R & D NOTES

Latent Heats of Supercritical Fluid Mixtures

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In the analysis of heat transfer measurements for mixtures of CO_2 and *n*-decane in the retrograde condensation region (Jones et al., 1987), we have found the need for values of the latent heat of condensation. However, the latent heat of condensation or vaporization for mixtures may be defined in different ways. In the thermodynamics literature of King (1969) or Bett et al. (1975), for example, equilibrium differential and integral latent heats for mixtures are defined and discussed. These definitions, based on the derivations of Strickland-Constable (1951), take changes in composition and temperature or pressure into account, as a differential or fixed quantity of mixture is progressively vaporized or condensed. Liquid and vapor are taken to be in thermal and phase equilibrium and, hence, to be homogeneous. The process is therefore reversible in the thermodynamic sense. In heat transfer studies, on the other hand, one is interested in the irreversible vaporization or condensation of mixtures at a phase interface on both sides of which temperature and composition gradients may exist, with accompanying heat and diffusional fluxes, while pressure is usually uniform. Only the material in a thin layer at the interface may be assumed to be in equilibrium with a similar layer in the adjacent phase. Latent heat is manifested by a discontinuity in the conductive heat flux at the interface. The process may or may not be at steady state, but it is indeed irreversible.

In this paper we use a conventional definition for the binary latent heat for phase change at an interface as encountered, for example, in film condensation and evaporation. We call this the transport latent heat to make a clear distinction from the equilibrium latent heat. We show that it must pass through zero and change sign at the right and left hand extrema (cricondenbars) on the isobaric temperature composition phase diagram.

Estimates of the transport latent heat are presented for CO_2 + *n*-decane using the Peng-Robinson equation of state (Peng and Robinson, 1976) with the interaction parameter adjusted to fit excess enthalpy data. We hope that the mixed success achieved in fitting these excess enthalpy data will stimulate further work on this subject to enable the computation of latent heats with more confidence.

Qualitative Properties of the Latent Heat

Consider a binary mixture at pressures above the critical pressure of each pure component but below the mixture critical pressure, and let $x^{(V)}$ and $x^{(L)}$ be the mole fractions of the more volatile component in vapor and liquid phases. With reference to Figure one, if $q^{(V)} - q^{(L)}$ is the discontinuity in the conductive heat flux normal to the vapor-liquid interface, then continuity of the total normal component of the energy flux, $q + N_1\bar{H}_1 + N_2\bar{H}_2$, requires that

$$q^{(V)} - q^{(L)} = N_1(\bar{H}_1^{(L)} - \bar{H}_1^{(V)}) + N_2(\bar{H}_2^{(L)} - \bar{H}_2^{(V)})$$
$$= N[z_1(\bar{H}_1^{(L)} - \bar{H}_1^{(V)}) + z_2(\bar{H}_2^{(L)} - \bar{H}_2^{(V)})] \quad (1)$$

In Eq. 1, N is the total normal molar flux, N_1 and N_2 are the normal components for species 1 and 2 and the z_i are their fractional values. $\bar{H}_i^{(L \text{ or } V)}$ are partial molar enthalpies for component i. It can be assumed in most cases that the mole fractions in the phase being produced are in the ratio of the molar fluxes, especially in some small region adjacent to the interface, in the absence of chemical reaction or vigorous backmixing. With this assumption, we may write Eq. 1 as

$$q^{(V)} - q^{(L)} = N[x^{(L)}(\bar{H}_1^{(L)} - \bar{H}_1^{(V)})$$
$$+ (1 - x^{(L)})(\bar{H}_2^{(L)} - \bar{H}_2^{(V)})] \quad (2)$$

We define the quantity in square brackets in Eq. 1 to be $\lambda^{T(V,L)}$, the transport latent heat of the phase change from vapor to liquid. We note that this definition is the established definition of latent heat in the transport literature—see, for example, Colburn and Drew (1937), Sparrow and Marschall (1969) and Slattery (1981). The transport latent heat differs in form and concept from the equilibrium latent heat, the latter containing an additional contribution for the restoration of phase equilibrium upon change of composition. In the remainder of the paper we shall use the form implicit in Eq. 2. $\lambda^{T(V,L)}$ can be evaluated immediately if partial molar enthalpies are available. We shall return to this calculation after discussing the qualitative behavior of the transport latent heat by consideration of the excess enthalpy $H^E(T, P, x)$, the quantity usually measured. In terms of this quantity, evaluated at the phase boundaries, the transport latent heat for the phase change may be written

$$\lambda^{T(V,L)} = H^{E(L)} - H^{E(V)} - (x^{(L)} - x^{(V)})(\partial H^E/\partial x)_{TP}^{(V)} \quad (3)$$

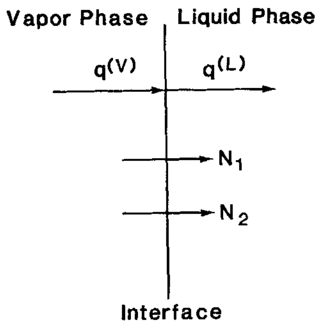

Figure 1. Heat and mole fluxes at a phase interface.

This expression follows from the definitions of H^E and $\bar{H}_i$. While Eq. 3 provides a means of obtaining transport latent heats directly from experimental data, in practice its utility is limited; excess enthalpy data of sufficient accuracy are not generally available in the retrograde region to carry out the indicated differentiations. On the other hand, Morrison et al. (1985) have shown that experimental excess enthalpy data are in conformity with some rather general rules which also have consequences for the transport latent heats. Their results are directly applicable here. In Fig 2, we show a qualitative sketch of the $T - x$ and $H^E - x$ plots for a pressure above the critical pressures of the pure components. Morrison et al. show first that the curvature of H^E is always negative at an upper critical solution temperature (UCST) and positive at a lower critical solution temperature (LCST). They then go on to discuss the changes in slope of the excess enthalpy isotherms at the boundary between single- and two-phase regions, making use of the Gibbs-Konovalow rule. This rule, applied to the discontinuity in enthalpy derivatives with respect to composition at a phase boundary, is

$$\left.\frac{dT}{dx}\right|_{P,\sigma} = \frac{-T\left(\dfrac{\partial^2 G}{\partial x^2}\right)_{TP}}{\dfrac{\Delta H^E}{\Delta x} - \left(\dfrac{\partial H^E}{\partial x}\right)^{(i)}_{TP}} \tag{4}$$

In eq. 4, G is the Gibbs free energy, $\Delta H^E/\Delta x$ is the tie-line slope in the two-phase region, $(\partial H^E/\partial x)^{(i)}_{TP}$ is evaluated in phase i at the phase boundary, and σ denotes differentiation along a phase boundary. Equation 4 is derived in Morrison et al. (1985). The denominator in Eq. 4 is precisely the right hand side of Eq. 3 divided by $(x^{(L)} - x^{(V)})$. In the normal part of the dew-point curve, $x^{(L)} < x^{(V)}$, and $dT/dx|_{P,\sigma}$ is negative. Furthermore, in view of the stability requirement $(\partial^2 G/\partial x^2)_{TP} > 0$, Eq. 4 requires that the tie-line slope in the two-phase region be greater (more positive) than the slope of H^E in the single-phase region where they connect. This is illustrated by the changes in slope on the right hand side of isotherms T_3, T_4 and T_5 of Figure 2. In the retrograde part of the dew-point curve, $dT/dx|_{P,\sigma}$ is positive, and hence the tie-line slope is less (more negative) than the slope of H^E, for example, isotherm T_1. In consequence, the transport latent heat of condensation as defined by Eq. 3 is positive in retrograde regions and negative in normal regions of the dew-point curve where liquid is being formed from vapor. Similarly, if we interchange the L, V superscripts in Eq. 3, the transport latent heat of vaporization along the bubble point curve is found to be positive in the normal region and negative in the retrograde region. Finally, at the right extremum of the dew-point curve and the left extremum of the bubble-point curve, $dT/dx|_{P,\sigma}$ is infinite, requiring that there be no change in the slope of H^E at the phase boundary. Then the transport latent heat by Eq. 3 is zero at these points, as it is also at the upper and lower extrema: the UCST and LCST. However, in the latter cases, it is zero by virtue of the fact that the two phases become identical in composition. It is somewhat surprising to find a phase change involving quite different compositions with no accompanying heat effect.

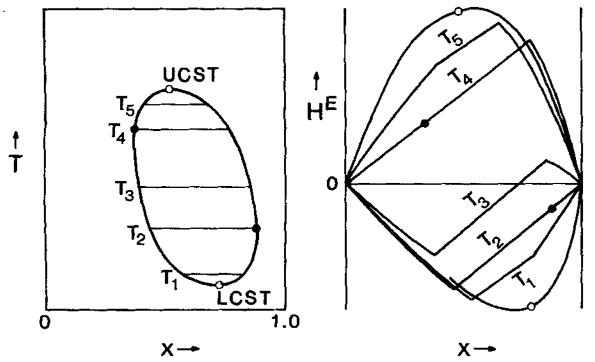

Figure 2. Qualitative diagram showing the relationship betwen isotherms in the $T - x$ plane and the form of the excess enthalpy isotherms, after Morrison et al. (1985).

Quantitative Estimate of the Transport Latent Heat

In order to make quantitative estimates of the transport latent heat, we calculated the partial molar enthalpies $(\partial H/\partial n_i)_{TPn_j}$ from the Peng-Robinson equation of state.

The Peng-Robinson specification of the enthalpy departure function is

$$H - H^0 = nRT(Z-1) + \frac{Td(n^2a)/dT - n^2a}{2\sqrt{2}\,nb}\ln\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \tag{5}$$

H is the enthalpy of the mixture, H^0 the enthalpy of the ideal gas mixture, n the number of moles of the mixture, and Z the compressibility factor. B is the quantity $bP/(RT)$ and $a(T, x)$ and $b(x)$ are the characteristic energy and volume parameters for the equation of state:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i x_i b_i \tag{7}$$

where

$$a_{ij} = (1 - k_{ij}) a_i^{1/2} a_j^{1/2}, \quad i \neq j \tag{8}$$

and k_{ij} is the empirically determined binary interaction coefficient. The composition dependence resides only in these parameters. See Peng and Robinson (1976) for details of the calculation of the a_i and b_i of the pure components.

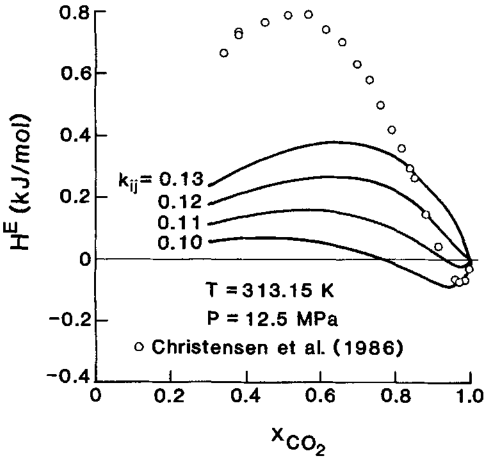

Figure 3. Experimental excess enthalpies vs. values computed from the Peng-Robinson equation of state for different values of the interaction parameter.

This isotherm lies entirely in the single-phase region below the LCST.

Since Eq. 5 is explicit in v rather than P, it was necessary to express the partial molar enthalpy in terms of derivatives at constant v by a change of independent variables. Thus,

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{TPn_j} = \left(\frac{\partial H}{\partial n_i}\right)_{VTn_j} - \frac{\left(\frac{\partial H}{\partial V}\right)_{nT}\left(\frac{\partial P}{\partial n_i}\right)_{VTn_j}}{\left(\frac{\partial P}{\partial V}\right)_{nT}} \tag{9}$$

with P given by the equation of state

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{10}$$

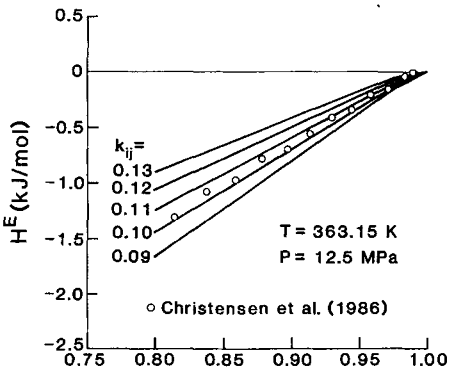

Figure 4. Experimental excess enthalpies vs. computed values for an isotherm in the two-phase region at a temperature just above the righthand extremum of the $T - x$ diagram.

This would be an isotherm between T_2 and T_3 of Figure 2.

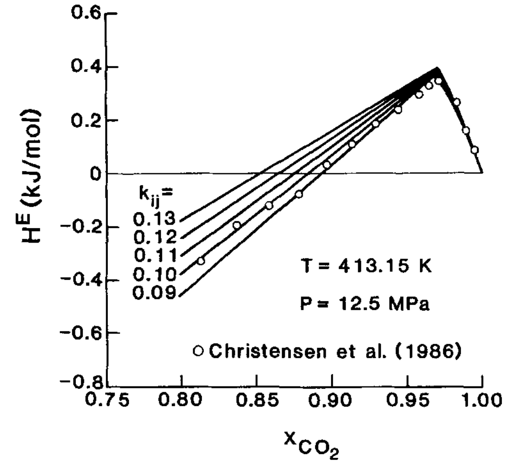

Figure 5. Comparison of experimental data with computations for an isotherm such as T_3 of Figure 2.

We performed the required differentiations on Eqs. 5 and 10, and thus derived algebraic expressions for the partial molar enthalpies $\bar{H}_i$ of each component. The differentiations are tedious but straightforward. The transport latent heat was finally calculated by substitution in the square-bracketed quantity in Eq. 2.

We optimized the value of the interaciton coefficient k_{ij} by calculating the excess enthalpy of the CO_2 + n-decane mixture and comparing the result with the experimental data of Christensen et al. (1986). These data were obtained at 12.5 MPa and various isotherms. A global fit was beyond the intended scope of this work, but comparisons with three isotherms of interest for various values of k_{ij} are shown in Figures 3, 4 and 5.

At the lowest temperature (313.15 K, single-phase region), the agreement between experimental values and those calculated from the Peng-Robinson enthalpy departure function is quite poor for all values of k_{ij}, although the calculated curves have the correct shape. In contrast, it is fairly good at the two higher temperatures, 363.15 and 413.15 K, for values of k_{ij} = 0.1. We were encouraged to find that this value of k_{ij} also gave the best fit to independent phase coexistence data of Reamer and Sage (1963) and Nagarajan and Robinson (1986). Note

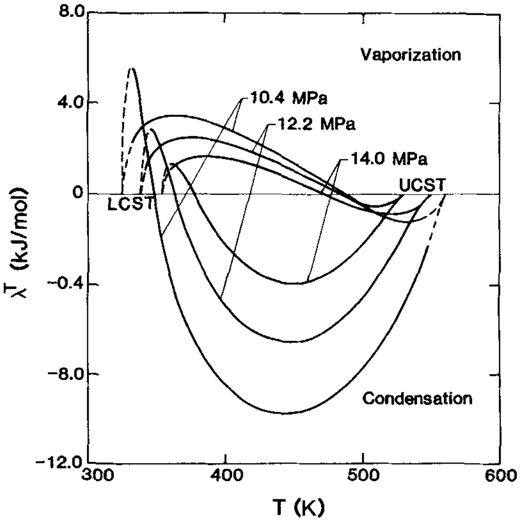

Figure 6. Computed transport latent heats of vaporization and condensation for CO_2 + n-decane at three pressures; k_{ij} = 0.10.

also that, according to the figures and the discussion above, these two temperatures must lie above the right hand extremum temperature of the $T - x$ plot, and phase change is normal, that is, not retrograde. At 363.15 K, the computed results indicate that the tie-line slope and single-phase slope are almost identical and, if we take into account the apparent imprecision, the data do not dispute this. Thus, the retrograde region must lie slightly below this temperature at 12.5 MPa. This is in accord with the phase coexistence data which give, by interpolation, a temperature of about 343 K for the right-hand extremum of the $T - x$ curve at this pressure. None of the data reported by Christensen et al. (1986) actually lie in the retrograde region, but they are close.

To illustrate the transport latent heats, we show in Figure 6 the predicted curves for condensation and vaporization for two pressures at which our heat transfer measurements were made: 10.4 and 12.2 MPa, and also at 14.0 MPa. This plot illustrates the qualitative features discussed above, and, in view of the agreement with excess enthalpy data at 363.15 and 413.15 K, we expect the estimates to be good in this vicinity. These results have been of value in analyzing our heat transfer measurements relative to classical film condensation theory where some estimate of transport latent heat is imperative.

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Notation

a, a_i, a_{ij} = characteristic energy parameters for the equation of state
b, b_i = characteristic volume parameters
G = Gibbs free energy
$\underline{H}$ = enthalpy
$\overline{H}_i$ = partial molar enthalpy
$\lambda^{T(V,L)}$ = transport latent heat for the phase change from vapor to liquid
k_{ij} = empirical binary interaction parameter
N, N_i = molar fluxes
n, n_i = number of moles
P = pressure
q = heat flux
R = gas constant
T = temperature
v, V = molar volume, total volume
x = mole fraction of more volatile component
x_i = mole fraction of component i
z_i = fractional molar flux = N_i/N

Superscripts

V = *vapor phase*
L = condensed phase
V, L = change from vapor phase to liquid phase
o = ideal gas state

Subscripts

i = component number
σ = phase boundary

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Appendix

The following are expressions derived from the Peng-Robinson equation of state for the partial derivatives required in the calculation of partial molar enthalpies.

$$\left(\frac{\partial P}{\partial n_i}\right)_{v,T,n_j} = -\frac{\hat{a}_i}{D} + \frac{RTb_i}{(v-b)^2} + \frac{2a(v-b)b_i}{D^2} + \frac{RT}{v-b}$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{v,T,n_j} = H_i^o - RT + v\left(\frac{\partial P}{\partial n_i}\right)_{v,T,n_j} + \frac{\ln(X/Y)}{2\sqrt{2}b}\left[(\hat{a}_i'T - \hat{a}_i) - (a'T - a)b_i/b\right] + \frac{(a'T - a)b_i}{2\sqrt{2}b}\,\frac{Y(\sqrt{2}+1) + X(\sqrt{2}-1)}{XY}$$

$$\left(\frac{\partial H}{\partial P}\right)_{n,T} = v + \left[P + \frac{(a'T - a)(Y - X)}{2\sqrt{2}bXY}\right] \Big/ \left(\frac{\partial P}{\partial v}\right)_{n,T}$$

$$\left(\frac{\partial P}{\partial v}\right)_{n,T} = \frac{-RT}{(v-b)^2} + \frac{2a(v+b)}{D^2}$$

where

$$\hat{a}_i = \sum_j 2x_j a_{ji}$$

$$a' = da/dT$$

$$\hat{a}_i' = \sum_j 2x_j da_{ji}/dT$$

$$X = v + (\sqrt{2}+1)b$$

$$Y = v - (\sqrt{2}-1)b$$

$$D = v(v+b) + b(v-b)$$

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