On the Calculation of Critical Liquid-Vapor Lines of Binary Mixtures

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The critical lines of binary mixtures of conformal fluids are calculated on the basis of the one-fluid Van der Waals theory. The conditions for the existence of the gas/gas equilibrium of the first and second type are shown and discussed. The analytical expressions for partial derivatives of Gibbs free energy with respect to concentration, up to the third order, are given in the appendix.

Key words: Conformal solution theory; corresponding states; critical point; gas/gas equilibria; mixtures; Van der Waals one fluid model.

1. Introduction

In this work we study the binary mixture at the gas/liquid critical line (the Plait point curve). Our emphasis will be on locating the line rather than discussing the behavior of the critical point itself [1][1]: it is felt that the former problem is of scientific and practical interest which has not yet been fully explored. Our procedure is based on one fluid Van der Waals conformal solution model since it is now well established [2-6] that phase equilibria in general can be predicted successfully by this method.

The organization of the paper is as follows: the corresponding states approach is recalled briefly in section 2 and the calculation of the critical lines is discussed in section 3 with the lengthy working equations relegated to the appendix. The phenomena of gas/gas equilibria are next discussed. In particular, some variations of the critical line over a range of pressure, P, temperature, T, and mole fraction, x, for various types of mixtures are described in section 4. Brief comparisons with the more restricted approach from simple equations of state [7,8] are given.

Throughout this discussion, argon is used as the reference substance [9]; results with other reference equations will be published in a forthcoming paper [10].

2. Conformal Solution Theory

A basic postulate of the Van der Waals one fluid theory is that if the components of a mixture—characterized by the usual parameters, ϵ and σ—separately obey corresponding states, then their mixture will also obey corresponding states as if it were a single substance. This hypothetical equivalent substance is characterized by some suitable composition dependent average parameters, $\langle \epsilon \rangle$ and $\langle \sigma \rangle$. The statistical mechanical basis behind the theory has been discussed by several authors, in particular by Henderson and Leonard [11], Leland, et al. [12], Jacucci and McDonald [13], and by Hanley and Evans [14]. The concept cannot be strictly valid but the model is nevertheless appealing and often successful in practice.

Accepting that the single component equivalent substance is a valid entity, its properties are then determined from those of a known reference substance via corresponding states. See, for example, references 3 and 5. For the Gibbs free energy the expressions are

$$G_m(T,P,x) = G_x(T,P) + RT \sum_i x_i \ell n x_i \tag{1}$$

$$G_x(T,P) = f_x G_o(T/f_x, Ph_x/f_x) - RT \ell n h_x \tag{2}$$

Here the subscript m refers to the mixture, x to the equivalent substance and o to the reference substance;

$$f_x = \frac{\langle \epsilon \rangle}{\epsilon_o} \quad \text{and} \quad h_x = \frac{\langle \sigma^3 \rangle}{\sigma_o^3}$$

are parameters of the equivalent substance with respect to the reference fluid. The Van der Waals mixing rules which express h_x and f_x are as follows:

[1] Figures in brackets refer to literature references at the end of this paper.

$$h_x = \sum_{i,j} x_i x_j h_{ij} \tag{3a}$$

$$f_x = \left(\sum_{i,j} x_i x_j f_{ij} h_{ij}\right)/h_x \tag{3b}$$

where

$$h_{ii} = \frac{\sigma_{ii}^3}{\sigma_o} = \frac{V_{ii}^c}{V_0^c}, \qquad f_{ii} = \frac{\epsilon_{ii}}{\epsilon_o} = \frac{T_{ii}^c}{T_0^c}$$

The parameters referring to unlike pairs are usually expressed in terms of a mixing rule:

$$h_{ij} = \eta_{ij}\left(\frac{1}{2} h_{ii}^{\frac{1}{3}} + \frac{1}{2} h_{jj}^{\frac{1}{3}}\right)^3 \tag{3c}$$

$$f_{ij} = \xi_{ij}\left(f_{ii}f_{jj}\right)^{\frac{1}{2}}$$

where η_{ij} and ξ_{ij} are semi-empirical correction factors which are close to unity; V_{ii}^c is the critical volume and T_{ii}^c is the critical temperature of the component i.

3. Critical Lines

Phase behavior of a mixture can be characterized by the course of the gas/liquid critical line in $(P-T-x)$ space joining (or not) the critical points of the pure components [15]. The line depends on the interactions between unlike $(i-j)$ molecules and on the relationship between the critical temperatures and critical volumes of the pure components. Many investigations have examined this question both from the theoretical and experimental viewpoint. See, for example, references [16] and [17]. Of special interest, Van der Waals [18] and Kamerlingh Onnes and Keesom [19] predicted that a phase separation could occur in a binary mixture at temperatures well above the critical temperature of either component. Hence the term gas/gas equilibria. [The effect was verified experimentally in 1940 for the system NH_3-H_2 [20] and one of the earlier theoretical discussions is reported in reference [21] for the system Xe-He.]

The wide range of possible phase behavior is covered by the extensive work of Scott and Van Konynenburg [7,22,23] who used the Van der Waals equation of state with the mixing rules

$$a_m = a_{11}x_1^2 + a_{22}x_2^2 + 2 x_1 x_2 a_{12}$$

$$b_m = b_{11}x_1^2 + b_{22}x_2^2 + 2 x_1 x_2 b_{12}$$

where a_{ij} and b_{ij} are the Van der Waals constants, to calculate critical lines as functions of T^c, V^c or of a and b. Further calculations of critical lines based on the Van der Waals and Guggenheim reduced equations of state were later reported and compared with experiment [8,24,25].

3.1. Equations

The critical point of a binary mixture at a given T,P and x is defined by the equations of diffusional or material stability [26]:

$$\left(\frac{\partial^2 Y_m}{\partial x^2}\right)_{T,P} = 0 \tag{4a}$$

$$\left(\frac{\partial^3 Y_m}{\partial x^3}\right)_{T,P} = 0 \tag{4b}$$

$$\left(\frac{\partial^4 Y_m}{\partial x^4}\right)_{T,P} > 0 \tag{4c}$$

where $Y_m = G_m/RT$, with G_m, the Gibbs free energy of the mixture: $x(\equiv x_2)$ is the mole fraction of the second component. The locus of the critical points is of course the critical line. Note that there is no formal difference between a liquid/liquid curve and a gas/liquid (plait point) curve.

Equation (4) can be solved in two ways, the first graphically. The Gibbs free energy is plotted versus mole fraction at T and P: the common tangent determines the boundary of the phase separation and a critical point is the T,P,x point at which the common tangent vanishes. The second way is to solve equations (4a) and (4b) directly, with the constraint of equation (4c). This is the procedure used here, coupled with the one fluid model.

Accordingly equations (1) and (2) are expressed in the following form:

$$Y_m(T,P,x) = Y_o(T_o,P_o) - \ell n h_x + x \ell n x + (1-x) \ell n(1-x)$$

$$Y_m(T,P,x) = G_m(T,P,x)/RT \tag{5}$$

$$Y_o(T_o,P_o) = G_o(T_o,P_o)/RT_o, \quad T_o = T/f_x, \quad P_o = P h_x/f_x$$

Equations (4a) and (4b), which are to be solved, are obtained explicitly by differentiation of equation (5) with respect to x—the mole fraction of the second component resulting in,

$$\left(\frac{\partial^2 Y_m}{\partial x^2}\right)_{T,P} = Y_{o,T,T}T_o'^2 + 2Y_{o,P,T}P_o'T_o' + Y_{o,P,P}P_o'^2 + Y_{o,T}T_o''$$

$$+ \; Y_{o,P}P_o'' - h_x'/h_x + (h_x'/h_x)^2 + 1/x(1-x) \tag{6a}$$

$$\left(\frac{\partial^3 Y_m}{\partial x^3}\right)_{T,P} = Y_{o,T,T,T}T_o'^3 + 3Y_{o,T,T,P}P_o'T_o'^2 + 3Y_{o,P,P,T}P_o'^2T_o'$$

$$+ \; Y_{o,P,P,P}P_o'^3 + 3Y_{o,T,T}T_o'T_o'' + 3Y_{o,T,P}(P_o'T_o'' + P_o''T_o')$$

$$+ \; 3Y_{o,P,P}P_o'P_o'' + Y_{o,T}T_o'' + Y_{o,P}P_o''' - h_x'''/h_x \tag{6b}$$

$$+ \; 3h_x'h_x''/h_x^2 - 2(h_x'/h_x)^3 - 1/x^2 + 1/(1-x)^2$$

where $Y_{o,T,T}$, etc., are defined in the appendix, the prime denotes the derivative with respect to x. The equations were solved numerically using the Newton method.

3.2 Gas/Gas Equilibria

Equation (4) and the one-fluid modifications are quite general and we have applied them to several systems of interest; for example, to mixtures of the noble gases, to the mixture N_2/CH_4 and to the mixture N_2/C_2H_6. These results will be discussed in a later publication [2]. Here, however, we report on the phenomenon of gas/gas equilibria for *model* systems. We refer to the classification of Scott [7]. *Type I*: Equilibria are classified by the behavior of the critical line in the P-T projection. For type I behavior, the line must begin from the critical point of the less volatile component with a positive slope, i.e.,

$$\left(\frac{dP}{dT}\right)_c > 0 \tag{7}$$

where subscript c denotes differentiation along the critical line.
Type II: For this class, the P-T projection has a minimum with respect to temperature as the pressure increases. Therefore a condition is

$$\left(\frac{dP}{dT}\right)_c = \pm \infty \tag{8}$$

Making use of equations (4a) and (4b) we obtain a necessary condition to satisfy equation (8). Namely at the critical point

$$dY_{m,x,x} = 0 \tag{9a}$$

$$Y_{m,x,x,x}dx + Y_{m,x,x,T}dT + Y_{m,x,x,P}dP = 0 \tag{9b}$$

$$\left(\frac{dP}{dT}\right)_c = -\frac{Y_{m,x,x,T}}{Y_{m,x,x,P}} \tag{9c}$$

Equation (9c) follows from equation (9b) because we are on the critical line, equation (4b). There is no reason for $Y_{m,x,x,T}$ to be infinite, thus to satisfy equation (8) we must have

$$Y_{m,x,x,P} = 0 \tag{10}$$

It follows that if the system of equations:

$$Y_{m,x,x} = 0$$
$$Y_{m,x,x,x} = 0 \tag{11}$$
$$Y_{m,x,x,P} = 0$$

has a solution at a temperature below the critical temperature of the less volatile component, then gas/gas equilibrium of the second type occurs.

In order to calculate $Y_{m,x,x,P}$, we derive from the one-fluid theory:

$$Y_{m,x,x,P} = Y_{o,T,T,P}T_o'h_x/f_x + 2Y_{o,P,T,P}P_o'T_o'h_x/f_x$$

$$+ \; Y_{o,P,T}(2P_o'T_o'/P + T_o''h_x/f_x) + Y_{o,P,P,P}P_o'^2h_x/f_x$$
$$\tag{12}$$

$$+ \; Y_{o,P,P}(2P_o'^2/P + P_o''h_x/f_x) + Y_{o,P}P_o''/P$$

Mixed Type: A third possibility can easily occur from our calculations, even though it has not been observed experimentally; namely a mix of type I and type II is permissible. For instance the derivative $(dP/dT)_c$ can be positive initially but then a maximum can occur with respect to the temperature at a relatively low pressure, and afterwards a temperature minimum is found at higher pressures.

4. Results

We calculated a critical point at a given state point via equations (4)-(6)—using the mixing rules of equation (3) with η^{ij} and ξ^{ij} set equal to unity—so that equations (7) and/or (8) were satisfied. In fact equation (6) was solved for a given fixed ratio of the critical volume of the pure components, and the ratio of the critical temperatures then varied until the minimum value of this temperature ratio was found which would satisfy equation (7) or (8). Table 1 lists the results, i.e., the appropriate value of T_{22}^c/T_{11}^c for fixed values of V_{22}^c/V_{11}^c between 0.7 and 4.5. As a matter of interest the overlapping results of Hicks and Young [24] are included.

TABLE I. *Minimal value of T_{22}^c/T_{11}^c for gas/gas equilibrium.*

V_{22}^c/V_{11}^c	First kind (Type I)	Mixed kind	Second kind (Type II)
0.7			1.88
0.8			2.07
0.9			2.25
1.0	7.06	4.8	2.42
	[14.0][a]		[2.5][a]
	[81.0][b]		[4.0][b]
1.05	7.40		
1.1	7.79		
1.15	8.22		
1.2	8.73		
1.25	9.38		
1.3	10.4		
1.35	14.2		
1.5		5.43	
1.66			3.47
2.0		5.86	3.95
2.5		6.18	4.60
3.75			5.85
4.0		6.73	6.06
4.2			6.23
4.5		6.87	

[a] Calculated [24] by means of the Guggenheim equation of state.

[b] Calculated [24] by means of the Van der Waals equation of state.

The results are perhaps clearer when shown in figure 1. Curve I is the plot of the temperature ratio in the second column of table 1 versus V_{22}^c/V_{11}^c. It represents a limiting critical point line above which and including which unambiguous first kind, or type I, of gas/gas equilibria occur. In other words if the temperature and volume ratios of the components of a binary mixture are such that they lie inside curve I, the Van der Waals one-fluid model will predict gas/gas equilibria of type I. Curve II is the limiting line above which and including which equilibria of type II
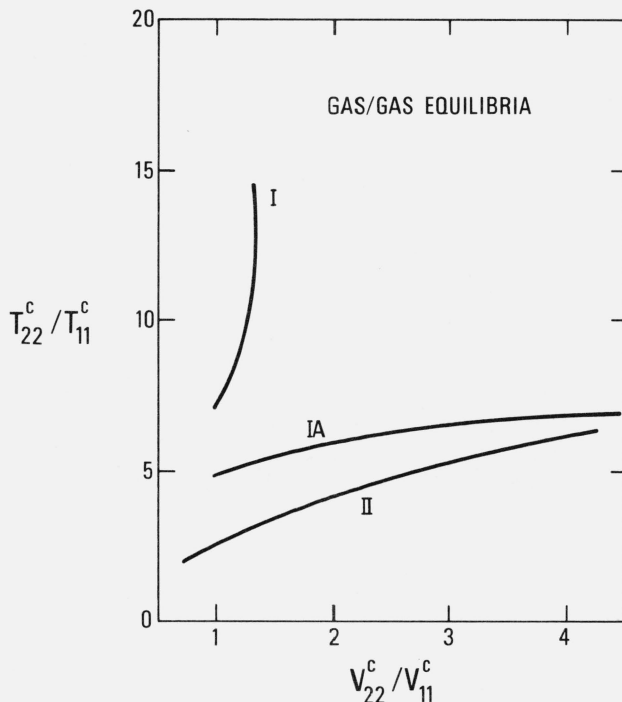

FIGURE 1. *Ratios of the temperature at fixed ratios of the critical volumes designating regions of different classes of behavior of the critical lines for gas/gas equilibria.*
Curve I—the lower limit of appearance of the gas/gas equilibrium of the first kind or type I [7].
Curve IA—the lower limit of appearance of the gas/gas equilibrium of the mixed kind.
Curve II—the lower limit of appearance of the gas/gas equilibrium of the second kind or type II [7].

will occur. Curve IA represents equilibria of the mixed kind. This curve is somewhat arbitrary since we required that equation (7) be satisfied at pressures between P_{22}^c and $P_{22}^c + \Delta P$ is arbitrary set at 7.5 MPa, and at temperatures greater than the critical of the less volatile component. We have determined, however, that curve IA with $\Delta P = 7.5$ MPa represents the *upper* boundary: Use of $\Delta P < 7.5$ MPa simply tended to collapse IA towards II.

Figures 2 and 3 show sample plots of the critical lines in the P-T projection. Curve I of figure 2 is typical of type I behavior: in this case with $V_{11}^c/V_{22}^c = 1.3$ and $T_{11}^c/T_{22}^c = 10.4$. Curve IA is typical of a mixed kind result with the volume and temperature ratio of 2.5 and 6.18, respectively. Figure 3 gives type II results for the ratios (1 and 2.42) and 1.25 and 2.59.

5. Discussion and Conclusions

Our first remark is that we have proposed a very efficient general procedure to calculate the critical lines of a mixture based on the one-fluid Van der Waals conformal solution theory. Computational time is rapid. As an example of the procedure we report results for the critical
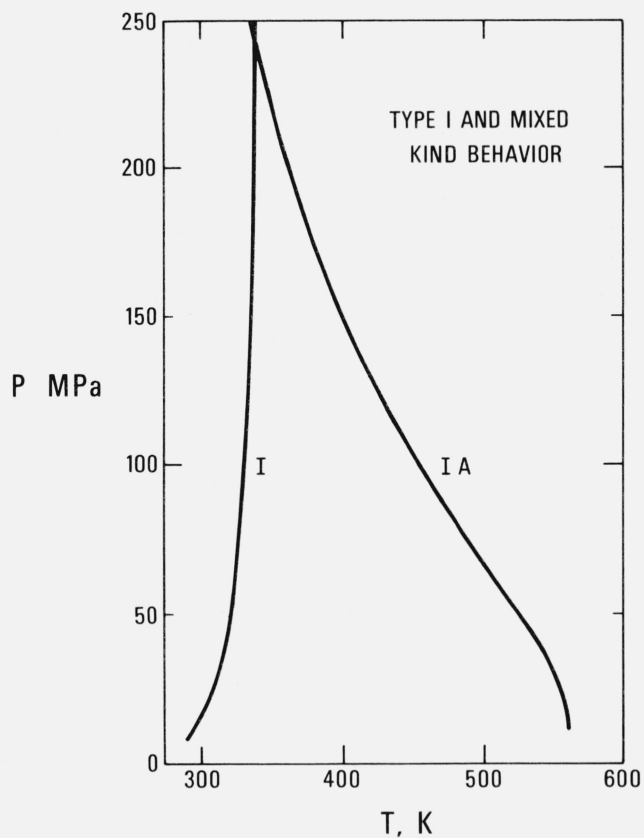
FIGURE 2. *P-T projection of type I, at $V_{22}^c/V_{11}^c=1.3$ and $T_{22}^c/T_{11}^c=10.4$, and of the mixed type, (Ia) at $V_{22}^c/V_{11}^c=2.5$ and $T_{22}^c/T_{11}^c=6.18$.*
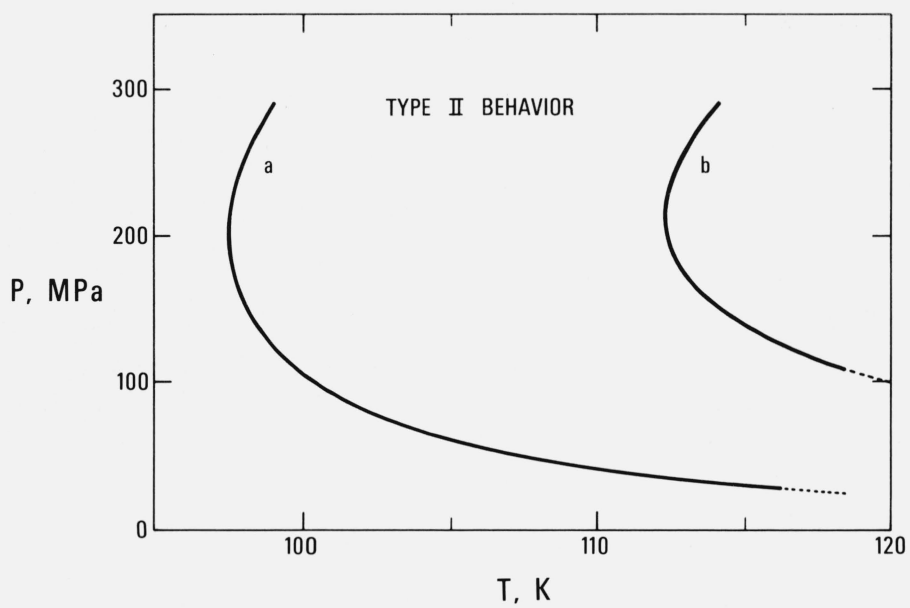

FIGURE 3. *P-T projection for type II behavior at $V_{22}^c/V_{11}^c=1.0$ and $T_{22}^c/T_{11}^c=2.42$ (curve a), and $V_{22}^c/V_{11}^c=1.25$ and $T_{22}^c/T_{11}^c=2.59$ (curve b).*

lines in gas/gas equilibria, but we have used the method to estimate gas/liquid and liquid/liquid lines for several hydrocarbon systems with success [2,25].

We next remark on the relationship of our curves with experiment. Unfortunately this is not clearcut for the following reasons:

(a) Conformal solution theory is not strictly valid and tends to break down for a mixture whose species differ widely in size, mass, and interaction energy [13,14]. Unfortunately such mixtures are the more likely to show gas/gas equilibria, especially mixtures with helium. Our predictions of type I behavior for mixtures of He-C_2H_6, He-CO_2 and He-Xe (for which $V_{22}^c/V_{11}^c \approx 4$ and $T_{22}^c/T_{11}^c \approx 30$) where not too satisfactory. Predictions of type II behavior for the mixtures Ne-Kr, Ne-Xe and Ne-CH_4 were somewhat better. Also the model correctly gave the negative result that mixtures whose components are not disparate, e.g., Ar-Kr, Ar-Xe and Kr-Xe, do not show gas/gas equilibria.

(b) Real mixtures do not obey corresponding states, although the method can be generalized to include the so-called shape factors introduced by Leland and coworkers [6].

(c) The procedure—common with all mixture procedures available at this time—requires interaction parameters such as the ξ_{12} and η_{12} of equation (3) and the numerical properties of a mixture are often, but not necessarily, extremely sensitive to a particular choice of ξ and η. We have set ξ and η equal to unity but their influence on the critical lines is quite pronounced, which is demonstrated in figures 4 and 5. The general tendency is: lowering ξ_{12} shifts the critical line towards a higher temperature, (the same qualitative effect is obtained by increasing the critical temperatures ratio with the critical volumes ratio held constant): increasing η_{12} increase the curvature of the critical line.
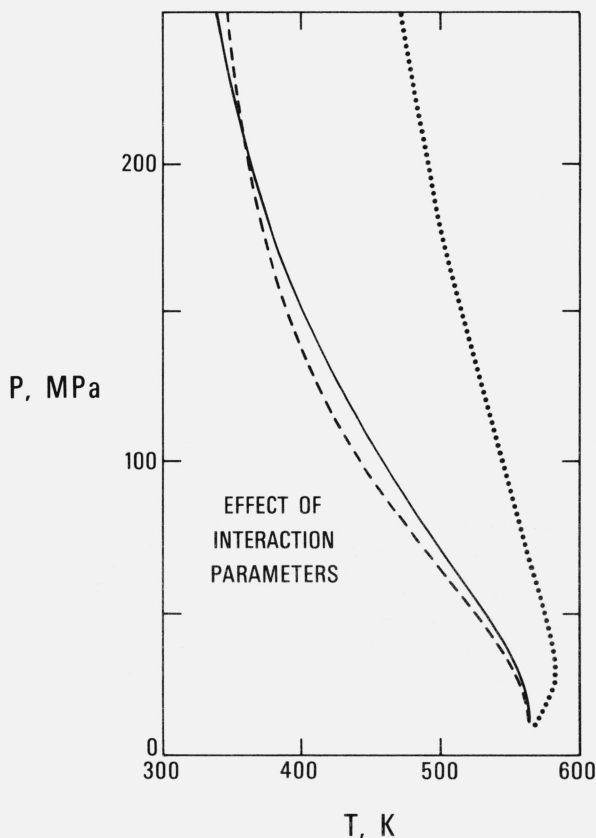
FIGURE 4.   *Effect of ξ_{12} and η_{12} on the projected P-T curve of the mixed kind. All calculations at $V_{22}^c/V_{11}^c = 2.5$ and $T_{22}^c/T_{11}^c = 6.18$ (see fig.2). Solid curve: $\xi_{12} = \eta_{12} = 1.0$, dashed curve: $\xi_{12} = 1.0$, $\eta_{12} = 1.08$, dotted curve: $\eta_{12} = 1.0$, $\xi_{12} = 0.8$.*
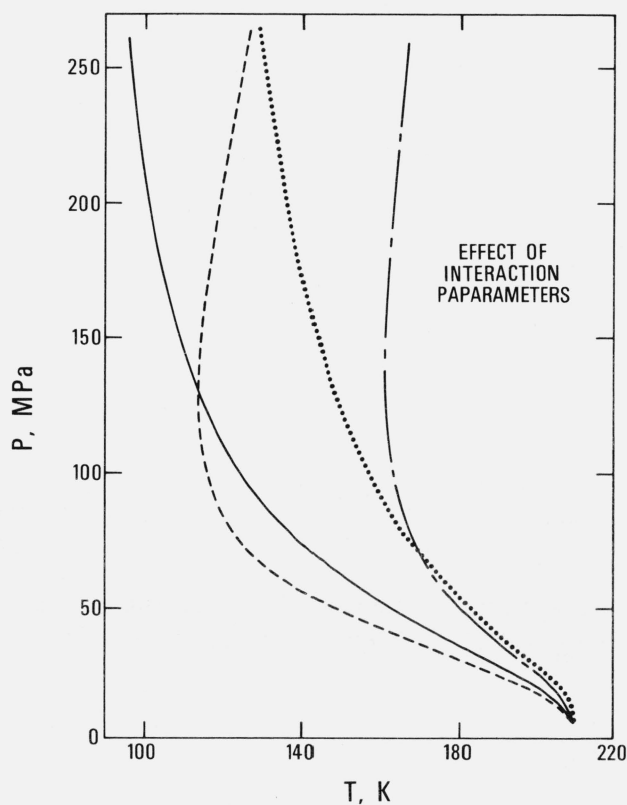

FIGURE 5.   *Effect of ξ_{12} and η_{12} on the projected P-T curve of type II. All calculations at $V_{22}^c/V_{11}^c = 2.18$ and $T_{22}^c/T_{11}^c = 4.71$. Solid curve: $\eta_{12} = \xi_{12} = 1.0$, dashed curve: $\xi_{12} = 1$, $\eta_{12} = 1.1$, dotted curve: $\eta_{12} = 1$, $\xi_{12} = 0.9$, dash-dotted curve: $\eta_{12} = 1.1$, $\xi_{12} = 0.9$.*

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7. Appendix

The partial derivatives of the function $Y_o(T_o, P_o)$ which are necessary for calculations of the second and third derivative of $Y_m(T, P, x)$ with respect to x are given in this appendix. H is the enthalpy, F the Helmholtz free energy and S the entropy. We define $Y_{o,i,j,k}$ as the derivative of Y_o with respect to i, j and k,

$$Y_{o,T} = -H(T,P)/RT,$$

$$Y_{o,P} = V/RT,$$

$$Y_{o,P,T} = -V/RT^2 + \left(\frac{\partial V}{\partial T}\right)_P /RT,$$

$$Y_{o,P,P} = \left(\frac{\partial V}{\partial P}\right)_T /RT,$$

$$Y_{o,T,T} = 2H(T,P)/RT^3 - \left(\frac{\partial S}{\partial T}\right)_P /RT,$$

$$Y_{o,T,T,T} = -6H(T,P)/RT^4 + 3\left(\frac{\partial S}{\partial T}\right)_P /RT^2 - \left(\frac{\partial^2 S}{\partial T}\right)_P /RT,$$

$$Y_{o,T,T,P} = 2V/RT^3 - 2\left(\frac{\partial V}{\partial T}\right)_P /RT^2 + \left(\frac{\partial^2 V}{\partial T^2}\right)_P /RT,$$

$$Y_{o,T,P,P} = -\left(\frac{\partial V}{\partial P}\right)_T /RT^2 + \left(\frac{\partial^2 V}{\partial P \partial T}\right) /RT$$

$$Y_{o,P,P,P} = \left(\frac{\partial^2 V}{\partial P^2}\right)_T /RT^2,$$

where we have omitted subscript o on the right hand side for brevity.

The equation of state of argon is:

$$P_o = P(T,\rho)$$

$$\rho_o = 1/V \tag{A1}$$

In this work P_o and T_o are used as the independent variables, thus for any given pair, equation (A1) is solved for ρ_o.

Calculation of $H_o(T_o, P_o)$.

$$G_o^{\text{res}}(T,P) = F^{\text{res}}(T,V) + RT(Z-1) - RT \ell nZ$$

$$Z_o = PV/RT \tag{A2}$$

$$F_o^{\text{res}}(T,V) = \int_o^\rho [P(T,\rho')/\rho'^2 - RT/\rho'] d\rho'$$

After integration of equation (A1) accordingly to equation (A2) we obtain $F_o^{\text{res}}(T,V)$ as a polynomial in T_o and ρ_o. The superscript "res" denotes the residual functions defined in general by $X_o^{\text{res}} = X(T,P) - X^{id}(T,P)$:

$$S_o^{\text{res}}(T,V) = -\left(\frac{\partial F^{\text{res}}(T,V)}{\partial T}\right)_V \tag{A3}$$

$$S_o^{\text{res}}(T,P) = S^{\text{res}}(T,V) + RT\ell nZ$$

$$G_o(T,P) = G^{\text{res}}(T,P) + RT\ell nP/kT$$

$$S_o(T,P) = S^{\text{res}}(T,P) - R(\ell nP/kT - 1)$$

$$H_o(T,P) = G^{\text{res}}(T,P) + TS^{\text{res}}(T,P) + RT \tag{A4}$$

Calculations of $\left(\dfrac{\partial S_o(T_o,P_o)}{\partial T_o}\right)_{Vo}$ *and* $\left(\dfrac{\partial^2 S_o(T_o,P_o)}{\partial T_o^2}\right)_{Vo}$

$$\left(\frac{\partial S_o(T_o,P_o)}{\partial T_o}\right)_{Po} = \left(\frac{\partial S(T,V)}{\partial T}\right)_V + \left(\frac{\partial S(T,V)}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$
$$= \left(\frac{\partial S(T,V)}{\partial T}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{A5}$$

since

$$\left(\frac{\partial S_o(T_o,V_o)}{\partial T_o}\right)_{Vo} = \left(\frac{\partial S_o^{\text{res}}(T_o,V_o)}{\partial T_o}\right)_{Vo}$$

this quantity is obtained by direct differentiation of the equation (A3) with respect to the temperature.

$$\left(\frac{\partial^2 S_o(T_o,P_o)}{\partial T_o^2}\right)_{Po} = \left(\frac{\partial^2 S(T,V)}{\partial T^2}\right)_V + 2\left(\frac{\partial^2 P}{\partial T^2}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$
$$+ \left(\frac{\partial^2 P}{\partial V \partial T}\right) \left(\frac{\partial V}{\partial T}\right)_P^2 + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{A6}$$

since

$$\left(\frac{\partial^2 S_o(T_o,V_o)}{\partial T_o^2}\right)_{Vo} = \left(\frac{\partial^2 S_o^{\text{res}}(T_o,V_o)}{\partial T_o^2}\right)_{Vo}$$

this quantity is obtained by differentiation of equation (A3).

Calculation of other derivatives. All derivatives of the pressure, P_o, are obtained by direct differentiation of the equation of state (A1). The derivatives of the volume V_o with respect to the temperature and pressure are reexpressed by the derivatives of the pressure P_o:

$$\left(\frac{\partial V_o}{\partial P_o}\right)_{To} = \left(\frac{\partial P}{\partial V}\right)_T^{-1} \tag{A7}$$

$$\left(\frac{\partial V_o}{\partial T_o}\right)_{Po} = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial V}\right)_T^{-1} \tag{A8}$$

$$\left(\frac{\partial^2 V_o}{\partial P_o^2}\right)_{To} = -\left(\frac{\partial P}{\partial V}\right)_T^{-3} \left(\frac{\partial^2 P}{\partial V^2}\right)_T \tag{A9}$$

$$\left(\frac{\partial^2 V_o}{\partial T_o^2}\right)_{Po} = -\left(\frac{\partial P}{\partial V}\right)_T^{-1} \left(\frac{\partial^2 P}{\partial T^2}\right)_V - 2\left(\frac{\partial^2 P}{\partial T \partial V}\right) \left(\frac{\partial P}{\partial T}\right)_V$$
$$\left(\frac{\partial P}{\partial V}\right)_T^{-1} + \left(\frac{\partial^2 P}{\partial V^2}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial P}{\partial V}\right)_T^{-1} \tag{A10}$$

$$\left(\frac{\partial^2 V_o}{\partial T_o \partial P_o}\right) = -\left(\frac{\partial P}{\partial V}\right)_T^{-2}\left[\left(\frac{\partial^2 P}{\partial T \partial V}\right) - \left(\frac{\partial^2 P}{\partial V^2}\right)_T\right.$$
$$\left.\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial V}\right)_T^{-1}\right] \tag{A11}$$