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REPORT

THERMODYNAMIC EQUILIBRIUM BE-  
TWEEN ICE AND WATER IN POROUS  
MEDIA

BY J.P.G.LOCH

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## PREFACE

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ABSTRACT

A derivation is given for the equation of thermodynamic equilibrium between ice and water in porous media. The equation accounts for a difference between the pressure of the ice phase and the total potential (in pressure units) of the water phase. Emphasis is laid on the distinction between this total potential and the hydrostatic pressure and osmotic pressure of the unfrozen soil solution. The difference between the hydrostatic pressure of the solution and the ice pressure is accounted for by the ice-water interfacial tension, as expressed by the generalized form of Laplace's equation. The resulting generalized form of the Clausius-Clapeyron equation is an equilibrium expression, whereas the Laplace equation only expresses a definition, valid under any circumstances. It is emphasized that all influences of the pore wall, whether working via the diffuse double layer or not, and which cause the liquid to have lower Gibbs free energy than the equilibrium liquid at the same temperature, are collected in the osmotic pressure term.

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*INTRODUCTION*

Recently an equation has been proposed for the thermodynamic equilibrium between ice and water in porous media (Miller, 1973; Kay and Groenevelt 1974). The equation allows for a difference in pressure between the two phases and has been called a generalized form of the Clausius-Clapeyron equation. The best justification for this equation was given by Miller, when he referred to the so-called phase barrier principle as treated by Lewis and Randall (1961) for a vapor/liquid system. A derivation of this equation for ice/water equilibrium in porous media seems lacking. Saetersdal (1973) expressed doubts about an equilibrium with differences in pressure between the phases. Rosenqvist (1971) illustrated in words that the equilibrium exists under a difference in pressure and he pointed out that the classical form of the Clausius-Clapeyron equation is not valid here. In the following we will derive the proposed equilibrium equation from basic thermodynamics.

*THEORETICAL DERIVATIONS*

A fundamental equation of thermodynamics gives the differential of the Gibbs Free Energy of a mono-component system as

$$dG = - SdT + Vdp \tag{1}$$

in which S = entropy of the system

T = absolute temperature

V = volume

p = pressure



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When the system consists of a mixture of components, for instance a binary system of salt and water, the expression for  $dG$  of the solution takes a more complicated form:

$$dG = - SdT + Vdp + \mu_s dn_s + \mu_w dn_w \quad (2)$$

in which  $n_s$  and  $n_w$  are the mass (in grams) of the components salt and water in the solution.

and  $\mu_s$  and  $\mu_w$  are respectively the chemical potentials of the salt and the water (on a mass basis).

The variable  $\mu_j$  needs some explanation. It is usually defined as,

$$\mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T, p, \mu_k, \mu_l, \dots} \quad (3)$$

for a mixture of components  $j, k, l, \dots$

In most cases  $N_j$  is the number of moles of component  $j$  in the system. In Eq. (2) we have chosen  $\mu_j$  to be the change in the Gibbs free energy of the solution due to a change of 1 gram in the amount of component  $j$  present.

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For the mixture we then know that

$$G = n_s \mu_s + n_w \mu_w \tag{4}$$

so that

$$dG = n_s d\mu_s + \mu_s dn_s + n_w d\mu_w + \mu_w dn_w \tag{5}$$

Combination of Eqs. (2) and (5) gives the Gibbs-Duhem equation

$$n_w d\mu_w + n_s d\mu_s = - SdT + Vdp \tag{6}$$

so

$$n_w d\mu_w = - SdT + Vdp - n_s d\mu_s \tag{7}$$

The chemical potential of the salt component can be written as (e.g. Castellan, 1966),

$$\mu_s = \mu_s^0(p, T) + \frac{RT}{M_s} \ln x_s \tag{8}$$

in which  $\mu_s^0(p, T)$  is the chemical potential for the pure salt at the same pressure and temperature.

$R$  = gas constant

$M_s$  = molecular weight of the salt

$x_s$  = mole fraction of the salt

$$x_s = \frac{N_s}{N_w + N_s} \approx \frac{N_s}{N_w} = \frac{M_w}{M_s} \frac{n_s}{n_w} \tag{9}$$

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Substitution of (9) into (8) gives,

$$\mu_s = \mu_s^o(p, T) + \frac{RT}{M_s} \ln \frac{M_s n}{M_s} + \frac{RT}{M_s} \ln \frac{n_s}{n_w} \quad (10)$$

and

$$d\mu_s = \frac{RT}{M_s} \cdot \frac{1}{n_s} dn_s$$

so

$$n_s d\mu_s = RTd \left( \frac{n_s}{M_s} \right) \quad (11)$$

Substitution of (11) into (7) gives,

$$d\mu_w = - \bar{S}dT + \bar{V}dp - RTd \left( \frac{n_s}{M_s n_w} \right) \quad (12)$$

in which  $\bar{S}$  = entropy of the solution per gram of water

$\bar{V}$  = volume of the solution per gram of water.

Rewriting Eq. (12) gives,

$$d\mu_w = - \bar{S}dT + \bar{V}dp - \bar{V}RTd \left( \frac{n_s}{M_s n_w} \right) \quad (13)$$

The osmotic pressure of dilute solutions is written as

$$\Pi = RTc = RT \frac{n_s}{M_s n_w \bar{V}} \quad (14)$$

where c is the salt concentration in moles per unit volume.

So we write Eq. (13) as,

$$d\mu_w = - \bar{S}dT + \bar{V}dp - \bar{V}d\Pi \tag{15}$$

Equation (15) gives the change in the chemical potential of the component water (on a mass base) due to a change in temperature, T, hydrostatic (or tensiometer-)pressure, p, and osmotic pressure,  $\Pi$ . We rewrite this equation as,

$$d\mu_w = - \bar{S}dT + \bar{V}dp_w \tag{16}$$

in which  $p_w$  is defined as

$$p_w = p - \Pi \tag{17}$$

$p_w$  is often called the "total potential" (energy on a volume basis) of the component water. It is the pressure which one would measure in a soil water solution with a tensiometer if the tensiometer cup were a perfect semipermeable membrane.

Since  $\bar{S} = \frac{\bar{H}}{T}$ , in which  $\bar{H}$  is the enthalpy per unit mass of the solution, integration of Eq. (16) between a reference level ( $T = T_o, p_w = 0$ ) and the actual temperature  $T = T_o + \Delta T$  and pressure  $p_w$ , gives

$$\mu_w = - \bar{H} \ln\left(1 + \frac{\Delta T}{T_o}\right) + \bar{V}p_w \tag{18}$$

or for small  $\Delta T$ ,

$$\mu_w = - \frac{\bar{H}\Delta T}{T_o} + \bar{V}p_w \tag{19}$$

In these equations  $T_o$  is the melting point of the pure solvent and  $\Delta T$  is the actual temperature in  $^{\circ}C$ .

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When we consider equilibrium between this solution and ice, then it is *this*  $\mu_w$  which one has to equate with  $\mu_i$ . This becomes clear when one carefully looks at the definition of  $\mu_w$ , as given below Eq. (3) and realizing that ice excludes solutes.

The condition for equilibrium between this solution and ice is,

$$\mu_w = \mu_i \tag{20}$$

Knowing that ice has no inclusions of solutes in it, we can write, *for bulk ice*, an equation similar to Eq. (15) but without the last term. This results in,

$$(\mu_i)_{\text{bulk}} = - \frac{\bar{H}_i \Delta T}{T_0} + \bar{V}_i p \tag{21}$$

Ice in fine pores is different from bulk ice in that its surface free energy plays a large (additional) role in its chemical potential (the surface area is large relative to its mass). So for pore ice we have to write (Everett, 1961),

$$\mu_i = (\mu_i)_{\text{bulk}} + \partial G_{\text{surface}} / \partial n_i \tag{22}$$

in which

$$G_{\text{surface}} = A \sigma_{iw} \tag{23}$$

where A = surface area

$$\sigma_{iw} = \text{interfacial energy ice/water}$$

The mass of the ice,  $n_i$ , can be written as,

$$n_i = V/\bar{V}_i \quad (24)$$

where  $V$  is the volume of the ice.

so

$$\frac{\partial G_{\text{surface}}}{\partial n_i} = \sigma_{iw} \bar{V}_i \frac{\partial A}{\partial V} \quad (25)$$

And Eq. (22) becomes,

$$\mu_i = - \frac{\bar{H}_i \Delta T}{T_o} + \bar{V}_i p + \bar{V}_i \sigma_{iw} \frac{\partial A}{\partial V} \quad (26)$$

Equilibrium exists when,

$$- \frac{\bar{H}}{T_o} \Delta T + \bar{V} p_w = - \frac{\bar{H}_i}{T_o} \Delta T + \bar{V}_i p + \bar{V}_i \sigma_{iw} \frac{\partial A}{\partial V} \quad (27)$$

Rearranging gives,

$$\bar{V}_i (p + \sigma_{iw} \frac{\partial A}{\partial V}) - \bar{V} p_w = - (\bar{H} - \bar{H}_i) \Delta T / T_o \quad (28)$$

$$\bar{H} - \bar{H}_i = L_f$$

where  $L_f$  = heat of fusion per unit mass.

In the first term of Eq. (28) we can define,

$$p + \sigma_{iw} \frac{\partial A}{\partial V} = p_i \quad (29)$$

which is a generalized form of the Laplace equation.

Now Eq. (28) becomes,

$$\bar{V}_i p_i - \bar{V} p_w = - \frac{L_f}{T_o} \Delta T \quad (30)$$

It should be emphasized that in Eqs. (17), (26) and (29)

$p$  is the hydrostatic pressure of the solution.



Equations (29) and (30) have their analogous forms in respectively the Laplace equation for the curved interface liquid/gas and the Clausius-Clapeyron equation for the equilibrium between bulk ice and pure bulk water. It may be inappropriate to call Eq. (30) a Clausius-Clapeyron equation, but it certainly correctly describes the equilibrium between ice and water solution in porous media. In fact, the best equation to be used is (28).

*INTERPRETATION OF THE TERM  $\Pi$*

The meaning of  $\Pi$  in this discussion can be generalized. We called  $\Pi$  the osmotic pressure of the solution. In a porous medium the solution is mainly the liquid film between mineral particle walls and the ice. In part it is also "islands" of liquid in pores, too narrow for ice to be stable in. In the films solutes are close enough to the pore wall to be strongly under the influence of the electrostatic force field emanating from the charged wall surface. In modern soil physics it is agreed among many that the combination of charged pore wall and solute ions constitutes a so called diffuse double layer. This diffuse double layer involves in most soils an elevated cation concentration, which, in clays, is responsible for the swelling phenomenon. In clays the diffuse double layer creates the necessary "suction" for water intake. In the frozen system

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the "suction" for water intake for heave is quite analogous to the swelling clay system. The adsorbed cations represent the osmotic pressure, so that the "suction" for water intake is  $p_w = p - \Pi$ .

For those who do not agree with the theory of the diffuse double layer and/or those who suspect other or additional adsorption forces to be responsible for water intake, we can generalize  $\bar{V} \cdot \Pi$  such that it stands for all these forms of energy together.

*THE MEANING OF EQUILIBRIUM*

Equation (30) is an equation for thermodynamic equilibrium. The equilibrium is disturbed when, due to changes in any of the variables  $T, p, \Pi$  or  $r$ , the situation

$$\mu_i \neq \mu_w \text{ is created.}$$

When ice is being formed in situ,  $\mu_i < \mu_w$ . This means that,

$$\bar{V}_i p_i - \bar{V}_w p_w < - \frac{L_f}{T_0} \Delta T \tag{31}$$

This is for instance the case when the temperature drops locally. Then, if  $p_i$  stays constant,  $p_w$  is less negative than one would predict from the equilibrium equation. It is the case when we deal with a penetrating frost front.



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$\mu_i < \mu_w$  also prevails when the radius of an ice/water interface is larger than the equilibrium radius. If this is a spherical particle in supercooled bulk water in a beaker-glass, this particle will continue to grow, so that  $r$  continues to increase and the ice will spontaneously fill the whole beakerglass.

$\mu_i < \mu_w$  with spontaneous local ice formation would also prevail when suddenly  $p_i$  or  $\Pi$  are dropped.

From this reasoning we also derive that Eq. (29) is not necessarily an equilibrium equation. It is only a definition of  $p_i$ , which is valid under all circumstances. As Rosenqvist (1971) pointed out, one should be careful to ascribe the surface energy to  $p_i - p$  instead of  $p_i - p_w$ .

Equation (30) represents *local* equilibrium. It is valid everywhere in the porous medium if at each *locality*  $p$ ,  $\Pi$ ,  $r$  and  $T$  do not change in time. This does not mean that these variables cannot change with location. We can, for instance, have a steady state temperature distribution with a gradient in temperature. In such a situation we derive from Eq. (30) that there exists a gradient in  $p_w$  across the system, which does not change with time. And since  $\text{grad } p_w$  is the driving force for water movement (Darcy's law), we get a steady flow of mass through our frozen system. This is the case in a freely heaving system, in which the frost front does not

penetrate further. It is obvious that then we can express the steady mass flow rate as a function of the temperature gradient (and of the gradient of  $p_i$  if it exists) - see Loch and Kay, 1977.

To emphasize again what was said before: Eq. (30) is not valid during frost front penetration, during increasing heaving pressure (=  $p_i$  at the ice lens) or during decreasing suction. Equation (30) was recently verified experimentally by Biermans et.al. (1976) who showed that, in order to stop steady water intake into their system at a constant temperature  $\Delta T^{\circ}\text{C}$  and ice pressure  $p_i$ , they had to reduce the pressure in their equilibrium reservoir to  $p_w$ .

#### *SUMMARY AND CONCLUSIONS*

A thermodynamic derivation was given of a generalized form of the Clausius-Clapeyron equation, applicable to ice/water equilibrium in frozen porous media. A careful distinction was made between various pressure terms in the equation. In the process of this derivation evolved a generalized form of the Laplace equation, which accounts for the ice/water interfacial energy.

It was pointed out that the former equation is an expression, only valid under thermodynamic equilibrium, whereas the latter is a definition, valid under non-equilibrium conditions as well.



It was emphasized under what conditions we have thermodynamic equilibrium; this can be a local equilibrium, allowing for gradients in the thermodynamic variables.

Finally it was emphasized that all influences of the pore wall on the system's liquid water can be symbolized by an osmotic pressure.

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