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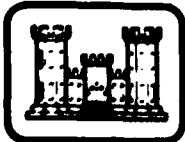
Samuel C. Colbeck

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UNITED STATES ARMY  
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**PREFACE**

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## NOMENCLATURE

$A$	Helmholtz free energy	$T$	temperature (K)
$C$	number of components	$T_i$	temperature of $i$ th phase (K)
$F$	Gibbs free energy	$T_m$	melting temperature ( $^{\circ}\text{C}$ )
$g$	acceleration due to gravity	$T_0$	reference temperature (K)
$h$	height above a free surface	$U$	internal energy
$H$	enthalpy	$v$	specific volume
$L$	latent heat	$v_i$	specific volume of $i$ th phase
$L_e$	latent heat of evaporation	$V$	volume; also molar volume
$m$	mass	$W$	work
$N_a, N_b$	mole fractions	$x_a$	mole fraction of solvent
$p$	pressure	$x_b$	mole fraction of solute
$p_i, p_j$	pressure of phases $i$ and $j$	$\theta$	contact angle
$p_0$	reference pressure	$\mu$	chemical potential
$P$	number of phases	$\mu_i$	chemical potential of $i$ th phase
$Q$	heat	$\pi$	osmotic pressure
$r_1, r_2$	radii of curvature of two mutually perpendicular sections	$\rho$	density
$r_p$	radius of particle	$\rho_i$	density of $i$ th phase
$r_v$	radius of a liquid vein	$\sigma_{ij}$	interfacial energy between $i$ th and $j$ th phases
$r_{\text{film}}$	mean radius of curvature of film	$\phi$	solid angle of portion of surface
$r_{ij}$	mean radius of curvature of phase boundary		
$R_1, R_2$	principal radii of curvature		
$S$	entropy		
$S_i$	entropy of $i$ th phase		
		<b>Subscripts</b>	
		$a, b, l, j$	indices for phases or components
		$g, l, s$	gas, liquid, solid, respectively

# INTRODUCTION TO THE BASIC THERMODYNAMICS OF COLD CAPILLARY SYSTEMS

Samuel C. Colbeck

## INTRODUCTION

The concepts of thermodynamics apply to a wide variety of cold regions materials in which radius of curvature effects are important (for example, frozen soils, snow, and ice fog). The basic principles applicable to these and many other important phenomena are reviewed here, and some example applications are given.

This report is intended to serve as a brief introduction or review of the elements of thermodynamics which are applicable to cold regions materials. References to additional sources of information are provided, since only an outline of thermodynamics is given here.

## THERMODYNAMIC PRINCIPLES

J. Willard Gibbs (1839-1903) greatly increased our understanding of thermodynamics, especially the thermodynamics of reversible processes (Gibbs 1928). Some of his most important contributions are reviewed here.

### The first law

The first law of thermodynamics expresses energy balance as

$$dU = dQ + dW \quad (1)$$

where  $dU$  is the change in internal energy of the system,  $dQ$  is a small amount of heat energy entering the system, and  $dW$  (usually taken as  $-pdV$ ) is the work done on the system by a change of volume  $dV$  against the pressure  $p$ . This equation is inexact since  $\int_A^B pdV$

depends on the path followed in going from  $A$  to  $B$  (except in reversible processes, where the integral is independent of path). We define enthalpy  $H$  as

$$H = U + pV. \quad (2)$$

Hence, another form of the first law is

$$\delta Q = dH - Vdp. \quad (3)$$

### The second law

From the second law of thermodynamics

$$\oint \frac{dQ}{T} < 0 \quad (4)$$

where the integration is over a closed path (that is, the integration starts and stops at the same point). The inequality applies if the process is irreversible (for example, losses due to friction or strain energy) and the equality applies if the process is completely reversible (for example, the adiabatic expansion and contraction of a perfect balloon). When a reversible process occurs, the integral must be independent of the path followed from  $A$  to  $B$ . We define entropy  $S$  as

$$S_B - S_A > \int_A^B \frac{dQ}{T} \quad (5)$$

where  $A$  and  $B$  are any two positions. Again, the inequality applies to an irreversible process. Therefore, entropy must always increase in any irreversible process in an isolated system. (In other words, the world is filling up with entropy!)

### Entropy maximum

Unless the system is in equilibrium, entropy will be increasing according to eq 5. Therefore, entropy is at its maximum at equilibrium. From eq 1 and 5,

$$\delta S > \frac{\delta U + p\delta V}{T} \quad (6)$$

or

$$\delta U + p\delta V - T\delta S < 0. \quad (7)$$

At constant volume ( $\delta V = 0$ ),

$$\delta U - T\delta S < 0 \quad (8)$$

or at constant volume and temperature,

$$\delta(U - TS) < 0. \quad (9)$$

The expression  $U - TS$  is the definition of the Helmholtz free energy  $A$ , so  $\delta A < 0$ . Accordingly, a system will move toward lower values of  $A$ , and at equilibrium  $A$  will assume a minimum.

If the system is at constant temperature and pressure but variable volume, then eq 7 is rewritten as

$$\delta(U + pV - TS) < 0. \quad (10)$$

The Gibbs free energy  $F$  is defined as

$$F = U + pV - TS \quad (11)$$

or

$$F = H - TS \quad (12)$$

or

$$F = A + pV. \quad (13)$$

In this system ( $\delta p = \delta T = 0$ ), the Gibbs free energy is at its minimum at equilibrium. It follows that when liquid, gaseous, and/or solid phases are in equilibrium, their free energies are equal. If they are not equal, the phase with the largest value of  $F$  will give up mass to the other phases until equilibrium is established.

### Maxwell's relations

We can derive a very useful form of the Gibbs equation. Differentiating eq 11

$$dF = dU + p\delta V + V\delta p - T\delta S - S\delta T \quad (14)$$

and rewriting eq 7 for a reversible process

$$dU + p\delta V - T\delta S = 0 \quad (15)$$

we find a very general relation

$$dF = V\delta p - S\delta T. \quad (16)$$

In a single-component system of two or three phases (for example, vapor, liquid and solid  $H_2O$ ), eq 16 can be applied to each phase or to the whole system at once. When the phases are in equilibrium, the free energies of the phases are equal.

### Chemical potential

If more than one component exists (for example,  $H_2O$  and  $SiO_2$ ), eq 16 can be generalized. Gibbs defined the chemical potential (or partial molal free energy)  $\mu$  as

$$\mu_{ab} = \frac{\partial F_b}{\partial m_{ab}} \quad (17)$$

where  $m$  is the number of moles per unit volume,  $a$  is the component,  $b$  is the phase. Phase changes occur spontaneously such that material is transferred from a phase at a high potential to a phase at a low potential. Equilibrium occurs when the potential of each component is the same in each phase. In general,

$$dF = -S\delta T + V\delta p + \sum_a \mu_a \delta m_a. \quad (18)$$

### Gibbs-Duhem equation

In another form, called the Gibbs-Duhem equation ( $dF = 0$  at equilibrium),

$$S\delta T - V\delta p + \sum_a m_a \delta \mu_a = 0. \quad (19)$$

In a system of ice, liquid water and moist air, there are two components (air and water), but the air component can be ignored. (If it is included, only the partial pressure of the dry air need be specified. Air dissolved in the liquid phase decreases the melting temperature by  $0.0024^\circ C$  when the liquid is saturated.) Then the Gibbs-Duhem equation reduces to a simple relation which is commonly used,

$$d\mu = v\delta p - S\delta T \quad (20)$$

where  $\mu$ ,  $v$  and  $S$  are expressed per unit mass. Equation 20 can be applied to each phase separately. Then

$$d\mu_i = v_i \delta p_i - S_i \delta T \quad (21)$$

where  $i$  is the solid, liquid or vapor phase. When only one component exists,

$$\mu_i = \frac{\partial F_i}{\partial m_i} \quad (22)$$

At equilibrium,  $F$  is at its minimum, so mass transfer will occur between the phases (mass will transfer away from phases of high potential) until the potential is the same for all phases. Thus, at equilibrium between phases  $i$  and  $j$ ,

$$\mu_i = \mu_j \quad (23)$$

#### Phase rule

Gibbs' phase rule tells us how many variables must be specified at equilibrium. When there are no chemical reactions, and  $C$  components (for example water, air,  $\text{SiO}_2$ , salts) and  $P$  phases (for example, solid, liquid, vapor) are considered independently, there are  $P(C+1)$  variables which must be specified at equilibrium. Since the phases are in equilibrium, there are  $C(P-1)$  restrictions because the chemical potentials must be equal. Also, since the temperatures of each phase must be equal, there are  $P-1$  additional restrictions. Thus, for a system with curved interfaces, there are  $P(C+1) - C(P-1) - (P-1)$  or  $C+1$  variables which must be specified at equilibrium. This is the number of "degrees of freedom" or the "variance" of the system. Note that for flat interfaces there are  $P-1$  additional restrictions, since the pressures must also be equal. Thus, for non-capillary systems, there are  $C+2-P$  degrees of freedom.

#### SURFACE FORCES

Since capillary systems have curved interfaces between the solid, vapor and/or liquid phases, pressure differences can occur among the phases. These pressure differences must be included in the derivation of the governing equations. Laplace's equation describes the pressure difference between two adjoining phases; it is derived here because of its basic importance in cold capillary systems. The pressure difference arises from the tension in the interfacial layer (surface free energy or surface tension) and from the curvature of the interface in much the same way that a stretched balloon supports a pressure difference between the inside air and the outside air.

Figure 1 depicts a curved surface between two phases ( $i$  and  $j$ ). Let the distance along the surface from the point  $P$  to the edge of the surface be everywhere equal to  $\rho$ . Let the two sections  $ABN$  and  $CDN$  be mutually perpendicular. Then the radii of curvature in these two sections ( $r_1$  and  $r_2$ ) completely describe the surface separating the phases  $i$  and  $j$ . According to Euler's theorem,

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{1}{R_1} + \frac{1}{R_2} \quad (24)$$

where  $R_1$  and  $R_2$  are the principal radii of curvature of the surface separating these two phases. The mean radius of curvature ( $r_{ij}$ ) is defined as

$$\frac{2}{r_{ij}} = \frac{1}{R_1} + \frac{1}{R_2} \quad (25)$$

Consider an element of length  $\delta l$  of the perimeter at  $A$ . The component along  $PN$  of the force on the element at  $A$  is  $\sigma_{ij} \delta l \sin \phi$  where  $\sigma_{ij}$  is the surface energy between phases  $i$  and  $j$ . Since  $\phi$  is small,

$$\sin \phi \approx \phi \approx \frac{\rho}{r_1} \quad (26)$$

Thus, the force along  $PN$  due to this element is  $\sigma_{ij} (\rho/r_1) \delta l$  and is positive in the direction of phase  $i$ . At points  $C$  and  $D$  there are similar forces equal to  $\sigma_{ij} (\rho/r_2) \delta l$ . Integrating around the perimeter of this section, we find that the total force directed towards phase  $i$  is  $\pi \rho^2 \sigma_{ij} [(1/r_1) + (1/r_2)]$ . This must be balanced by a pressure difference between the phases, or

$$\pi \rho^2 (p_i - p_j) = \pi \rho^2 \sigma_{ij} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (27)$$

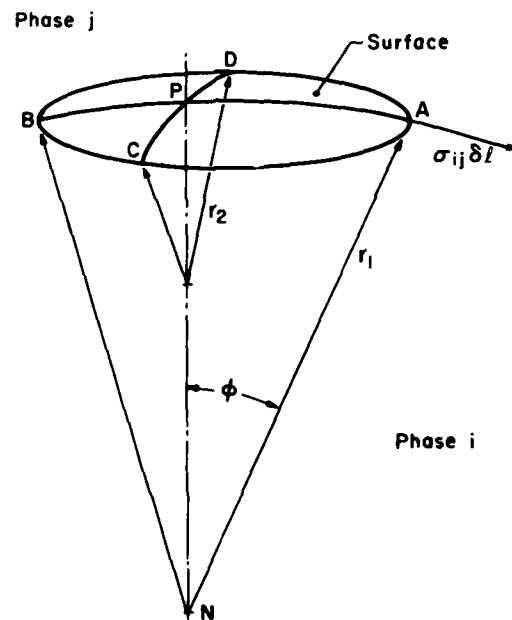


Figure 1. Portion of the surface dividing phase  $i$  (below) from phase  $j$  (above).

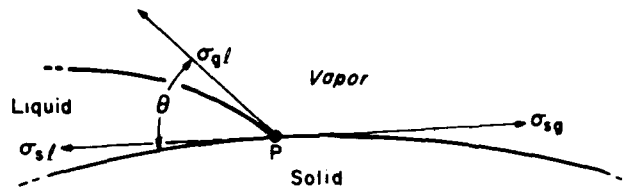


Figure 2. Force equilibrium at a point of liquid-vapor contact on a solid surface.

or

$$p_i - p_j = \sigma_{ij} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (28)$$

or finally, Laplace's equation,

$$p_i - p_j = \frac{2\sigma_{ij}}{r_{ij}} \quad (29)$$

where  $r_{ij}$  is the mean radius of curvature between phases  $i$  and  $j$ . By convention, we call  $r_{ij}$  positive when phase  $i$  is on the concave side of the interface.

Now consider the line of contact of three adjacent phases. Summing forces along the tangent to the surface at the point of contact  $P$  in Figure 2,

$$\sigma_{sg} = \sigma_{sl} + \sigma_{gl} \cos \theta. \quad (30)$$

This is Young's equation. Since for most materials the contact angle ( $\theta$ ) is small (that is,  $\cos \theta \approx 1$ ),

$$\sigma_{sg} \approx \sigma_{sl} + \sigma_{gl} \quad (31)$$

or  $\sigma_{sg}$  is generally much greater than either  $\sigma_{sl}$  or  $\sigma_{gl}$ . Surface energies  $\sigma_{sg}$  and  $\sigma_{sl}$  cannot be measured directly but must be deduced by methods such as measurement of  $\theta$  and  $\sigma_{gl}$  or grain boundary observation.

There is some controversy over the correct interpretation of  $\sigma_{sg}$  and  $\sigma_{sl}$ . In the derivation of Laplace's equation (eq 29), we assumed that only isotropic stresses (or pressures) occur in the phases. Therefore, the equation may only be applied in the absence of deviatoric stress; application to solids must be done carefully.

## GENERAL APPLICATIONS

### Clausius-Clapeyron equation

For a liquid and solid with a flat surface in common, eq 21 shows that

$$d\mu_s = v_s dp_s - S_s dT_s \quad (32)$$

and

$$d\mu_l = v_l dp_l - S_l dT_l.$$

The  $d\mu$ 's vanish at equilibrium. For a flat surface,  $p_l = p_s$ , and from eq 5, the difference in entropy at constant temperature is related to the latent heat of fusion  $L$  (usually assumed to be constant) by

$$S_l - S_s = L/T. \quad (33)$$

Thus,

$$(v_s - v_l) dp + (S_l - S_s) dT = 0$$

or

$$(v_l - v_s) dp = L (dT/T).$$

Integrating from  $p = 0$  (gauge) and  $T = T_0$  (273.15K) and assuming that  $L$  is not dependent on pressure or temperature,

$$\ln \frac{T}{T_0} = \frac{v_l - v_s}{L} p \quad (34)$$

where  $T$  and  $T_0$  are in kelvins. We define the melting temperature  $T_m$  in  $^{\circ}\text{C}$  as

$$T_m (^{\circ}\text{C}) = T (\text{K}) - T_0 (\text{K}). \quad (35)$$

Now

$$\begin{aligned} \ln \frac{T}{T_0} &= \ln \frac{T_m + T_0}{T_0} \\ &= \ln(1 + T_m/T_0) \end{aligned}$$

or since  $T_m \ll T_0$ ,

$$\ln \frac{T}{T_0} \approx \frac{T_m}{T_0}. \quad (36)$$

Combining eq 34 and 36 to get the Clausius-Clapeyron equation,

$$T_m = \frac{T_0}{L} \left( \frac{1}{\rho_l} - \frac{1}{\rho_s} \right) p \quad (37)$$

where the density  $\rho$  is the inverse of the specific volume  $v$ . For ice in contact with liquid water,

$$T_m \approx -0.00736 p \text{ (}^\circ\text{C/bar)}.$$

Since  $\rho_l > \rho_s$ , the melting temperature of water decreases with increasing pressure. This is probably the best known result of phase equilibrium thermodynamics.

#### Kelvin's equation

For liquid and vapor in contact at a constant temperature at equilibrium, eq 21 gives

$$\begin{aligned} v_g dp_g &= v_l dp_l \\ v_g dp_g &= v_l dp_l - v_l dp_g + v_l dp_g \\ (v_g - v_l) dp_g &= v_l (dp_l - dp_g). \end{aligned} \quad (38)$$

Using  $v_g \gg v_l$  and Laplace's equation (eq 29),

$$v_g dp_g = v_l d \left( \frac{2\sigma_{gl}}{r_{lg}} \right) \quad (39)$$

where  $r_{lg}$  is positive when measured from the liquid side of the interface.

For one mole of a perfect gas,

$$v_g p_g = RT \quad (40)$$

so

$$RT \frac{dp_g}{p_g} = v_l d \left( \frac{2\sigma_{gl}}{r_{lg}} \right). \quad (41)$$

For a flat interface,  $r_{lg}$  is infinite and the pressure is  $p_0$ . Thus eq 41 can be integrated to give Kelvin's equation

$$\ln \frac{p_g}{p_0} = \frac{v_l}{RT} \frac{2\sigma_{gl}}{r_{lg}}. \quad (42)$$

This shows that the vapor pressure increases as  $r_{lg}$  decreases. Thus, large droplets of water in the atmosphere have lower vapor pressures than small droplets, and the larger droplets tend to grow at the expense of the smaller droplets (that is, the small droplets evaporate because of their large vapor pressure, while the vapor condenses on the large droplets).

If the radius of curvature  $r$  is measured from the air side of the interface,

$$\ln \frac{p_g}{p_0} = - \frac{v_l}{RT} \frac{2\sigma_{gl}}{r_{gl}} \quad (43)$$

In a capillary system, smaller pores have smaller (but positive) values of  $r_{gl}$  and lower vapor pressures. Thus the larger pores are preferential sites for evaporation.

#### Capillary rise

In a capillary system, gravity must be considered, because the system height is large compared to the size of a meniscus. When the liquid is connected throughout the pore space,

$$p_l = p_0 - \rho_l gh \quad (44)$$

where  $h$  is the height above a free surface ( $p_0 = p_l = p_g$  at the free surface) and  $g$  is the acceleration due to gravity. From eq 21 for a capillary system at a constant temperature at equilibrium,

$$v_g dp_g = v_l dp_l$$

so

$$v_g dp_g = v_l (-\rho_l g dh).$$

Using  $v_l = (1/\rho_l)$  and eq 40,

$$RT \frac{dp_g}{p_g} = -g dh.$$

Integrating from 0 to  $h$  and  $p_0$  to  $p_g$ ,

$$\ln \frac{p_g}{p_0} = - \frac{g}{RT} h \quad (45)$$

or

$$p_g = p_0 \exp(-gh/RT). \quad (46)$$

Thus the vapor pressure decreases with height above a free surface. This is an alternate form of Kelvin's equation.

Consider the vapor pressure  $p_g$  as constant in a capillary system and let  $p_g = p_l = p_0$  at a free surface. Above the free surface,  $p_l$  decreases according to eq 44, while  $p_g$  is nearly constant. Then

$$p_g - p_l = p_g - (p_0 - \rho_l gh)$$

or

$$p_g - p_l = \rho_l gh. \quad (47)$$

Since  $\rho_l gh > 0$ ,  $p_g - p_l > 0$ . By Laplace's equation,

$2\sigma_{gl}/r_{gl} < 0$ ; hence,  $r_{gl} > 0$ . In other words, the vapor/liquid interface must have a positive radius of curvature.

#### Menisci and grains

In a meniscus between two rounded particles (Fig. 3),  $r_{gl} > 0$ , but a liquid film cannot cover the particle without violating this condition. The mean curvature is given by

$$\frac{2}{r_{gl}} = \frac{1}{r_1} - \frac{1}{r_2} \quad (48)$$

where  $r_1$  and  $r_2$  are the principal radii. Both are positive values as long as  $1/r_2$  is subtracted from  $1/r_1$ . Remember,  $r_{gl}$  is measured from the vapor side. However, if a film of water surrounds the grain of radius  $r_p$ , the mean radius of the film is given approximately by

$$\frac{2}{r_{film}} = -\frac{1}{r_p} - \frac{1}{r_p} \quad (49)$$

or

$$r_{film} = -r_p \quad (50)$$

Thus  $r_{film} < 0$ , which violates the condition  $r_{gl} > 0$ . Therefore, if a film exists, it must not have the properties of a liquid; that is, it can support elastic stresses.

#### Dissolved impurities

When another component exists in the form of a dissolved solid, eq 19 must include its mass and chemical potential. At equilibrium the chemical potentials of the two components are equal, but the mass of the dissolved solid must still be considered. In effect, another term is added to equations like eq 37 and 42. This term reduces the equilibrium temperature by an amount which depends on the quantity of the impurity and the particular geometry of the system.

In soil science it is popular to describe the effect of dissolved salts using the term "osmotic pressure." The effect of salts (at constant temperature and pressure) is to decrease the free energy. This decrease can be restored at a constant temperature by raising the pressure an amount  $\pi$ ; that is, a pure liquid will be in equilibrium with a solution if the solution is at an osmotic pressure  $\pi$  higher than that of the pure liquid.

For a pure liquid, the free energy change with pressure is

$$\Delta F = RT \ln p/p_0 \quad (51)$$

In general, the dependence of free energy at constant

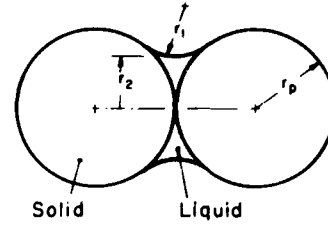


Figure 3. Liquid meniscus between two rounded particles.

temperature is expressed by

$$\left(\frac{\partial F}{\partial p}\right)_T = V \quad (52)$$

where  $V$  is the volume per mole. Thus for a pressure increase  $\pi$ ,

$$\Delta F = V\pi \quad (53)$$

Adding eq 51 and eq 53 so that the decrease (due to salinity) and the increase (due to pressure) balance,

$$\pi + \frac{RT}{V} \ln(p/p_0) = 0 \quad (54)$$

From Raoult's observations,

$$p/p_0 = x_a \quad (55)$$

where  $x_a$  is the mole fraction of solvent. The total fraction is

$$1 = x_a + x_b \quad (56)$$

where  $x_b$  is the mole fraction of solute. For dilute solutions it immediately follows that the ratio of the mole fractions  $N$  is

$$\ln x_a \approx -N_b/N_a \quad (57)$$

so  $\pi = RTN_b/(N_a V)$  or the osmotic pressure is proportional to the number of moles of solute per unit volume of dilute solution at a constant temperature.

## COLD REGIONS APPLICATIONS

### Frozen soils

A number of important topics have already been discussed, including capillary condensation, capillary rise, meniscus shape and ionic impurities. In these cases we assumed constant temperature and examined

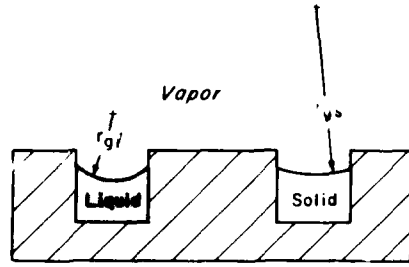


Figure 4. Coexisting ice- and liquid-filled pores.

variations in pressure and geometry. As an alternative to this approach, we can assume constant vapor pressure and look at the dependence of equilibrium temperature on variations in geometry. When all three phases of water are present, there is one equation (eq 21) for each phase. When three phase boundaries occur, there is one equation (eq 29) for each boundary. These equations can be combined in various ways to derive equations which are applicable to particular situations. For example, when each pore in a soil is either ice- or water-filled (Fig. 4),

$$T_m = \frac{T_0}{L} \left( -\frac{v_s \sigma_{sg}}{r_{gs}} - \frac{v_l \sigma_{lg}}{r_{gl}} \right) \quad (58)$$

Thus the temperature at which the system comes to equilibrium is determined by the radii of both the ice/vapor and liquid/vapor interfaces in the pores.

In a pore containing both solid and liquid (Fig. 5), the equilibrium temperature and geometry are related by

$$T_m = \frac{T_0}{L} \left( -\frac{v_s \sigma_{sl}}{r_{sl}} - (v_l - v_s) \frac{\sigma_{gl}}{r_{gl}} \right) \quad (59)$$

where  $L_e$  is the latent heat of evaporation.

These are only two of many equations which can be derived for a variety of situations. Note that to define equilibrium unambiguously, it is necessary to specify the nature of the interfaces actually existing in the soil.

#### Grain growth in snow

In snow at a subfreezing temperature, the vapor pressure over an ice surface depends on the radius of curvature of the surface. (In the absence of an imposed temperature gradient, snow is nearly isothermal, so Kelvin's equation applies.) By analogy with eq 42, the vapor pressure over the curved surface of a snowflake is

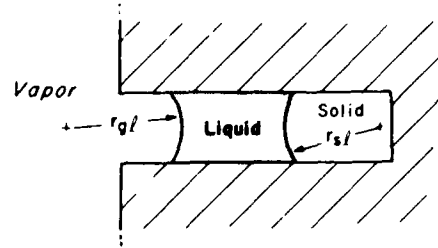


Figure 5. Pore with both ice and liquid.

$$\ln(p_g/p_0) = \frac{v_s}{RT} \frac{2\sigma_{gs}}{r_{sg}} \quad (60)$$

so larger vapor pressures prevail over surfaces of smaller particles. As the water vapor is removed by condensation on the larger particles, the smaller particles evaporate; grain growth proceeds by this mechanism.

When the pore space of snow is filled with liquid rather than vapor, the fluid pressure is essentially constant but large temperature differences arise among the particles. For a constant liquid pressure, the temperature of each particle is given by

$$T_m = -\frac{2T_0}{L\rho_s} \frac{\sigma_{sl}}{r_p} \quad (61)$$

where  $r_p$  is the radius of the ice particle. Since the smaller particles are at lower temperatures than the larger particles, heat flows towards the smaller particles, causing them to melt, while the larger particles grow by accretion. This mechanism causes rapid grain growth and grain rounding in liquid-saturated snow.

#### Liquid-filled veins

Metallurgists discovered some time ago that liquid-filled veins can occur at three-grain boundaries in crystalline materials (Fig. 6). These veins also occur in ice, whose dihedral angle is about  $20^\circ$ . Veins provide a fluid path and render ice permeable, even at subzero

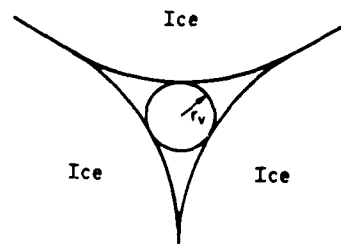


Figure 6. Liquid-filled vein at a three-grain boundary.

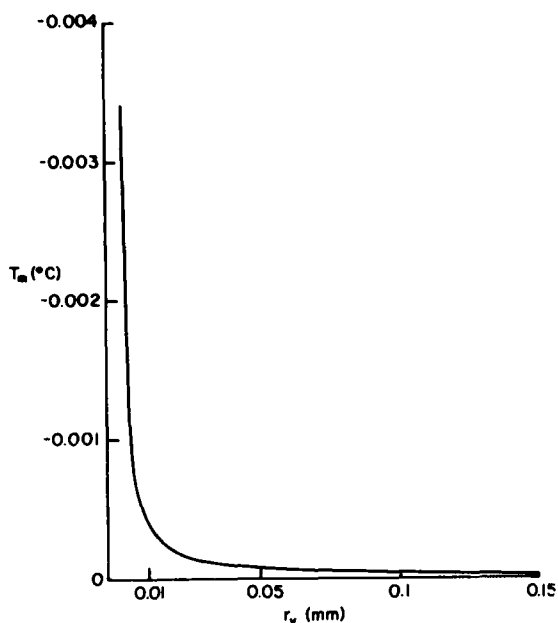


Figure 7. Equilibrium temperature of a liquid-filled vein as a function of vein size.

temperatures. The temperature of a two-dimensional vein is given by

$$T_m = -0.137 \frac{T_0 \sigma_{s\ell}}{\rho_Q L r_v} \quad (62)$$

where the coefficient is determined by the geometry and  $r_v$  is the radius of the largest circle which will fit in the vein. The temperature-radius relation shown in Figure 7 is an important part of the "candling" of lake ice. As the internal ice temperature rises by radiation absorption and heat conduction, the veins enlarge. Thus, grain boundary strength decreases and permeability increases with increasing temperature.

#### Ice clouds

As stated earlier, equilibrium can only be defined unambiguously when the nature of the interfaces is known. For example, ice particles in clouds can grow either from the vapor or the liquid (Fig. 8). When an ice particle is surrounded by liquid, no solid/vapor interface exists, so one less equation is available to specify equilibrium. In this case the three equations from eq 21 and two equations from eq 29 are combined to give the temperature at which equilibrium occurs, yielding

$$T_m = \frac{2}{L} \left[ \frac{(\nu_R - \nu_S) \sigma_{g\ell}}{r_{\ell g}} - \frac{\nu_S \sigma_{s\ell}}{r_{s\ell}} \right] T_0. \quad (63)$$

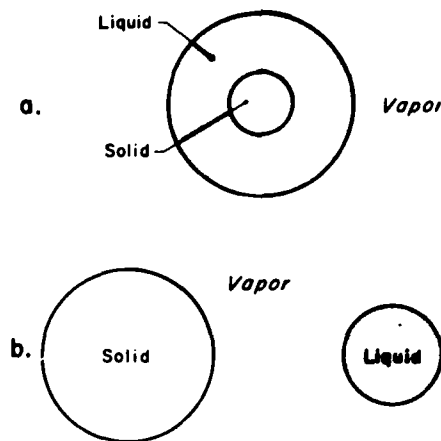


Figure 8. Ice particle enclosed in liquid (a) and a separate ice particle and water droplet (b).

When the liquid droplets and ice particles are separate, the three equations from eq 21 and three equations from eq 29 are combined to give the equilibrium temperature

$$T_m = \frac{2}{L} \left[ \frac{\nu_S \sigma_{g\ell}}{r_{\ell g}} - \frac{\nu_S \sigma_{s\ell}}{r_{s\ell}} \right] T_0. \quad (64)$$

These two cases differ significantly, since the effect of the radius of the liquid droplet is very small (and negative) in the first case but large (and positive) in the second case.

#### CONCLUSION

The principles given here can be applied to a wide range of cold regions problems. These basic ideas concerning the laws of thermodynamics and Laplace's equation explain a large number of capillary phenomena. No doubt many future observations will be enriched by these well tested concepts.

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