

# Thermodynamic Correction for Salts in Variably Saturated Porous Media

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**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 relationships are 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 nearsurface geologic materials.

**Key words:** sodium chloride (NaCl), saline, brine, vapor depression, thermodynamic correction, constitutive relation, unsaturated.

## Notation

### *Variables*

|   |   |
|---|---|
| $U$   | internal energy.  |
| $S$   | entropy.  |
| $T$   | absolute temperature.   |
| $P$   | pressure.   |
| $V$   | volume.   |
| $\mu^i$   | chemical potential of the $i$ th constituent.   |
| $N^i$   | mole number of the $i$ th constituent.  |
| $X^{iG} = \frac{N^{iG}}{N^G}$                           | the mole fraction of $i$ in the gas.  |
| $a^{iL}$  | the activity of constituent $i$ 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<br>(or the density of gas–liquid interface). |

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|                               |   |
|-------------------------------|---|
| $\tilde{P}^L \equiv P^L(S^L)$ | equivalent liquid pressure neglecting changes in surface tension<br>(see discussion following Equation (33)). |
| $\rho^{wG}$                   | molar density of water in a gas.  |
| $m$                           | molality of salt in water.  |

### *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.<br>(i.e., infinite radius of curvature).                 |
| 0        | reference condition corresponding to known salt content.<br>(generally zero or negligible amount of salt). |

## **1. 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 (Nassar and Horton, 1989; Bear and Gilman, 1995; Olivella *et al.*, 1996), 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 Section 5. The result of this work

is a general analytic relationship that aids in the conceptual understanding of the underlying physics, as well as providing a methodology to be used for computation of high strength salt effects. All necessary relations are derived herein, and the theory may be subsequently applied to particular salts for computation (e.g., Burns *et al.*, 2005b, submitted). Such computations show when non-negligible effects due to high salt strengths may be expected to occur. The following derivation is terse, and the reader is referred to Burns (2004) for a detailed derivation.

## 2. Derivation of Constitutive Relationships

### 2.1. 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. During the derivation, three sets of assumptions are stated defining the quite general applicability of the results. The assumptions are stated in the order they are employed in the derivation. While the assumptions may appear overly restrictive at first glance, they are quite general. The reason for this is that each assumption need only be valid on the timescale of the problem (e.g., chemical equilibrium is assumed to be achieved arbitrarily fast when compared to the rates of diffusion, advection, etc.). This is known as a quasi-static process, and it is consistent with the local equilibrium assumption. Assumptions 1–5 give sufficient (though not necessary) conditions to use equilibrium thermodynamics.

*Assumption 1:* The total system is closed to mass transfer (i.e., diffusion and advection are very slow relative to local exchanges between the phases).

*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). The quasi-static assumption applies here also, so the porous medium may deform very slowly compared to chemical exchanges.

*Assumption 4:* Equilibrium between the phases is reached much faster than changes driven by external forcing (i.e., the quasi-static process assumption).

*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 so general that it is necessary to define the system of interest further before

computations may be made. Assumptions 6–12 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.,  $\mu^{\text{hL}}$ ) and mole numbers (e.g.,  $N^{\text{hL}}$ ) 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  $V^{\text{L}} = V^{\text{L}}(N^{\text{wL}}, N^{\text{hL}})$  such that if any two of the values ( $V^{\text{L}}, N^{\text{wL}}, N^{\text{hL}}$ ) are known, then the third variable may be computed.

These assumptions allow derivation of several important results for liquid–gas–salt constitutive relations. 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 a sufficiently large gas volume such that  $\left| \int_{0\infty}^B \frac{V^{\text{L}}}{N^{\text{wL}}} dP^{\text{L}} \right| \gg \left| \int_{0\infty}^B \frac{V^{\text{L}}}{N^{\text{wL}}} dP^{\text{G}} \right|$ .

*Assumption 14:* Assume that surface tension ( $\sigma^{\text{LG}}$ ) is a function of salt content and temperature only, and  $\frac{dA^{\text{LG}}}{dV^{\text{L}}}$  is only a function of saturation.

Assumptions 13 and 14 may appear cryptic at this point, but during the course of derivation, the relations arise naturally. The limitations and considerations for application of these two assumptions are discussed more fully in the text where they are applied.

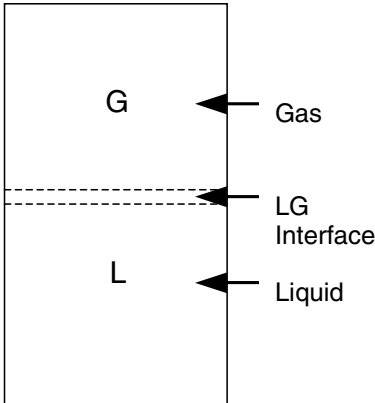


Figure 1. Schematic representation of a system composed of both a liquid and a gas.

## 2.2. DERIVATION OF CONSTITUTIVE RELATIONS

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 1–5 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):

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

where the index  $i$  includes every chemical constituent in the homogeneous mixture, and the symbols are defined in the “Notation” section. Another well-known fact that may be used is that under the above conditions, the Gibbs–Duhem relation also holds (Callen, 1960):

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

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

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

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

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

The corresponding Gibbs–Duhem relations are:

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

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

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

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

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

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

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

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

Re-iterating Assumptions 1–5 in mathematical form yields the following relations.

Conservation of mass:

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

Conservation of volume with negligible interface volume:

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

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

Thermal and chemical equilibrium:

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

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

Closed system except for heat flux:

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

where Callen's (1960) representation of the heat flux,  $\delta Q = TdS$ , has been used. From the above, the commonly accepted form of the mechanical equilibrium condition across an interface may be derived:

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

In order to develop the Gibbs–Duhem relations further, it is necessary to make additional assumptions that adequately describe the real physical system of interest. Assumptions 6–12 are used to describe exactly what is assumed to be true for a saline liquid. Brief discussions of the limitations imposed by these assumptions and of the necessary steps to relax the assumptions are included in the following where appropriate. Assumption 6 implies:

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

Assumption 7 greatly simplifies notation, allowing the utility of the results to be shown easily. The theory developed here extends naturally to multiple salts (e.g.,  $N_1^{\text{hL}}$ ,  $N_2^{\text{hL}}$ ,  $N_3^{\text{hL}}$ , ...), via appropriate definitions of chemical affinities (c.f., DeHoff, 1993).

Assumptions 8 and 9 give  $N^{\text{hG}} = 0$  and  $N^{\text{aL}} \cong 0$ . 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  $dT = 0$ . While this assumption appears limiting, the goal of this research is to evaluate non-dilute salt concentration effects and not temperature effects. The theory may be extended to anisothermal conditions later (see Section 5).

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:

$$P^G = P^{wG} + P^{aG}. \quad (17)$$

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

$$X^{iG} P^G = \frac{N^{iG}}{N^G} P^G = \frac{N^{iG} RT}{V^G} = P^{iG} \quad \text{for all } i. \quad (18)$$

Solving Equation (4b) for the chemical potential of water yields:

$$d\mu^{wG} = \frac{1}{P^{wG}} (RT dP^G - P^{aG} d\mu^{aG}). \quad (19)$$

For gases at low pressure, the following relation holds:

$$\mu^{iG} = \mu_0^{iG} + RT \ln \left( \frac{P^{iG}}{P_o^{iG}} \right) \quad \text{for all } i. \quad (20)$$

It is more convenient here to write Equation (20) in its differential form:

$$d\mu^{iG} = RT d(\ln P^{iG}) = RT \frac{dP^{iG}}{P^{iG}} \quad \text{for all } i. \quad (21)$$

Substituting Equation (21) for the air constituent into Equation (20), and using Equation (17) yields:

$$d\mu^{wG} = \frac{RT}{P^{wG}} (dP^G - dP^{aG}) = RT \frac{dP^{wG}}{P^{wG}}. \quad (22)$$

The result of this derivation is not surprising since it is the expected result of just writing down Equation (21) 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.

Solving Equation (4a) for the chemical potential term yields:

$$d\mu^{wL} = \frac{V^L}{N^{wL}} dP^L - \frac{X^{hL}}{X^{wL}} d\mu^{hL}. \quad (23)$$

By definition, the analogous version of Equation (21) for aqueous solutions is:

$$d\mu^{iL} = RT d(\ln a^{iL}) \quad \text{for all } i. \quad (24)$$

Now, all of the groundwork has been laid to derive some constitutive relations. This is accomplished by using Equation (13) for the water constituent, which may be written:

$$\int_{\mu_0^{\text{wL}}}^{\mu^{\text{wL}}} d\mu^{\text{wL}} = \mu^{\text{wL}} - \mu_0^{\text{wL}} = \mu^{\text{wG}} - \mu_0^{\text{wG}} = \int_{\mu_0^{\text{wG}}}^{\mu^{\text{wG}}} d\mu^{\text{wG}}. \quad (25)$$

Note that it is critical that the limits of integration correspond to the same equilibrium states. 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.

Substituting Equations (22) – (24) into (25) gives:

$$\int RT \frac{dP^{\text{wG}}}{P^{\text{wG}}} = \int \frac{V^{\text{L}}}{N^{\text{wL}}} dP^{\text{L}} - \int \frac{X^{\text{hL}}}{X^{\text{wL}}} RT d(\ln a^{\text{hL}}), \quad (26)$$

where the limits of integration are from some reference state to some final state. Now, by imposing physical constraints, Equation (26) may be used to develop constitutive relations. Notice that the first integral is purely a function of vapor pressure, and the last integral is a purely a function of salt concentration (because  $X^{\text{wL}} + X^{\text{hL}} = 1$ ). In principle, these integrals may be evaluated as functions of only one variable. However, the integrand of the liquid pressure integral is one over the molar density of water in the liquid. Commonly, this integrand is assumed to be constant (i.e., liquid density is constant) such as occurs for dilute solutions, and all three integrals may be evaluated to yield the dilute approximation (c.f. Burns, 2004). In general, and for non-dilute salt solutions, the integrand is not constant and is a function of multiple variables.

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.” Use of this assumption is consistent with the notion that salt concentration will dominate the system for high salt concentrations (e.g., Bear and Gilman, 1995), and this assumption can be shown to be unnecessary for dilute systems (Burns, 2004). Using Equations (23) and (24), the thermodynamic relation for non-dilute salt content over a flat interface is derived is:

$$d \ln (a^{\text{wL}}) = - \frac{X^{\text{hL}}}{X^{\text{wL}}} \ln (a^{\text{hL}}) \quad (27)$$

This is particularly convenient since chemists commonly develop relations describing the activity of water as a function of salt concentration.

By invoking the proposition of Guggenheim, Equation (26) is immediately reduced to:

$$RT \ln \left( \frac{P^{\text{wG}}}{a^{\text{wL}} P_{0\infty}^{\text{wG}}} \right) = \int \frac{V^{\text{L}}}{N^{\text{wL}}} dP^{\text{L}}. \quad (28)$$

Notice here that if the integrand is sufficiently close to constant, then the integral is trivial to evaluate. For zero salt concentration, it is easy to show that the psychrometric equation is recovered, and for dilute salt concentrations, the dilute approximation is also recovered (Burns, 2004). However, for the case of NaCl at 25 C, Heyrovská (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.

### 3. Vapor pressure for a Non-dilute Solution with Non-negligible Interface Curvature in an Unsaturated Porous Media

In order to determine a constitutive relationship for this general case, it becomes necessary to account for the effects of salt concentration on the integrand and the variable of integration for the liquid pressure integral in Equation (28). This will then allow the appropriate choice of integration limits. For this exercise, the physics imposed by porous media geometry are used.

Suppose the specific volume (analogously, density) is uniquely defined by the salt to water ratio and also assume the pressure-saturation curves are well-defined. 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. In general, the integration in (28) must occur from an initial state A to a final state B. It is convenient to integrate along the path ACB (see Figure 2), where path AC is a constant salt content path, and CB is a constant water content path. Letting A be the zero salt, flat interface condition (i.e.,  $0\infty$ ), the integrand is the zero salt specific volume of water, which may be assumed to be constant along the path AC. Equation (28) may be rewritten as:

$$RT \ln \left( \frac{P^{\text{wG}}}{P_{0\infty}^{\text{wG}}} \right) = RT \ln a^{\text{wL}} + \frac{V_0^{\text{L}}}{N_0^{\text{wL}}} (P_0^{\text{L}} - P_{0\infty}^{\text{L}}) + \int_C^B \frac{V^{\text{L}}}{N^{\text{wL}}} dP^{\text{L}} \quad (29)$$

Hereafter, the integral in Equation (29) 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

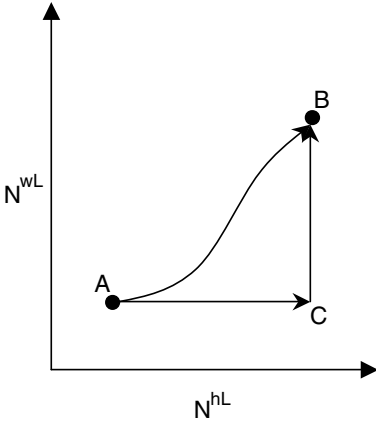


Figure 2. Diagram showing the change in state between two arbitrary states A and B, and another path AC followed by CB.

approximation to the integral in (28)). The **activity term** is self explanatory, and the term on the left-hand side of the equality is the desired resulting **vapor depression term**.

**4. 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:

$$dP^G - dP^L = d \left( \sigma^{LG} \frac{dA^{LG}}{dV^L} \right). \tag{30}$$

Recall that assumption 13 is precisely:

$$\left| \int_{0\infty}^B \frac{V^L}{N^{wL}} dP^L \right| \gg \left| \int_{0\infty}^B \frac{V^L}{N^{wL}} dP^G \right|. \tag{31}$$

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 (though not necessary) 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

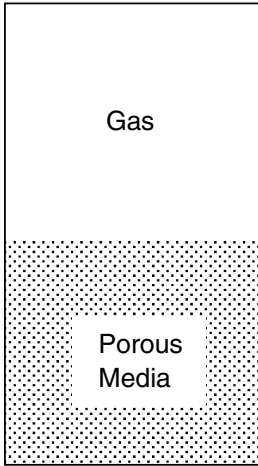


Figure 3. Schematic representation of a partially saturated porous media overlain by a gas filled space.

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 (31). 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. It may be shown for sodium chloride salt (Burns *et al.*, 2005b) that the integral term in (29) is only important for very dry conditions (this is a relative term that depends on soil texture, but even for strongly influenced fine textured soils, this refers to saturations <5%). Under dry conditions, the assumption that the soil gas is well connected to the atmosphere is valid for many near-surface geologic formations. Here, sufficient, though not necessary, conditions to satisfy Assumption 13 have been given. Assumption 13 is a very subtle condition, which will likely permit application of the derived relations to a broad range of applications for which gas pressures are consistent with the ideal gas assumption. Physically, the condition is requiring that changes in the liquid–gas interface are more strongly coupled to variations in liquid pressure than to variations in gas pressure. For the derivations in this paper, use of (30) and (31), allows use of the following approximation for evaluation of the integral in (29):

$$dP^L \cong -d\left(\sigma^{LG} \frac{dA^{LG}}{dV^L}\right). \quad (32)$$

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

$$P^L(S_0^L) = -\sigma_0^{\text{LG}} \frac{dA^{\text{LG}}}{dV^L}(S_0^L). \quad (33)$$

Notice that for porous media, Equation (33) is simply the water saturation–pressure relationship that is often experimentally determined. Define  $\tilde{P}^L \equiv P^L(S_0^L)$ , and note 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 (33) 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. In general, liquid pressure may be written:

$$P^L(N^{\text{hL}}, S^L) = \frac{\sigma^{\text{LG}}(N^{\text{hL}})}{\sigma_0^{\text{LG}}} \tilde{P}^L(S^L) = -\frac{\sigma^{\text{LG}}(N^{\text{hL}})}{\sigma_0^{\text{LG}}} \left( \sigma_0^{\text{LG}} \frac{dA^{\text{LG}}}{dV^L}(S^L) \right). \quad (34)$$

Noting that the integrand in the volume correction term in Equation (29) 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  $V^{\text{pore}} \equiv 1$  (units to be chosen based on available empirical relationships). Then saturation may be defined as  $S^L \equiv \frac{V^L}{V^{\text{pore}}}$ . Since  $V^{\text{pore}}$  is a constant, this relation allows the application of Assumption 12 to the saturation, so  $S^L = S^L(N^{\text{wL}}, N^{\text{hL}})$ . Since water content is constant in the volume correction term, the integral in (29) may be written as a function of the single variable, salt concentration.

$$\int_C^B \frac{V^L}{N^{\text{wL}}} dP^L = \int_0^{N^{\text{hL}}} \frac{S^L(N^{\text{hL}}) V^{\text{pore}}}{N^{\text{wL}}} d \left( \frac{\sigma^{\text{LG}}(N^{\text{hL}})}{\sigma_0^{\text{LG}}} \tilde{P}^L(S^L(N^{\text{hL}})) \right), \quad (35)$$

where the appropriate limits of integration are obviously from zero salt to the desired final salt concentration, and the implicit dependence of  $\tilde{P}^L$  on

salt concentration has been made explicit. The meaning and use of all of the terms in Equation (35) may be clarified by examination of an example calculation (see Burns 2004; or Burns et al. 2005b). Now, recognizing that Equation (34) is a constitutive relation for  $P^L$ , leads to the conclusion that Equation (29) 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:

$$P^{wG} = P_{0\infty}^{wG} a^{wL} \exp\left(\frac{V_0^L}{N_0^{wL} RT} (P_0^L - P_{0\infty}^L)\right) \times \exp\left(\frac{1}{RT} \int_0^{N^{hL}} \frac{S^L V^{\text{pore}}}{N^{wL}} d\left(\frac{\sigma_{0\text{LG}}^{LG}}{\sigma_0^{LG}} \tilde{P}^L\right)\right), \quad (36a)$$

$$P^L = \frac{\sigma_{0\text{LG}}^{LG}}{\sigma_0^{LG}} \tilde{P}^L, \quad \text{where } \tilde{P}^L = -\sigma_0^{LG} \frac{dA^{LG}}{dV^L}. \quad (36b)$$

#### 4.1. DERIVATIVES

The constitutive relations (36a) and (36b) 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 ( $\nabla P^L$  and  $\nabla P^{wG}$ , respectively). 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. Since the derivation is routine (see Burns, 2004), only the results are presented here for completeness of the theoretical development. These results are subsequently used in applications in Burns et al. (2005a, b). Since relations between salt concentration and volume must be taken from the literature (for use in applications), it is found that  $S_0^L$  (water saturation) and  $m$  (molality) are convenient variables. Subject to the fourteen assumptions above, the resulting equations are:

Differential of water vapor pressure

$$\frac{dP^{wG}}{d\cdot} = \left(\frac{\partial P^{wG}}{\partial m}\right) \frac{dm}{d\cdot} + \left(\frac{\partial P^{wG}}{\partial S_0^L}\right) \frac{dS_0^L}{d\cdot} \quad \text{with} \quad (37)$$

$$\frac{\partial P^{wG}}{\partial m} = P^{wG} \left( \frac{\partial (\ln a^{wL})}{\partial m} + \frac{\partial}{\partial m} \left( \frac{1}{RT} \int_C^B \frac{V^L}{N^{wL}} dP^L \right) \right), \quad (38a)$$

$$\frac{\partial P^{\text{wG}}}{\partial S_0^{\text{L}}} = P^{\text{wG}} \left( \frac{\partial}{\partial S_0^{\text{L}}} \left( \frac{V_0^{\text{L}}}{N_0^{\text{wL}} RT} (P_0^{\text{L}} - P_{0\infty}^{\text{L}}) \right) + \frac{\partial}{\partial S_0^{\text{L}}} \left( \frac{1}{RT} \int_C^B \frac{V^{\text{L}}}{N^{\text{wL}}} dP^{\text{L}} \right) \right). \quad (38b)$$

Differential of liquid pressure

$$\frac{dP^{\text{L}}}{d\cdot} = \left( \frac{\partial P^{\text{L}}}{\partial m} \right) \frac{dm}{d\cdot} + \left( \frac{\partial P^{\text{L}}}{\partial S_0^{\text{L}}} \right) \frac{dS_0^{\text{L}}}{d\cdot} \quad (39)$$

with

$$\frac{\partial P^{\text{L}}}{\partial m} = \frac{1}{\sigma_0^{\text{LG}}} \left( \tilde{P}^{\text{L}} \frac{\partial \sigma^{\text{LG}}}{\partial m} + \sigma^{\text{LG}} \frac{\partial \tilde{P}^{\text{L}}}{\partial m} \right), \quad (40a)$$

$$\frac{\partial P^{\text{L}}}{\partial S_0^{\text{L}}} = \frac{\sigma^{\text{LG}}}{\sigma_0^{\text{LG}}} \frac{\partial \tilde{P}^{\text{L}}}{\partial S_0^{\text{L}}}. \quad (40b)$$

## 5. 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 equation that would be given by neglecting the volume correction term in (29). 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 is valid, it is necessary to compute the value of the integral in Equation (29) and to compare the magnitude of the integral with the magnitude of the other terms. This is done in Burns (2005b) for sodium chloride.

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 can be shown to be reasonable for cases where sodium chloride salt gradients dominate in the region

of interest (Burns, 2004b) and is likely true for other salts of interests. Bear and Gilman's resulting equation is similar to the one derived here (assuming a negligible volume correction term) 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 which is generally assumed to be valid for dilute solutions. Bear and Gilman also have a temperature correction term that includes the latent heat of vaporization, while Olivella et al. and Nassar and Horton both compensate for temperature with empirical relations, but separate out the latent heats and other energy transfers for inclusion in energy conservation equations.

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 (29). The methodology developed herein results in the general relations Equations (36a) and (36b). 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 (36a, b), (38a, b), and (40a, b) 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.* (2005b), or for a more complete discussion, Burns (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 develop the general equations necessary to allow evaluation of when non-dilute effects are appreciable, the single concentration derivation was used for clarity.

The extension of these results to an-isothermal conditions (where changes in temperature occur via a quasi-static path) is of interest to environmental applications. Since it is possible to conduct the experiments necessary to define the above relations at multiple fixed temperatures, a surface in the  $n$ -dimensional space defined by the  $n$  state variables (where  $T$  is one of the variables) may be constructed, allowing an empirical functional form for the temperature dependence to be derived. This is analogous to the temperature correction used by Olivella et al. and the net result of this

procedure is a constitutive relation for mass exchange between the phases for an-isothermal conditions.

## 6. 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.

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