to deform the volume of the system. If it were, there would be double counting of pressure-like potentials, which would be unacceptable. In an ideal gas, chemical potential does not change pressure by changing the volume (i.e., advection), but rather, chemical potential gradients result in diffusions, and the ideal gas law requires that pressure and temperature reach a new equilibrium value. So, it is sufficient to think of chemical potential as an escape potential.

Assuming that density is essentially a constant (say 1 g/cm^3), this implies that $\nabla \cdot \bar{w}^L \approx 0$ (by conservation of mass) and that $\nabla \mu^L$ is arbitrarily small (zero if the liquid is truly incompressible, but this violates the thermodynamic definition of pressure). This implies that (73) reduces to:

$$(74) \quad \rho^L c^L \nabla T^L \approx 2\eta^L \nabla \cdot \bar{D}^L$$

which is just a statement that the viscous losses result in a thermal gradient (i.e., viscous losses generate heat). On the other hand, the usual relation (72) reduces to:

$$(75) \quad 0 \approx \rho^L s^L \nabla T^L + \nabla P^L$$

Since $\rho^L s^L > 0$, this implies that the pressure gradient must point opposite the temperature gradient. Since there is no externally applied thermal gradient, the only thermal gradient is the result of the pressure gradient or the resulting flow. If it is the result of the pressure gradient, it is known that an increase in pressure results in an increase in temperature, which is a contradiction of the required gradient directions. Therefore, the thermal gradient must be the result of the flow and possibly conduction of generated heat.

It is known that for steady laminar flow through a capillary tube, that the gradient in pressure is constant at all points. If the thermal conductivity coefficient is assumed to be constant for a sufficiently large set of conditions (a reasonable assumption) and the heat generated by viscous dissipation is linear, then the gradient in temperature is also constant at all points. Solving equation (75) for entropy density, the result is the ratio of the gradient of pressure over the gradient of temperature. But, these are both constant, implying that the entropy density is constant at all points along the tube. This contradicts the notion that entropy is increasing during this irreversible process. As a result, it seems unlikely that equation (72) is correct. This is unsurprising if the generalized intensive variable associated with entropy is not temperature in this case. The assumptions above are idealizations of the system used to facilitate analysis, but arguments involving a poorly understood variable such as entropy are a very subtle thing. After all, if entropy changes only a little bit over the capillary tube, then to a first approximation, it may be approximately constant. For this reason, the contradiction is not as strong as is desired. What is clear is that equation (74) corresponds to the physical notion that temperature is related to viscous deformation, while equation (75) provides no physical insight into the physics of the problem.

If the contradiction of the previous paragraph is tacitly assumed to be correct, and if only the assumption that temperature is the generalized intensive variable associated with entropy is relaxed for the “usual” relations, (72) becomes:

$$(76) \quad 0 = \rho^L s_{\tilde{e}}^L \nabla Z_{\tilde{e}}^L + \rho^L c^L \nabla T^L + \nabla P^L + \rho^L \nabla \mu^L$$

and the above reasoning yields:

$$(77) \quad 0 \approx \rho^L s_{\tilde{e}}^L \nabla Z_{\tilde{e}}^L + \rho^L c^L \nabla T^L + \nabla P^L$$

If one assumes that the intensive variable associated with entropy increases as the system relaxes, then the gradient of this variable should be in the opposite direction to ∇P^L , with the temperature term only returning a portion of the energy, making the above relationship feasible. Unfortunately though, it is not a particularly useful relationship because both the entropy and its associated intensive variable are poorly defined.

The Gibbs Relation for Flow of an Idealized Liquid with Mass Conserved

For the new theory, it is desired to check the results also for the Gibbs Relation. The Gibbs Relation for the liquid is:

$$(78) \quad T^L \left[(\rho^L c^L)_t + \nabla \cdot (\rho^L c^L \tilde{w}^L) \right] + P^a (\nabla \cdot \tilde{w}^L) + \mu^L \left[(\rho^L)_t + \nabla \cdot (\rho^L \tilde{w}^L) \right] \\ + \left(\frac{1}{2} \tilde{w}^L \cdot \tilde{w}^L \right) \left[(\rho^L)_t + \nabla \cdot (\rho^L \tilde{w}^a) \right] + (\tilde{g} \cdot \tilde{x}) \left[(\rho^L)_t + \nabla \cdot (\rho^L \tilde{w}^a) \right] = - \sum_k \nabla \cdot \vec{j}_k^L + \hat{E}^L$$

Since mass is conserved, the chemical, kinetic, and gravitational terms are all zero, yielding:

$$(79) \quad T^L \left[(\rho^L c^L)_t + \nabla \cdot (\rho^L c^L \bar{w}^L) \right] + P^\alpha (\nabla \cdot \bar{w}^L) = - \sum_k \nabla \cdot \bar{j}_k^L + \hat{E}^L$$

If the only non-advective flux is via heat conduction, and if the heat source/sink term may be written as $\hat{E} = \bar{P}^L : \bar{D}^L$, then (79) becomes:

$$(80) \quad T^L \left[(\rho^L c^L)_t + \nabla \cdot (\rho^L c^L \bar{w}^L) \right] + P^\alpha (\nabla \cdot \bar{w}^L) = - \nabla \cdot \bar{j}^{LHD} + \bar{P}^L : \bar{D}^L$$

Utilizing the identity $\bar{P}^L : \bar{D}^L = P^\alpha (\nabla \cdot \bar{w}^L) + \bar{V}^L : \bar{D}^L \equiv P^\alpha (\nabla \cdot \bar{w}^L) + \Phi$ where this defines Φ (the well-known dissipation function) yields:

$$(81) \quad T^L \left[(\rho^L c^L)_t + \nabla \cdot (\rho^L c^L \bar{w}^L) \right] = - \nabla \cdot \bar{j}^{LHD} + \Phi$$

Since mass is conserved, the left-hand side of (81) may be rewritten, yielding:

$$(82) \quad \rho^L T^L \frac{Dc^L}{Dt} = - \nabla \cdot \bar{j}^{LHD} + \Phi$$

Equation (82) is exactly Serrin's equation (34.3) (1959) with s^L replaced with c^L , and in fact, this was what was used to provide the postulated relationship: $\hat{E} = \bar{P}^L : \bar{D}^L$.

Notice that the dissipation function is a "product" of only the viscous and compressible terms with the rate of deformation. It contains no conservative work terms, and therefore is consistent with the idea that only deformations generate heat.

Notice that no assumption of incompressibility was used, and in fact, if Serrin's postulated relation (33.3) is true, (82) is quite general. Equation (82) is consistent with

(74) in that the only heat source term results from losses due to mechanical deformation (i.e., heating due to viscosity and compressibility), and equation (82) is the heat flow equation corresponding to the general Navier-Stokes Equation. The derivation of (33.3) is complete in Serrin, and it is commonplace in continuum mechanics textbooks, so this derivation is not completed here. Subsequent application of the Onsager relations allows rewriting the heat flow equation in terms of intensive variables if desired.

Discussion

Two new notions have been developed above. First, there is the notion that temperature is not the generalized intensive variable associated with entropy. Second, the a-priori assumption that (33b) is true has been questioned, and an alternate method of derivation of thermodynamic relations has been postulated. When two new ideas are developed simultaneously, it is sometimes difficult to separate the effects without considering all of the various permutations. Such an approach is tedious and time-consuming for no good purpose in this case, because the examples worked are largely unaffected by the first assumption.

The first notion is gratifying in that it is no longer necessary to attempt to force arbitrary dissipations into a term that utilizes temperature as the corresponding intensive variable. Creating a separate temperature term related to the specific heat also alleviates the problem of carrying $\frac{1}{T^\alpha}$ terms through the entropy inequality (which is commonly the case with most derivations of the entropy inequality). In the new theory, (52) may be used to properly define the conditions necessary for equilibrium, without the need for the $\frac{1}{T^\alpha}$ terms.

Questioning the validity of (33b) has resulted in a more axiomatic framework for development of the thermodynamic relations. If this method of generating the relations can be shown to be correct, then the proper method of incorporating more

thermodynamic variables is more straightforward. In general, all that would be required is for the scientist to have a good understanding of all of the possible extensive or intensive variables that may be important. If the intensive variable is known, as in the case of temperature, the existence of a (localized) extensive counterpart may be postulated. Once this is done, unit analysis allows formulation of the extensive variable (e.g., the specific heat), which in turn leads to an intuition about how the extensive variable should behave.

If the extensive variable is known, as in the case of the chemical potential terms, then the intensive variable may be defined in the usual way. However, this leads to some confusion about the nature of the intensive variable. This confusion required the discussion (above) about the relationship between pressure and chemical potential. If instead, an "escape potential" (Γ^α) had been postulated as the potential to chemically react (either through phase change, chemical recombination, or diffusion) to form a substance of new chemical configuration (e.g. different phase, oxidation state, or concentration of mixture), then a specific energy of formation (say g^α) could be postulated as the extensive variable. This is consistent with the notion that a chemical reaction occurs spontaneously only under favorable energetic conditions. With this sort of derivation, energy production/exchange from latent heats arise more naturally. There is the remaining problem of defining and measuring an appropriate escape potential. The convenience the chemical potential (μ^α) is that chemists have already defined many relationships for the physical scientist to use. The notion of escape potential and corresponding formation energies is trivial to add to the theory above. This was not done in this paper to avoid adding yet a third new notion to the derivations.

The question then becomes: "How many variables should be altered?" As few as possible. If the existing variables are sufficient (e.g., the ideal gas law), then none should be altered. If, for a given problem, the intensive variable does not directly

correspond to the extensive variable (e.g., temperature and entropy), then alterations must occur. Also, if intensive variables and corresponding extensive variables are not consistent with other terms, then some alteration should occur. An example of this inconsistency is latent heat transfers. Certainly, there are no extensive variables in the above derivations that correspond to a transfer of latent heat (i.e. isothermal consumption of formation energies) so that appropriate balance equations may be written.

It is curious to note that with rare exception (c.f., deGroot and Mazur (1962), Luikov (1966), and Gray (1999)), there is no attempt to utilize Gibbs-Duhem Relations in computations. This is likely due to the fact that in historic derivations, temperature has erroneously been assumed to be the generalized intensive variable associated with entropy. This may lead to such contradictions as those discussed in the paragraph following (75). Certainly, if the resulting Gibbs-Duhem Relations are wrong, it would lead to problems with the equations in many cases. This begs the question of whether or not a particular Gibbs-Duhem equation is correct. Here, it has been shown that for most of the simple examples examined, that the method of selection of variables appears to be consistent with physical intuition.

But, what if other variables were selected as the extensive variables? An example of this might be to select momentum as an extensive variable for the kinetic term. Certainly, this is a reasonable extensive variable. Notice that momentum cannot be held constant when taking a partial derivative with respect to the density of a constituent of a phase. For this reason, the mathematics becomes increasing complex, but this may still provide viable answers.

Also, implicit to the derivations above, is the idea that the entropy terms of any two formulations cannot both be negligible unless the difference (in the remaining terms) between the two equations is also negligible. Implicitly, this is the idea that was used to show that both formulations work for the steady advective flow of ideal gases. So,

a comparison of two different formulations should be complete if either differences in the equations are shown to be negligible or if both entropy terms can be shown to be negligible.

It might be asked why the contradiction found for (75) does not apply to the ideal gas example? The simple answer to this is that in the ideal gas, it is assumed that pressure, temperature, and density are always assumed to be in their local equilibrium configuration. Equation (70) is merely a statement of this requirement. For the liquid, there is no such law, and a pressure gradient does not necessarily imply a corresponding temperature gradient that acts in the opposite direction and of the exact magnitude to counter the pressure gradient.

Instead of formulating and using a Gibbs-Duhem Relation, most authors formulate an entropy inequality along with the energy equation. Then, to get the equilibrium condition, the equations are divided by temperature yielding an unwieldy form of the resulting equations. Certainly, the new theory is consistent with the formulation of an entropy inequality, since (44) may still be used. Instead of actually solving the energy or entropy equations, the Onsager Relations are then used to formulate the proper relationships between all of the intensive variables. It is a direct consequence of the derivation that each general thermodynamic “flux” is associated with a *primary potential* (intensive variable, or sometimes called a “force”) in the Onsager theory. This primary intensive variable is always on the main diagonal at the position corresponding to its flux (e.g., pressure is the primary intensive variable associated with volumetric flux). It might be argued that there can be no flux without a gradient in the corresponding intensive variable (e.g., thermal heating increases pressure, resulting in a volumetric flux). Such a construction of the Onsager Matrix will ensure that operation of the matrix and differential operators on the vector of intensive variables will act as a contraction (in the mathematical sense) as long as the system acts in a dissipative manner. For this reason, the entropy inequality is not the required condition for Onsager’s ideas to work. Even if equality is achieved the system is still

dissipative, and the Onsager Relations may still be derived and used with assurance of success. The Onsager Relations just ensure that the terms are properly coupled.

Lastly, appropriateness of the standard use of the homogeneous first-order property has been questioned also. Certainly, the general theory of thermodynamics shows that even if this property is only “weakly” satisfied, that reasonable results are often obtained from derivations. Such is the case above.

Summary

Utilizing mixture theory, continuum mechanics, and the thermodynamics of irreversible processes a very general set of governing equations have been developed. It has been shown that temperature may not always be the generalized intensive variable associated with entropy, and that the entropy variable may be different depending on the choice energy equation. Further, the a-priori assumption of validity of (33a) has been examined. It has been found that selection of different extensive variables affects the form of the Gibbs-Duhem Relation, and that it is possible that at least some of these formulations may be wrong (e.g., see discussion following (75)).

The “usual” relations and the relations resulting from the new theory have been applied to simple examples to assess model correctness. The examples are worked for both an ideal gas and a slightly compressible single phase Newtonian liquid. In most cases, the usual results and the new results are the same, but the steady-flow of a liquid problem resulted in an apparent failure of the existing theory, while the new theory performed adequately. More work needs to be accomplished on the topic of selection of appropriate variables since a very small correction to the existing theory showed that feasible results may be obtained (e.g., 77).

Acknowledgements

The author wishes to thank the authors de Groot & Mazur and L.C. Woods for their outstanding books. These books provide the rigorous foundation for this work (and work by many others), so it would have been impossible to complete this work without their careful and comprehensive derivations. Also, thanks to Brian Wood, Stephen Whitaker, Bill Gray, Majid Hassanizadeh, Ian Turner, and Bill Williams for all correspondence in person or via email on the topics contained herein. They were very helpful and kind when faced with my ignorance. My discussions with them greatly aided my understanding of the topics covered.

Notation

Variables and Parameters

\vec{x} = position vector

t = time

ρ = mass density

m = mass

ϕ = volume fraction

X = mass fraction

V = volume

B = surface (boundary) of V

\vec{n} = unit normal vector to a surface S pointing outward from V

$\vec{w} = \vec{x}_t$ = velocity

\vec{j} = non-advective flux

\bar{T} = the stress tensor

\bar{P} = the pressure tensor

\bar{D} = the rate of deformation tensor

\vec{b} = the body forces per unit mass

\vec{g} = gravitational body force

ψ = gravitational potential

\hat{M} = source/sink term of mass

$\hat{\hat{Q}}$ = source/sink term of momentum

\hat{Q} = source/sink term of momentum corresponding to phase exchange

e = specific total energy (i.e., energy per mass)

u = specific internal energy

s = specific entropy

c = specific heat energy

v = specific volume

T = temperature

P = pressure

μ = chemical potential (important: chemical potential in this paper is defined in terms of mass density, so care must be taken when inserting functional forms)

Z = the generalized intensive variable associated with entropy in the new theory

R = ideal gas constant

N = number of moles, or sometimes used as the maximum number of elements of a set

\bar{R} = modified ideal gas constant (modified by multiplication or the ideal gas constant by the molar mass of the gas; it is constant for a given fixed composition gas)

η = dynamic viscosity (sometimes called first viscosity)

$\hat{\eta}$ = lame constant of compressibility (sometimes called second viscosity)
 \hat{E} = energy source/sink term (e.g., latent heats utilized during phase change)
 \hat{C} = heat source/sink term
 Tr = function that sums the elements on the main diagonal

Superscripts and modifiers

γ = generic index
 α = index over a consistent set of phases
 β = index over a consistent set of constituents
 $\beta\alpha$ = denotes property of β in α (e.g., $\rho^{\beta\alpha}$ is density of constituent β in phase α)
 B = indicates the value is a bulk value (i.e., is the true value times the volume fraction)
 \sim = indicates conversion of a specific property to a density by multiplication by mass density
 S = solid phase of a mixture
 L = liquid phase of a mixture
 G = gaseous phase of a mixture
 ss = non-reactive structural solid constituent of a mixture (e.g., silica sand upon which salt precipitates)
 h = precipitated salt (anhydrous) constituent of a mixture (h is for halite or table salt)
 w = pure water or H_2O constituent of a mixture
 a = dry air constituent of a mixture

Subscripts

t = partial derivative with respect to time
 i and j = component of a vector in a Cartesian coordinate system (in general = 1,2,3)
 0 = reference condition
 V = for fixed volume
 P = for fixed pressure
 \tilde{e} = used to specify that entropy and its associated intensive variable depend on the functional form of the energy density

References

- Bear, J., 1972. *Dynamics of Fluids in Porous Media*, corrected reprint by Dover Publications, Inc., New York, NY, U.S.A.
 Bowen, R.M., 1976. "Theories of Mixtures" in *Continuum Physics*, Ed. By A.C. Eringen, V. III, Academic Press, New York, pp. 2-122.

- Callen, H.B., 1960. *Thermodynamics*, John Wiley and Sons, Inc., New York, NY.
- Chapman, S., and T.G. Cowling, 1970. *The Mathematical Theory of Non-Uniform Gases: An Account of the Kinetic Theory of Viscosity, Thermal Conduction, and Diffusion in Gases*, 3rd Ed., Cambridge University Press, London, England.
- Fung, Y.C., 1994. *A First Course in Continuum Mechanics*, 3rd Ed., Prentice Hall, Englewood Cliffs, NJ.
- de Groot, S.R., and P. Mazur, 1962. *Non-Equilibrium Thermodynamics*, corrected reprint by Dover Publications, Inc., New York, NY, U.S.A.
- Kellogg, C.D., 1929. *Foundations of Potential Theory*, 1st Ed., reprinted in 1967, Springer-Verlag, Berlin, Germany.
- Kestin, J., 1966. *A Course in Thermodynamics*, Blaisdell Publishing Co., Waltham, MA, USA.
- Luikov, A.V., 1966. *Heat and Mass Transfer in Capillary-porous Bodies*, translated by P.W.B. Harrison, Pergamon Press, Oxford, England.
- Onsager, L., 1931. "Reciprocal Relations in Irreversible Processes. I.," *Physical Review*, v. 37, pp. 405-426.
- Onsager, L., 1931. "Reciprocal Relations in Irreversible Processes. II.," *Physical Review*, v. 38, pp. 2265-2279.
- Prigogine, I., 1967. *Introduction to Thermodynamics of Irreversible Processes*, 3rd Ed., John Wiley and Sons, New York, NY, U.S.A.
- Serrin, J., 1959. "Mathematical Principles of Classical Fluid Mechanics," *Handbuch Der Physik (Encyclopedia of Physics)*, v. 8, no. 1, pp. 125-263.
- Whitaker, S., 1998. "Coupled Transport in Multiphase Systems: A Theory of Drying," *Advances in Heat Transfer*, v. 31, pp. 1-104.
- Woods, L.C., 1975. *The Thermodynamics of Fluid Systems*, Oxford University Press, London, England.

Chapter 6 – Conclusion

The goal of this work has been to further the understanding of the physics of flow of saline solutions in variably saturated porous media. Chapter 2 provides a general derivation of the effects of salt on vapor pressure and liquid pressure in porous media. The derivation results in an additional term necessary to account for non-dilute effects. Chapter 3 provides an example of use of the relations in chapter 2 for sodium chloride (NaCl), complete with an analysis of when salt must be accounted for and when the non-dilute correction term is important. Chapter 4 provides a derivation of the necessary thermodynamic corrections for Darcy-type laws for saline solutions in isothermal unsaturated porous media. An example is again worked for NaCl for the data of Scotter (1974). The results show good agreement, though there appear to be a couple of possible confounding factors: 1) hysteresis effects, and 2) chemical interactions between the saline solution and the chemically reactive fines in the loamy sand of Scotter. In chapter 5, the notions necessary to extend the above derivations to continuous non-isothermal systems are developed. Analysis of the classical assumption that temperature is the generalized intensive variable associated with entropy is examined, as well as the assumption of an a-priori form of the differential of the total energy density. Alternatives to each of these classical assumptions are proposed and the results are examined by analyzing two examples: 1) the ideal gas, and 2) an isotropic Newtonian fluid. The new results and the “usual” (classical) results are the same for the ideal gas; but the Newtonian fluid shows possible problems for the “usual” theory, while the new theory appears consistent.

The results of chapter five are far from conclusive. In particular, questions remain about: 1) whether or not the homogeneous first-order property is truly satisfied, or if this is even important for the cases presented here; and 2) whether the selection of intensive and corresponding extensive variables results in a unique formulation or the problem, or if there are a variety of appropriate choices (as long as the mathematics is

carried through correctly). The example calculations showed that either formulation seems viable for many different simple scenarios.

Bibliography

- Apelblat, A., and Korin, E., 1998. "The Vapour Pressures of Saturated Aqueous Solutions of Sodium Chloride, Sodium Bromide, Sodium Nitrate, Sodium Nitrite, Potassium Iodate, and Rubidium Chloride at Temperatures from 227 K to 323 K," *J. Chem. Thermodynamics*, v. 30, pp. 59-71.
- Bear, J., 1972. *Dynamics of Fluids in Porous Media*, corrected reprint by Dover Publications, Inc., New York, NY, U.S.A.
- Bear, J., and A. Gilman, 1995. "Migration of Salts in the Unsaturated Zone Caused by Heating," *Letters in Mathematical Physics*, v. 19, pp. 139-156.
- Belton, J.W., 1935. "The Surface Tensions of Ternary Solutions. Part I. The Surface Tensions of Aqueous Solutions of (a) Sodium and Potassium Chlorides, (b) Sodium chloride and Hydrochloric Acid." *Transactions of the Faraday Society*, no. 174, pp. 1413-1419.
- Bowen, R.M., 1976. "Theories of Mixtures" in *Continuum Physics*, Ed. By A.C. Eringen, V. III, Academic Press, New York, pp. 2-122.
- Brooks, R.H. and A.T. Corey, 1964. "Hydraulic Properties of Porous Media." *Hydrology Papers*, Colorado State University, Ft. Collins.
- Burns, E.R., 2004. "Thermodynamic Correction for Salts in Variably Saturated Porous Media." Thesis for M.S. in mathematics. Oregon State University, Corvallis, OR.
- Burns, E.R., J.-Y. Parlange, J.S. Selker, and R.B. Guenther, 2004. "Thermodynamic Correction for Salts in Variably Saturated Porous Media." Submitted to *Transport in Porous Media*.
- Burns, E.R., J.S. Selker, J.-Y. Parlange, and R.B. Guenther, 2004. "Effects of Sodium Chloride (NaCl) on Constitutive Relations in Variably Saturated Porous Media." Submitted to *Water Resources Research*.
- Callen, H.B., 1960. *Thermodynamics*, John Wiley and Sons, Inc., New York, NY.
- Carsel, R.F., and R.S. Parrish, 1988. "Developing Joint Probability Distributions of Soil Water Retention Characteristics," *Water Resources Research*, V. 24, No. 5, pp. 755-769.

- Chapman, S., and T.G. Cowling, 1970. *The Mathematical Theory of Non-Uniform Gases: An Account of the Kinetic Theory of Viscosity, Thermal Conduction, and Diffusion in Gases*, 3rd Ed., Cambridge University Press, London, England.
- DeHoff, R.T., 1993. *Thermodynamics in Materials Science*, McGraw-Hill, Inc., New York, N.Y.
- Edlefsen, N.E., and A.B.C. Anderson, 1943. "Thermodynamics of Soil Moisture," *Hilgardia*, v. 15, no. 2, pp.31-298.
- Fung, Y.C., 1994. *A First Course in Continuum Mechanics*, 3rd Ed., Prentice Hall, Englewood Cliffs, NJ.
- de Groot, S.R., and P. Mazur, 1962. *Non-Equilibrium Thermodynamics*, corrected reprint by Dover Publications, Inc., New York, NY, U.S.A.
- Guggenheim, E.A., 1977. *Thermodynamics: An Advanced Treatment for Chemists and Physicists*, Sixth Edition, North-Holland Publishing Company, Amsterdam.
- Harkins, W.D., and H.M. McLaughlin, 1925. "The Structure of Films of Water on Salt Solutions I. Surface Tension and Adsorption for Aqueous Solutions of Sodium Chloride," *J. Amer. Chem. Soc.*, v. 47, pp. 2083-2089.
- Heyrovska, R., 1996. "Physical Electrochemistry of Strong Electrolytes Based on Partial Dissociation and Hydration: Quantitative Interpretation of the Thermodynamic Properties of NaCl(aq) from "Zero to Saturation"," *J. Electrochem. Soc.*, v. 143, no. 6, pp. 1789-1793.
- Kellogg, C.D., 1929. *Foundations of Potential Theory*, 1st Ed., reprinted in 1967, Springer-Verlag, Berlin, Germany.
- Kestin, J., 1966. *A Course in Thermodynamics*, Blaisdell Publishing Co., Waltham, MA, USA.
- Kestin, J., H.E. Khalifa, and R.J. Correia, 1981. "Tables of the Dynamic and Kinematic Viscosity of Aqueous NaCl Solutions in the Temperature Range 20-150° C and the Pressure Range 0.1-35 MPa," *J. Phys. Chem. Ref. Data*, v. 10, no. 1, pp. 71-87.
- Li, Y.G., 1999. "Reply to "Comments on 'Surface Tension Model for Concentrated Electrolyte Solutions by the Pitzer Equation'"", *Ind. Eng. Chem. Res.*, v. 38, pp. 4137-4138.

- Luikov, A.V., 1966. *Heat and Mass Transfer in Capillary-porous Bodies*, translated by P.W.B. Harrison, Pergamon Press, Oxford, England.
- Luikov, A.V., 1975. "Systems of Differential Equations of Heat and Mass Transfer in Capillary-Porous Bodies (Review)," *Int. J. Heat Mass Transfer*, v. 18, pp. 1-14.
- Matubayasi, N., H. Matsuo, K. Yamamoto, S. Yamaguchi, and A. Matazawa, 1999. "Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions: I. Aqueous Solutions of NaCl, MgCl₂, and LaCl₃," *Journal of Colloid and Interface Science*, v. 209, pp.398-402.
- Nassar, I.N., and R. Horton, 1989. "Water Transport in Unsaturated Nonisothermal Salty Soil: II. Theoretical Development," *Soil Sci. Soc. Am. J.*, v. 53, pp. 1330-1337.
- Olivella, S., J. Carrera, A. Gens, and E.E. Alonso, 1996. "Porosity Variations in Saline Media Caused by Temperature Gradients Coupled to Multiphase Flow and Dissolution/Precipitation," *Transport in Porous Media*, v. 25, pp. 1-25.
- Onsager, L., 1931. "Reciprocal Relations in Irreversible Processes. I.," *Physical Review*, v. 37, pp. 405-426.
- Onsager, L., 1931. "Reciprocal Relations in Irreversible Processes. II.," *Physical Review*, v. 38, pp. 2265-2279.
- Parlange, J.Y., 1973. "Movement of Salt and Water in Relatively Dry Soils," *Soil Science*, v. 116, no. 4, pp. 249-255.
- Pitzer, K.S., and J.C. Peiper, 1984. "Thermodynamic Properties of Aqueous Sodium Chloride Solutions," *J. Phys. Chem. Ref. Data*, V. 13, no. 1, pp.1-102.
- Prigogine, I., 1967. *Introduction to Thermodynamics of Irreversible Processes*, 3rd Ed., John Wiley and Sons, New York, NY, U.S.A.
- Scotter, D.R., 1974. "Salt and Water Movement in Relatively Dry Soil," *Aust. J. Soil Res.*, v. 12, pp. 27-35.
- Scotter, D.R., and P.A.C. Raats, 1970. "Movement of Salt and Water Near Crystalline Salt in Relatively Dry Soil," *Soil Science*, v. 109, no. 3, pp.170-178.
- Serrin, J., 1959. "Mathematical Principles of Classical Fluid Mechanics," *Handbuch Der Physik (Encyclopedia of Physics)*, v. 8, no. 1, pp. 125-263.
- van Genuchten, M.T., 1980. "A closed form equation for predicting the hydraulic conductivity of unsaturated soils," *Soil Sci. Soc. Am. J.*, v. 44, pp. 892-898.

- Washburn, E.W. (Ed.). Numerical Data, Physics, Chemistry and Technology: First Electronic Edition.
- Weisbrod, N., R. Nativ, E.M. Adar, and D. Ronen, 2000. "Salt Accumulation and Flushing in Unsaturated Fractures in an Arid Environment," *Groundwater*, v. 38, no. 3, pp. 452-461.
- Whitaker, S., 1998. "Coupled Transport in Multiphase Systems: A Theory of Drying," *Advances in Heat Transfer*, v. 31, pp. 1-104.
- Woods, L.C., 1975. *The Thermodynamics of Fluid Systems*, Oxford University Press, London, England.