Capillary Condensation of Water Vapor Within a Particulate Bed

For situations in which capillary condensation of water occurs (e.g., within porous media), the thermodynamics can usually be studied by means of the Laplace and Young equations and a compressibility equation. We show here that the compressibility equation for the liquid does not reflect the criteria of equal gas and liquid phase potential changes at equilibrium, for departures from a specified reference state.

Carman (1953) concluded that the capillary condensate can exist in a state of tension for large vapor-liquid pressure differentials and may exhibit physical properties that differ substantially from normal values. The familiar Kelvin equation is used to calculate the capillary curvature and is derived from the general Laplace and Young relationship. Melrose (1966) has obtained this relationship by matching the coefficients of the internal free energy and hydrostatic balances of the system shown in Figure 1.

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Total free energy balance:

$$dA = -P_g\,dV + (P_g - P_\ell)dV_\ell = (\sigma_{s\ell} - \sigma_{sg})d\Omega_{s_\ell} + \sigma_{\ell g}\,d\Omega_{\ell g} \quad (1)$$

where A is the total Helmholtz free energy. It is composed of an external component $P_g dV$, and an internal component which equals zero for an isothermal, closed, and reversible system. The liquid meniscus is given by the following

$$K\,d\bar{V}_\ell + d\Omega_{\ell g} = \cos\theta_{s\ell}\,d\Omega_{s\ell} \quad (2)$$

The internal component and Eq. 2 are compared to given the Laplace and Young relationship

$$P_g - P_\ell = \sigma_{\ell g}K \quad (3)$$

Thus, the mean curvature K is simply given in terms of the pressure differential $P_g - P_\ell$. The reference is specified by a flat, unconstrained surface in equilibrium with its vapor at saturation, $K = 0$, $P_g = P_g^o = P_\ell = P_\ell^o$. For a specified departure from a state of reference

$$\Delta P_g - \Delta P_\ell = -\sigma_{\ell g}K \quad (4)$$

Since both fluid phases are assumed nonideal, a (truncated) virial equation and a modified compressibility equation describe the state properties of the vapor and liquid phases. Equivalently, gas phase departures from the reference state are also given by the respective chemical potentials as follows:

$$\Delta\mu_g = \mu_g^o - \mu_g = B\Delta P_g - RT\ln\alpha \quad (5)$$

where $\Delta P_g = P_g^o(1 - \alpha)$, α being the relative saturation and

$$\rho^o\Delta\mu_\ell = \rho^o\Delta\mu^c{}_\ell + \Delta P_\ell \quad (6)$$

for the liquid phase where $\Delta\mu_\ell^c$ is the correction for liquid nonideality. Equation 6 may be rewritten in terms of the isothermal susceptibility and relative density

$$\Delta\mu_\ell = \int_\eta^1 x_\ell\,d\ln\eta \quad (7)$$

where

$$\Delta P_\ell = \rho^o\int_\eta^1 \chi_\ell\,d\eta, \quad \chi_\ell = \frac{\partial P_\ell}{\partial\rho}, \quad \eta = \frac{\rho}{\rho^o} \quad (8)$$

Equation 7 is the modified (compressibility) state equation for the liquid and is completely evaluated provided the relationship between χ_ℓ and η is known. The second virial coefficient B in Eq.

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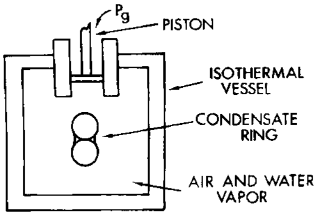

Figure 1. Arrangement of the thermodynamic system.

5 and $\Delta\mu_\ell^c$ in Eq. 6 account for nonideal behavior. The criterion of equilibrium between the two phases requires that

$$BP_g^o(1-\alpha) - RT\ln\alpha = \int_\eta^1 \chi_\ell \, d\ln\eta \tag{9}$$

Decreasing values of the relative saturation α corresponds to decreasing values of P_ℓ (increasing K). When $\Delta P_\ell > P_\ell^o$, $\Delta\mu_\ell$ is negative and the liquid is in a state of tension. This change in α is also accompanied by decreasing η and χ_ℓ (since P_ℓ changes more rapidly than η). Generally, a linear representation for χ_ℓ as a function of η is a convenient approximation (Melrose, 1966) and is readily obtained. For water, the empirical Kell-Whalley (1965) equation may be used to obtain coefficients K_1, K_2:

$$\chi_\ell = K_1\eta - K_2 \tag{10}$$

Where $K_1 = 1.95 \times 10^6$ cc·atm/mol and $K_2 = 1.60 \times 10^6$ cm^3·atm/mol at 126.7°C.

However, such an extrapolation is strictly valid for positive liquid pressures ($\Delta P_\ell < P_\ell^o$). The volume of the condensate ring in Figure 1 is assumed to be sufficiently large (macroscopic) in this region so that a thermodynamic relationship may be used. An example is the Kelvin equation, which relates the curvature K to the relative saturation α. In this case both the gas and liquid are assumed to be ideal and $\Delta P_g \ll -RT\ln\alpha$. Under these conditions:

$$\Delta P_\ell = \rho_\ell \cdot \Delta\mu_g \tag{11}$$

and with appropriate substitution into Eq. 4 one gets the Kelvin equation,

$$K = \frac{-RT\ln\alpha}{\sigma_{\ell g} \cdot \tilde{v}_\ell} \tag{12}$$

The conditions under which Eq. 12 is appropriate are suggested by the equation itself, namely that $\sigma_{\ell g}$ and $\tilde{v}_\ell$ are invariant with α (or K). As α decreases, K increases and the geometry of Figure 1 suggest that the capillary ring shrinks in size. However both $\alpha_{\ell g}$ and $\tilde{v}_\ell$ vary (Buff and Kirkwood, 1950) when the liquid is in appreciable tension. That the liquid experiences tensile stresses is indicated in Figure 2 where $\Delta P_\ell \geq P_g^o$ even for small departures from the reference state ($\alpha \leq \alpha_o$).

Melrose (1966) has used the compressibility equation, Eq. 7, and the linear interpolation, Eq. 10, to determine the variation of $\tilde{v}_\ell$ with α. This method of computation covers the entire region $1 \leq \alpha \leq \alpha_{\min}$, where $\alpha_{\min}$ corresponds to the vanishing of the isothermal susceptibility ($\chi_\ell = 0$). This is the criterion of mechanical instability of the liquid. For $\chi_\ell = 0$, $\eta_{\min} = K_1/K_2$ from Eq. 10.

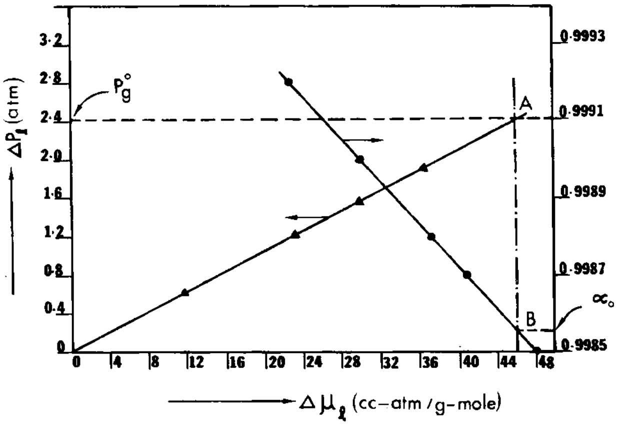

Figure 2. Variation of ΔP_ℓ and relative saturation α and $\Delta\mu_\ell$ for small departures. *A* and *B* are values of ΔP_ℓ and α where $P_\ell = 0$, $T = 126.7$°C.

It was determined by Shukla (1980) that a linear $\chi_\ell - \eta$ relationship as in Eq. 10 is not valid for low values of α. For example, at $\alpha = 0.4$, $T = 126.7$°C, the total potential departure from the reference state (saturation) $\Delta\mu_\ell$ equals 2.94×10^4 cm^3·atm/mole. The calculation of ΔP_ℓ, which incorporates Eq. 10, yields a value of 1.44×10^3 atm (145.91×10^3*kPa*) negative pressure (at $\eta = 0.88$). The potential correction term $\Delta\mu_\ell^c$ given by Eq. 13 is 1.48×10^4 cm^3·atm/mole.

$$\Delta\mu_\ell^c = K_1\left(\frac{1}{2} - \eta + \frac{1}{2}\eta^2\right) + K_2(1 - \eta + \ln\eta)\Bigg|_\eta^1 \tag{13}$$

This satisfies the assumption of relatively small departures from ideality, so that $\Delta\mu_\ell^c \ll \Delta\mu_\ell$. However, the large value of ΔP_ℓ for $\alpha = 0.4$ indicates an improbably high pressure within the condensate. The stability of the physical system is suspect under this condition. This situation partly results either from the linear dependence of the isothermal susceptibility χ_ℓ upon the relative density η, or from the assumption that parameter values K_1, K_2 in Eq. 10 are valid for negative pressures. It is therefore necessary to use an alternative method to determine χ_ℓ.

Kell and Whalley (1965) have published a nineteen-parameter polynomial that relates the specific volume of water to its pressure and temperature. This polynomial [which works well for positive pressure up to 1,000 atm (101.3 MPa)] was used to calculate the isothermal compressibility for the region of tension at various temperatures. The liquid density ρ, and therefore η, is calculated at each pressure and χ_ℓ is obtained as the ratio of the incremental pressure to the incremental density. $\eta_{\min}$, the minimum relative density, is the ratio of K_1, K_2, which are now obtained from the results of the iteration at negative pressures. Table 1 shows the results of such a calculation at $T = 65.6$°C.

Once again, ΔP_ℓ is very large near the limiting condition of $\eta_{\min} = 0.795$ and χ_ℓ is far greater than its expected value of zero. All other factors being equal, ΔP_ℓ increases with falling temperature. In this case, assuming that a capillary does exist, it would be reasonable to expect that liquid properties have significantly changed so that the liquid departs radically from ideal behavior. The ideal part of the phase chemical potential change, $\Delta\mu_\ell^{id}$ as

Table 1. Liquid Phase Parameters Near Estimated Point of Rupture at 65.6°C

$\eta_{\min}$ (ρ/ρ_o)	ν cm^3/g	ΔP_l atm	X_l cm^3 · atm/mol	$\Delta\mu_l$ cm · atm/mol
0.795	1.286	3,275	2.38×10^5	8.09×10^2

SI conversion: kPa = atm × 101.325.

expressed in Eq. 7 may therefore be expected to be a minor component. Additionally, for the region of tension, $\alpha < \alpha_o$, no agreement was found between the χ_ℓ values predicted by the coefficients in Eq. 10 for 65.6°C and those of the Kell-Whalley polynomial extrapolated to negative pressures. Both sets of χ_ℓ values were unreasonably high as η approaches $\eta_{\min}$ in the two cases. The basis of the equations used, namely $\mu_\ell^c \ll \mu_\ell$, is not valid and the utility of extrapolating into the negative pressure region, using state property parameters like K_1 and K_2 or state relationships, is questionable.

Evaluation of the integral in Eq. 7 presupposes a relationship between χ_ℓ and η. In view of the failure of the compressibility equation, an alternative equation must be used for the region of tension. One such equation is the van der Waals relationship, which has been applied with considerable success by Benson and Gerjuoy (1949) and Temperley (1947). For water this equation at least enables a crude estimate of the maximum tension (tensile strength) it can sustain before rupture at $\chi_\ell = 0$. It is calculated from the reduced form of the van der Waals equation.

$$P_r = 3/\hat{V}_r^3 - 2/\hat{V}_r^3 \tag{14}$$

$$T_r = 1/4\,[3\hat{V}_r - 1)^2/\hat{V}_r^3] \tag{15}$$

At 126.7°C the van der Waals equation predicts a tensile strength of approximately 500 atm (50.66 MPa). The ideal liquid phase chemical potential, given by $(\Delta P_\ell/\rho_\ell^o)$, is 9.7×10^3 cm^3·atm/mol. If the compressibility equation were valid with $\mu^c \ll \mu_\ell$, then χ_ℓ is required to vanish at this point. Instead the isothermal susceptibility has a large value of 2.98×10^5 cm^3·atm/mol. It therefore appears that either the (van der Waals) tensile strength, or the liquid potential change using the compressibility equation, is underestimated. Alternatively, if indeed $\eta_{\min} = 0.8223$ so that χ_ℓ equals zero at the point of rupture, then $\Delta\mu_\ell$ equals 3.26×10^4 cm^3·atm/mol from the compressibility equation. The calculated negative pressure at 126.7°C under these conditions is large (1,700 atm [172.25 MPa]). In other words the compressibility equation predicts that both $\Delta\mu_\ell$ and ΔP_ℓ change by the same order of magnitude in Eq. 6 so that the liquid exhibits relatively near ideal behavior. These assumptions, which are true near atmospheric pressure, are of questionable validity at high negative pressures.

The advantage of the van der Waals equation is that liquid ideality is not assumed, thus removing the need for a definition of ideal behavior for these calculations. There is no inconsistency in this procedure, unlike the compressibility equation, and it predicts a more conservative tensile strength of 500 atm (50.66 MPa). Additionally, potential changes in the gas phase at low values of the relative saturation are more compatible with the van der Waals estimate of $\Delta\mu_\ell$ than that calculated by the compressibility equation.

The utility of the van der Waals equation may be extended a step further to estimate the liquid chemical potentials. The isothermal potential departure from the reference state (P_ℓ^o) is given as:

$$(\Delta\mu_\ell)_T = \int_{\hat{\nu}_{\ell\min}}^{\nu_1^\ell} \nu_1 \left(\frac{\partial P}{\hat{\partial}\nu_1}\right)_T \mathrm{d}\nu_1 \tag{16}$$

Introduction of the critical constants and substitution of the derivative from the van der Waals equation results in:

$$(\Delta\mu_\ell)_T \approx P_c\hat{\nu}_c \int_{\hat{\nu}_{\ell\min}}^{\hat{\nu}_r^o} \hat{\nu}_r \left[\frac{-24T_r}{(3\hat{\nu}_r - 1)^2} + \frac{6}{\hat{\nu}_r^3}\right] d\,\nu_r \tag{17}$$

The lower limit $\nu_{\ell\min}$ is the minimum liquid volume corresponding to $\chi_\ell = 0$ and is obtained from Benson and Gerjuoy (1949). The expression estimates the "tensile state" chemical potential, and the upper limit $\hat{\nu}_r^o$ corresponds to the transition from the positive to the negative pressure region for the liquid phase. With these limits, the liquid potential is estimated to be 10^6 cm^3·atm/mol at 126.7°C. The departure occurs at a negative pressure of 500 atm (50.66 MPa) and it is much larger than the value obtained from Eq. 6. Additionally, $\Delta\mu_\ell$ increases (as α decreases) at a rate much higher than $\Delta P_\ell/P_\ell^o$.

The foregoing indicates the inappropriateness of the extension of the compressibility equation to large negative pressures. To circumvent this problem, the van der Waals relationship was invoked with some justification. However this presents a computational difficulty in the evaluation of the potential departure by Eq. 17 when ν_r is near or less than $1/3$. The reduced form is physically meaningful for the region $1/3 < \hat{V} < 2/3$, and the integral in Eq. 17 exhibits a discontinuity at $\hat{V}_r = 1/3$. Also, assumptions concerning the constants a and b must be based on molecular considerations. For example, the tensile strength at absolute zero, represented by $-a/b^2$, is extremely large. This calculation ignores the sensitivity of a to temperature. Similarly the excluded volume b varies with temperature. Due to variations in these constants, which are normally obtained from critical data, it is reasonable to expect that they will affect the calculated tensile strength.

For the geometry of Figure 1 the use of any conventional equation of state is constrained, due to decreasing condensate volume with the decreasing relative saturation α. A reduction in α lowers the volume to the point that the condensate cannot be assumed to be a bulk phase. Under these conditions properties of the liquid phase change. For example, surface tension (Hill, 1950) is not invariant with meniscus curvature as assumed in the Helmholtz energy balance, Eq. 1. This leads to interfacial free energy changes in addition to those of the pressure-volume type, and these changes must be accounted for in the description of the physical system.

Notation

A = Helmholtz free energy
B = second virial coefficient
K = curvature of liquid meniscus
K_1, K_2 = empirical constants, cm^3·atm/gmol
P = pressure, atm (101.325 kPa)
T = temperature, °C
R = gas constant
$\bar{V}$ = specific volume, cm.^{3}/g

Greek letters

α = relative saturation, P_g/P_g^o
Δ = departure from saturation
η = relative density, ρ/ρ_o
θ = angle of contact
μ = chemical potential, $cm^3 \cdot atm/gmol$
$\tilde{\nu}$ = molar volume $cm^3/gmol$
ρ = molar density, mol/cm^3
σ = interfacial tension
χ = isothermal susceptibility, $\partial P_\ell/\partial \rho$ $cm^3 \cdot atm/gmol$
Ω = interfacial area

Subscripts and superscripts

c = correction
g = gas
id = ideal
ℓ = liquid
o = saturation (reference)
r = reduced
s = solid

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