the exponential in Equation (1). A decrease of 3% in the surface tension of a mixture would lower the prediction of the kinetic limit of superheat by about 1°C. The prediction was only a little less sensitive to errors in the vapor pressure; an increase of 4% in the vapor pressure decreased the limit of superheat by 1°C. A 5% change in the molar volume of the liquid did not noticeably affect the prediction of the limit of superheat.

Considering the method used to obtain the values for the surface tension of the mixtures at high temperatures, the surface tensions could easily be about 5% off. Because of errors in the bubble points, critical temperatures, critical pressures, and the Riedel-Plank-Miller correlation, the vapor pressures are probably in error by about the same factor. These sources of errors easily account for the differences between the experimental and theoretical limits of superheat for *n*-hexane-cyclohexane and benzene-cyclohexane. However, the difference between the theoretical curve and the experimental points for benzene *n*-hexane may be partially due to solubility effects.

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Critical Points of Mixtures: An Analogy with Pure Fluids

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The thermodynamic properties of vapor-liquid equilibrium (VLE) states near the critical locus of mixtures are correlated in very close analogy with the techniques used to correlate the properties of pure fluids near a critical point. The only mixture parameters used in the correlation are the values of pressure, volume, temperature, and mole fraction (*PVTx*) along the physical critical locus. We illustrate the power of the present approach by correlating the rather extensive *PVTx* data that exist near the critical loci of the binary mixtures: CO_2-C_2H_6, SF_6-C_3H_8, and C_8H_{18}-C_3H_8. Nearly all the data within 10% of the critical temperature may be described within their accuracy despite the occurrence of critical azeotropy or large regions of retrograde condensation.

SCOPE

The primary objective of this study was to find some relatively simple techniques through which several very general, recent developments in the theory of critical points might be applied to correlating data in the engineering literature. In this work, we apply correlation techniques based on physical ideas of general applicability to experimental data and obtain representations of the data which are economical in terms of number of parameters. Furthermore, we find that the quantity of data needed to describe phase equilibria in the critical region is thereby significantly reduced. The representations may be used with confidence for interpolation, integration, or differentiation. This approach should facilitate the development of new engineering processes by reducing the time and expense required to obtain the VLE data that may be required for a mixture which has not been studied heretofore.

Our approach to correlating data in binary mixtures is adapted from that used to describe He^3-He^4 mixtures by Leung and Griffiths (1973) and by Doiron et al. (1976). We formulate a thermodynamic potential for a binary mixture which has *the same functional form* as the potential which has been used near critical points of pure fluids. The coefficients in this potential (and the critical parameters) are assumed to vary very smoothly as the particular mixture considered is taken from one pure component to the other. This assumption may be considered as an extension of the idea of corresponding states. It should be noted that to be consistent with current theoretical ideas about the critical point (Griffiths and Wheeler, 1970; Leung and Griffiths, 1973), the parameter, which is held constant

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as a particular mixture is taken through its various thermodynamic states, cannot be the mole fraction x. In fact, it cannot be any simple function of x nor (in the language of Griffiths and Wheeler) can it be any other thermodynamic density variable characterized by having values which are not equal in the coexisting phases. Instead, the parameter which defines what is meant by a particular mixture for a given set of values of $PVTx$ must be a function (again, in the language of Griffiths and Wheeler) of thermodynamic field variables, that is, variables which are the same in coexisting phases. Such variables are combinations of temperature, pressure, and chemical potentials. The utility of using a constant value of a thermodynamic field variable to define a mixture is implicit in the recent empirical discovery of a particular law of rectilinear diameters for some binary liquid mixtures (Won and Prausnitz, 1974). The use of thermodynamic field variables to map one fluid state into correspondence with another is the primary feature which distinguishes the present treatment from other extensions of corresponding states (Rowlinson and Watson, 1969).

The Leung-Griffiths equation of state for He^3-He^4 mixtures has been used with minor alterations by D'Arrigo et al. (1975) in carbon dioxide-ethylene. The present treatment differs in several practical details from these earlier applications of the field variable ideas. Here, a reduced equation of state is used, and a simple recipe for generating the coefficients in that equation is provided. The critical parameters of the mixtures are the only sensitive parameters adjusted to fit the data, and, in this work, an attempt is made to do this within the accuracy of the data. The power laws in our formulation occur with the variable $(T - T_c)$ in contrast with the variable $(T - T_c)^{-1}$ used by Leung and Griffiths. The present choice fits density data for pure fluids over a wider temperature range. It also allows us to use published correlations to obtain pure fluid parameters.

CONCLUSIONS AND SIGNIFICANCE

The particular recipe we have developed describes most of the $PVTx$ data of the three binary mixtures we have studied. In each case, for data within 10% (in temperature) of the critical locus, the difference between the description and experimental data is close to the accuracy of the data. The description is successful despite the occurrence of critical azeotropy in two of the systems (CO_2-C_2H_6 and SF_6-C_3H_8) and a fairly large region of retrograde condensation in the third (C_8H_{18}-C_3H_8). The most sensitive correlating parameters which we determine by fitting the data are the values of the pressure, volume, and temperature of the physical critical loci of the mixtures. These parameters will also be the most important ones in any correlation of transport properties which have anomalies that occur near critical loci.

On the basis of our experience, we expect the particular recipe we have used to apply for any binary mixture with a liquid-vapor critical locus which extends continuously and reasonably smoothly from one pure component to the other. A probable exception, which we have not yet investigated, is the case in which two critical loci approach each other near a tricritical point (for example, in carbon dioxide rich mixtures of CO_2-$C_{13}H_{28}$).

Our approach to the correlation of binary data can be generalized to deal with data on ternary or multicomponent mixtures. Unfortunately, there are few complete sets of data near the critical loci of such mixtures to test such a generalization.

The central idea of this work, the use, for mixtures, of a thermodynamic potential whose parameters are smooth functions of thermodynamic field variables rather than smooth functions of mole fractions, this idea is, in principle, useful outside of the critical region. Our illustration of the practical utility of this idea in dealing with phase equilibria in the critical region should lead to further investigations of its utility elsewhere in the $PVTx$ surface.

PHYSICAL IDEAS AND CORRELATING EQUATIONS

The correlation scheme which we have used to represent mixture data makes use of the following:

1. The physical critical parameters of each mixture must be adjustable parameters in any accurate representation of critical region data.

2. Power laws are an economical description of the anomalous thermodynamic properties near critical points.

3. Thermodynamically consistent power laws may be generated from a thermodynamic potential which obeys scaling laws (defined below).

4. The power laws (and the thermodynamic potentials) used for pure fluids may be generalized to mixtures by allowing the coefficients in these functions to vary smoothly with some thermodynamic field variable as the mixture under consideration is taken from one pure fluid to the other pure fluid.

5. For the simple mixtures we are considering, the coefficients in the thermodynamic potential may be obtained by a kind of linear interpolation between the corresponding coefficients for the pure fluids. We will now discuss each of these ideas in turn.

The physical critical parameters $T_c(x)$, $P_c(x)$, and $\rho_c(x)$ will play a central role in any accurate representation of mixture data in the critical region. Both thermodynamic and transport properties have power law anomalies which originate at the physical critical locus. Thus, in any correlation of critical region data, the location of the critical locus will be varied (implicitly if not explicitly) to obtain agreement with the data.

The usefulness of a power law representation for the equilibrium densities of coexising liquid and vapor phases has long been recognized for pure fluids. An expression for the reduced density difference as a function of the reduced temperature $[t = (T - T_c)/T_c]$ such as

$$(\rho_{\text{liquid}} - \rho_{\text{vapor}})/(2\rho_c) = C_1(-t)^\beta \qquad (1)$$

together with the law of the rectilinear diameter

$$(\rho_{\text{liquid}} + \rho_{\text{vapor}})/(2\rho_c) = 1 + C_2t \qquad (2)$$

is sufficient to represent the coexisting densities of many pure fluids with an accuracy of a few tenths of 1% within a temperature range $0.0001 < -t < 0.1$. These simple rules may be used with reduced accuracy to represent liquid densities of some fluids to the triple point; however they fail badly for ρ_{vapor} less than say, 0.1 ρ_c to 0.2 ρ_c. The best values of the exponent β in (1) appear to be in the range of 0.32 to 0.38. There are indications that the smaller values of β are found as T_c is approached (Hocken and Moldover, 1976).

Another power law describes the scaled isothermal compressibility as a function of temperature:

$$P_c\rho^2K_T \equiv P_c(\partial\rho/\partial\mu)_T = \Gamma^{\pm}|t|^{-\gamma} \qquad (3)$$

Here the + sign refers to the compressibility along the critical isochore above T_c, while the − sign refers to the compressibility of either the liquid or vapor phase at saturation. In the temperature range $10^{-4} < t < 0.1$ above T_c, data for many pure fluids will fit such a law within a few percent. Below T_c, the range of approximate validity is again much greater in the liquid phase than in the vapor phase. Typical values for γ are in the range 1.14 to 1.20.

Other thermodynamic quantities such as C_V also show power law divergences near the critical point. In an effort to represent all such anomalies in an accurate and consistent way a phenomenology known as scaling has been developed. On the basis of very simple and plausible assumptions (primarily, that the thermodynamic potential is analytic everywhere except at the critical point), it has been shown that only two exponents are independent and hence that only two are required to represent the thermodynamic anomalies for all properties asymptotically close to the critical point. One can choose as these two exponents the density exponent [β in Equation (1)] and the compressibility exponent [γ in Equation (3)].

Particular examples of scaling equations of state with unique choices for exponents have been shown to describe a large body of data on diverse fluids within the accuracy of the data (Levelt Sengers et al., 1976). Because the critical exponents actualy measured depend upon both the quantity under consideration (for example, C_V or K_T) and the path of approach to the critical point (for example, a path of constant volume, a path of constant pressure, etc.), a very large number of power laws are contained in scaling equations of state. Although the data are well represented with scaling equations, the exponents used are significantly different from the exponents predicted by all equations of state which have Taylor series expansions at the critical point itself. Thus, simple equations of state, such as the Redlich-Kwong equation, cannot represent data accurately in the critical region. A striking example of the superiority of scaling representations of the critical region over Taylor series representations is provided by the temperature dependence of C_V measured at the critical volume.

At the critical temperature, a discontinuous decrease in C_V is expected from all analytic equations. The experimental results for xenon, argon, He^3, He^4, oxygen, nitrogen, carbon dioxide, water, and ethane (Levelt Sengers, 1977) are all consistent with a power law of the form

$$C_V = A^{\pm}|t|^{-\alpha} + D \qquad (4)$$

(The + and − signs refer to temperatures above and below T_c, respectively.) Such a law is found to represent the data with an accuracy in the order of 1% in the temperature range $0.001 < |t| < 0.1$. Analysis of experimental data indicates that the exponent α has a value near 0.1 in all these fluids, in near agreement with the prediction of a scaling description based on equation of state data.

At first sight, scaling equations of state appear to be hopelessly complicated for applications involving mixtures. We enumerate their apparent disadvantages before outlining our approach to circumventing them. In their present form, scaling equations of state require a discouragingly large amount of input data. In the comparatively simple formulation of Leung and Griffiths (1973), the thermodynamic potential is divided up into a singular part and an analytic background part. The singular part requires the specification (for each fluid) of two scale factors [for example, C_1 in Equation (1) and Γ^- in Equation (3)]. The functional form of the singular part, including the two exponents, is to a reasonable approximation, the same for a wide variety of fluids in the narrow temperature range $10^{-4} < t < 0.05$. The regular part of the potential requires the specification of the critical parameters P_c, ρ_c, T_c, and many additional parameters depending upon the range of data to be fit. The minimum number of parameters required for phase equilibria alone in a practical application include the slope of the rectilinear diameter [C_2 in Equation (2)] and two derivatives of the vapor pressure equation near T_c. A further feature which discourages the application of scaling equations of state to mixtures in that in their present formulation they do not reduce to desirable limiting forms, for example, at very low or very high densities. Thus, from a user point of view, scaling equations of state have much in common with the virial equation of state. They each provide economical and accurate representations of data in a limited range of thermodynamic states. They each are awkward to extend beyond that range. They each require many parameters for a given fluid (for example, the parameters which determine the temperature dependence of the higher virials) which have little physical significance.

Thus, it would appear to be impractical to determine most of the parameters in a scaling equation of state for mixtures from mixture data alone. Instead, another scheme such as a version of a law of corresponding states must be used.

In formulating an appropriate version of the law of corresponding states for phase equilibria in mixtures, we shall rely heavily on the geometrical ideas of Griffiths and Wheeler (1970). We shall interpret these ideas graphically in Figures 1 and 2. The essential idea is: The thermodynamic properties of fluid mixtures can be expressed in simple analogy with the thermodynamic properties of pure fluids if one uses variables such as chemical potentials (or fugacities) as the independent variables which specify the mixture under consideration.

In Figure 1 we show three contrasting representations of the *P-T* surface for two phase mixtures of ethane in carbon dioxide. In Figure 1 (left) the pressure is shown as a function of temperature and mole fraction x. Because the liquid and vapor phases in equilibrium at a given temperature and pressure usually have different compositions, the *P-T-x* surface has upper and lower sheets which come together smothly at a critical line. They also come together with knife edges at the vapor pressure curves for each pure component ($x = 0$ and $x = 1$). In this mixture, the sheets also come together accidentally (in a sense to be discussed below) at an azeotropic line which intersects the critical line near $x = 0.32$. The critical locus in Figure 1 (left) usually does not occur at the maximum temperature or pressure of sections at constant x of the figure. Because the chemical potential (or fugacity) of each component is the same in the two phases, replacement of the mole fraction by any function of those variables will cause the surface in Figure 1 (left) to collapse to a single sheet bounded by the critical locus and vapor pressure curves. Figure 1 (center) illustrates this for the variable ζ, which is defined in terms of fugacities or chemical potentials by

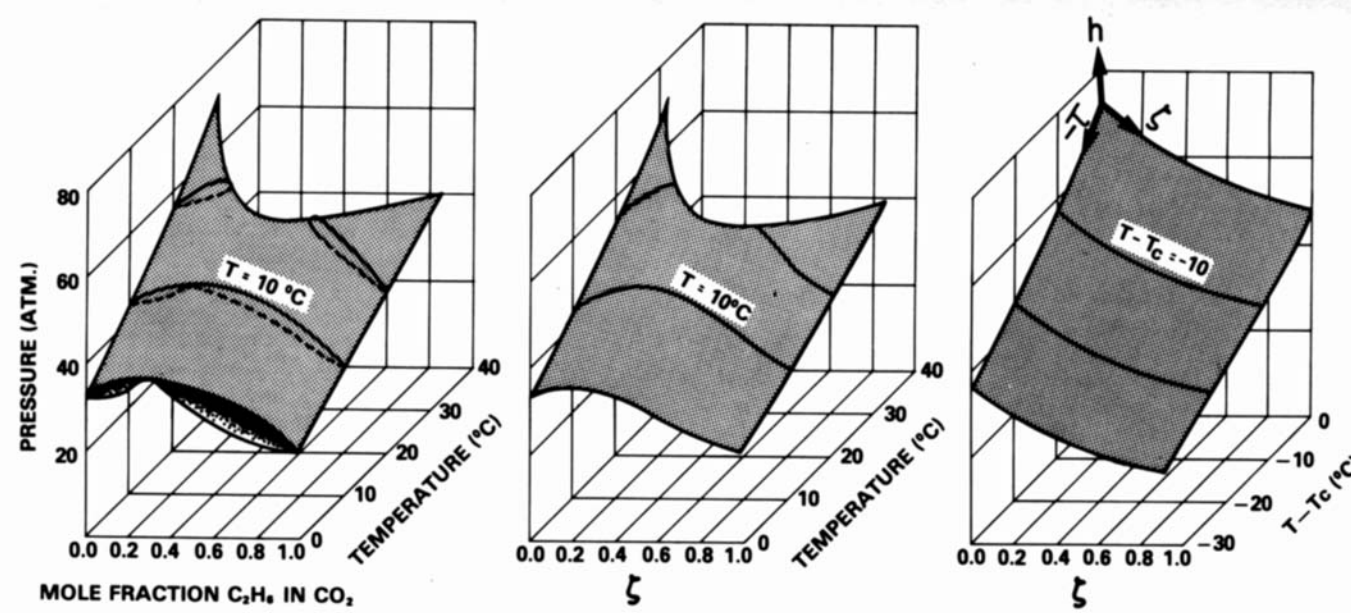

Fig. 1. Vapor-liquid equilibrium states near the critical locus of carbon dioxide-ethane. Left: values of P-T-x; center: values of P-T-ζ. Here all states with two coexisting phases are on a single surface. The azeotrope is the ridge in this surface. The critical locus is the upper boundary of this surface. Right: same as center with temperature scale changed to T-$T_c(\zeta)$. All signs of the azeotrope have disappeared.

$$\zeta \equiv f_1/(Kf_2 + f_1) = e^{\mu_1/RT}/(Ke^{\mu_2/RT} + e^{\mu_1/RT}) \quad (5)$$

The subscripts 1 and 2 stand for the first and second components, ethane and carbon dioxide, respectively. The presence of the constant K in Equation (5) emphasizes the fact that the numerical values assigned to ζ depend on the choice of the reference states for the chemical potentials, although physical properties do not.

In Figure 1 (center), each cross section at constant ζ has the same qualitative shape as the vapor pressure curve of a pure fluid. One might imagine that each section at constant ζ could be represented by a vapor pressurelike equation whose coefficients are smooth functions of ζ. Indeed, we will make such an assumption below. Instead of ζ, other combinations of the thermodynamic field variables, P, T, μ_1, and μ_2, could have been used for the horizontal axis of Figure 1 (center) without changing the qualitative features of the figure. The variable ζ is convenient because it is always in the range $0 \leq \zeta \leq 1$ and because it is easy to formulate a thermodynamic potential in terms of ζ, which is consistent with Henry's law in the limit of dilute solutions.

The right side of Figure 1 also shows the coexistence surface of carbon dioxide-ethane mixtures in the thermodynamic field variables. In this illustration, the absolute temperature T has been replaced with a variable $T - T_c(\zeta)$ which vanishes along the critical locus. In these variables, the surface is quite smooth. Thus, this is one of the surfaces we will model below.

In Figure 2, we show a schematic representation of the ρ-T-ζ surface for VLE states of carbon dioxide-ethane. Tie lines, which would connect coexisting densities, are unnecessary on this saddle shaped surface. (If we had drawn tie lines connecting coexisting phases, they would be horizontal lines lying in constant ζ sections of the figure. It follows that a zero length tie line, that is, a critical point, must occur at the top of a constant ζ section.) Cross sections of the ρ-T-ζ surface at constant ζ have the same general shape as T-ρ curves in a pure substance. We will assume that all constant ζ sections may be described by the same power law, Equation (1), which works so well for pure fluids. The curved sheet which intersects the saddle in Figure 2 represents the values of ρ, T, and ζ available to a mixture of a given composition x. In general, the critical point of a mixture of constant composition occurs on a shoulder of the curve of intersection. Thus, retrograde condensation is the rule for mixtures. One exception to this rule occurs when a sheet of constant x happens to be perpendicular to the ζ axis at the critical point. This case is critical azeotropy.

We now consider our particular thermodynamic model. In order to represent the P-T-ζ and the ρ-T-ζ surfaces algebraically, we first define a ζ dependent reduced temperature

$$t = [T - T_c(\zeta)]/T_c(\zeta) \quad (6)$$

where T_c (ζ) is the critical temperature corresponding to the composition given by ζ. Then we write the ζ dependent generalization of Equations (1) and (2):

$$\rho/\rho_c(\zeta) = 1 \pm C_1(-t)^{0.355} + C_2 t \quad (7)$$

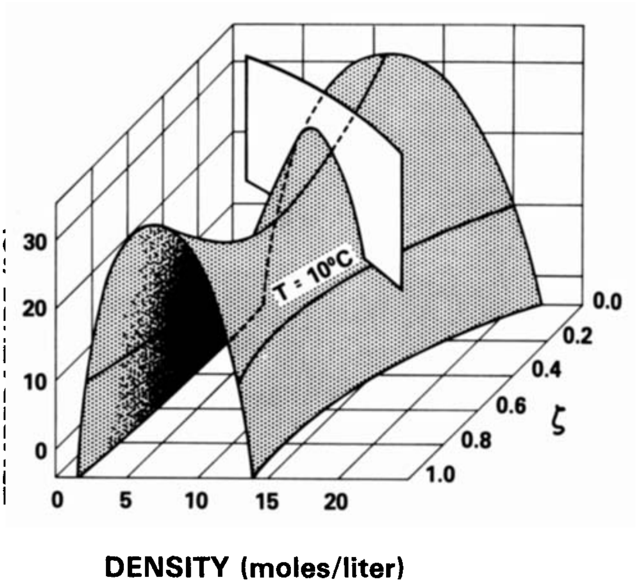

Fig. 2. Vapor-liquid equilibria states near the critical locus of carbon dioxide-ethane. Values of ρ-T-ζ fall on a saddle shaped surface. The critical locus is the heavy curve along the top of the saddle. The curved sheet intersecting this surface represents, schematically, all states of a given mole fraction x.

(The + sign refers to the more dense liquidlike phase, and the − sign refers to the vaporlike phase.) The numerical value for the exponent β (0.355) is consistent with the correlation of Levelt Sengers et al. (1976). Note that both here and in what follows, the coefficients C_i are ζ dependent. Our underlying hypothesis that the coexistence surface is smooth in the field variables led us to take the simplest possible form for $C_i(\zeta)$, namely, linear. For the mixtures which we are considering, this appears to be satisfactory. Thus, the value of C_i is found by interpolation between its values for the pure components:

$$C_i = (C_i^2 - C_i^1)\zeta + C_i^1 = C_i'\zeta + C_i^1 \qquad (8)$$

We have chosen to write the ζ dependent vapor pressure equation in the form

$$\frac{P}{T}\frac{T_c(\zeta)}{P_c(\zeta)} = 1 + C_3\,(-t)^{1.9} + C_4 t + C_5 t^2 + C_6 t^3 \quad (9)$$

The numerical value of the noninteger exponent 1.9 is consistent with the measured trend of the C_v divergence of pure fluids at their critical points and was used in the correlation of Levelt Sengers et al. The terms in ascending powers of t were chosen for our convenience. It is possible that some other form might be more efficient.

Once the functions $T_c(\zeta)$, $\rho_c(\zeta)$, and $P_c(\zeta)$ describing the critical line are supplied, Equations (6) to (9) define the P-T-ζ and ρ-T-ζ surfaces. In order to relate these surfaces to the P-T-x and ρ-T-x surfaces, we need relations between ζ and x. In a mixture of ideal gases at constant temperature, one has

$$x = 1 - \zeta \qquad (10)$$

Somewhat more generally, in situations where Henry's law applies, Equation (10) will hold at both ends of the critical locus if appropriate values of K or, equivalently, the Henry's law constant are chosen. The general form of the relation between ζ and x is not intuitively obvious (to us). We have followed Leung and Griffiths (see Appendix A) to obtain

$$x = (1-\zeta)\left\{1 - \zeta\left[\frac{\overline{Q}(\zeta, t)}{\rho} - \frac{\overline{Q}(\zeta, t=0)}{\rho_c} - \overline{H}(\zeta, t)\right]\right\} \qquad (11)$$

With our specific choice for the thermodynamic potential, the quantity $\overline{Q}$ becomes

$$\overline{Q} = \frac{dx_c}{d\zeta}\frac{P}{RT}\frac{T_c}{P_c}\frac{d(P_c/T_c)}{dx} + \frac{P_c}{RT_c}[C_3'(-t)^{1.9} + C_4' t + C_5' t^2 + C_6' t^3] + \frac{dx_c}{d\zeta}\frac{P_c}{R}\frac{d(1/T_c)}{dx}(1+t)$$

$$\times\,[-1.9\,C_3(-t)^{0.9} + C_4 + 2C_5 t + 3C_6 t^2] \quad (12)$$

[This is obtained from Appendix A by differentiating the sum of (A10) and (A11) as indicated in (A6).]

We have found that the $PVTx$ data for all three mixtures we studied may be satisfactorily described by choosing $\overline{H}(\zeta, t)$ identically equal to zero along the critical locus. This is equivalent to two very simple relations: $x = 1 - \zeta$ from Equation (11) and $dx_c/d\zeta = -1$ in Equation (12). In general, these simplifications cannot be expected. One may use standard, rather tedious approximation methods to estimate $\overline{H}$. This amounts to estimating μ_1 and μ_2 along the critical locus. Along paths parallel to the critical locus, the chemical potentials have no singularities. Thus, the predicted phase equilibria are not expected to be very sensitive to $\overline{H}$. Our experience bears this out.

Only for the propane rich mixtures of C_3H_{18}-C_8H_8 were nonzero values of $\overline{H}$ required. There we chose to treat $\overline{H}$ as an additional function to be adjusted to fit data. We studied the form

$$\overline{H}(\zeta, t) = \overline{H}_1 + \overline{H}_2\,\zeta + \overline{H}_3(\zeta)t \qquad (13)$$

but ultimately set $\overline{H}_1 = \overline{H}_2 = 0$. We found the choice $\overline{H}_3 = 25\ T_c^{-1}\ (dT_c/dx)$ significantly improved the fit to the data. In Appendix B we discuss procedures for estimating $\overline{H}(\zeta, t)$.

Equations (6) to (13) comprise our recipe for correlation of $PVTx$ data in mixtures. In this recipe, the mole fraction x appears as a dependent variable in Equation (11). This equation was derived by differentiating a thermodynamic potential P/T, whose independent variables are $1/T$ and μ_i/T. (The potential we used is given in Appendix A.) In the application of this recipe it is, in fact, not necessary to know properties such as P_c as a function of either μ_i or of ζ. It is convenient to think of ζ as a parameter relating the measured quantities $PVTx$ (and others such as C_{Vx}, K_{Tx}) to one another. It would be convenient to eliminate ζ in favor of x so as to obtain a dependence on experimental quantities only. This would require the inversion of Equation (11). Although we cannot eliminate ζ from the equations algebraically, we can do so numerically.

A simple approach when the functions $T_c(x)$, $\rho_c(x)$, and $P_c(x)$ are available is to calculate isothermal sections of the coexistence surface. One merely chooses successive values of ζ between 0 and 1. Equation (11) then relates the chosen value of ζ to x along the critical locus. The functions T_c, ρ_c, P_c, $d(P_c/T_c)/dx$, and $d(1/T_c)/dx$ are then evaluated at that value of x. The coefficients C_i are evaluated at the chosen values of ζ [Equation (8)]. The values of P, ρ_l, ρ_v, x_l, and x_v for the chosen values of T and ζ may then be found by evaluating Equations (6), (7), (9), (12), and (11) successively. Thus, isothermal

TABLE 1. CONSTANTS FOR PURE COMPONENTS

Substance	CO_2	SF_6	C_2H_6	C_3H_{18}	C_8H_{18}
Property (units)					
T_c (°K)	304.17	318.82	305.34	369.88	569.20
ρ_c (mole/l)	10.62	5.034	6.880	4.927	2.005
P_c (atm)	72.894	37.157	48.076	41.983	25.694
C_1	2.009	1.980	1.924	1.947	2.159
C_2	−0.995	−0.859	−0.834	−0.861	−1.493
C_3	30.87	29.98	28.84	29.57	30.00
C_4	6.00	5.97	5.45	5.704	6.90
C_5	−26.13	−25.90	−25.94	−25.75	−20.62
C_6	−5.49	−14.06	− 8.13	−6.29	0

sections of the coexistence surface may be generated without an iterative root finding process.

DATA FOR THE PURE COMPONENTS

In order to apply our correlation scheme, we need the critical parameters and the six coefficients C_i for each pure component. The values we have selected for these constants are listed in Table 1. We have made neither an exhaustive search of the literature, nor have we attempted to evaluate the data we did find critically. Such care was not required at this time, since our purpose was to develop and test an approach rather than use it at its ultimate accuracy. Thus, the tabulated numbers are not the best in any particular sense. The fact that the coefficients C_1 to C_6 vary only slightly from fluid to fluid attests to the utility of our use of reduced expressions for the coexisting densities and vapor pressure curves. This fact also suggests that fewer coefficients would be required of a more sophisticated vapor pressure equation were used. The small variation of C_1 to C_6 from fluid to fluid makes our assumption of a linear ζ dependence for these coefficients seem plausible. It is exactly this linearity assumption that has enabled us to cope with the scaled equation of state's requirement for many coefficients.

To obtain values of T_c, ρ_c, C_1, and C_2 we fit data for the coexisting densities to Equations (1) and (2). As a criterion of goodness of fit, we simply used the minimum in the sum of the squares of the fractional density deviation for all the data in the range $0 > t > -0.12$. The data used came from the following sources: carbon dioxide from Michels et al. (1937); SF_6 and C_3H_8 from Clegg et al. (1955), ethane from Douslin and Harrison (1973), and C_8H_{18} from McMicking and Kay (1965).

Table 2. Mixture Critical Constants
These constants, which specify the location of the critical loci, are defined in Equations (15) to (17)

Mixture	CO_2-C_2H_6	SF_6-C_3H_8	C_8H_{18}-C_3H_8
ρ_1 (mole/l)	−3.152	−0.054	−0.8
ρ_2 (mole/l)	−0.988	−0.466	0.5
ρ_3 (mole/l)	0.0	0.0	3.0
P_1 (mole/l)	−0.2929	0.1542	1.1
P_2 (mole/l)	−0.1537	−0.4418	−1.6
P_3 (mole/l)	0.0	0.0	1.0
T_1 (mole/l atm)	0.0075	0.006027	−0.01291
T_2 (mole/l atm)	−0.00112	0.002947	0.00990
T_3 (mole/l atm)	−0.00188	0.0	−0.00770

In principle, values for P_c and C_3 to C_6 can be obtained from vapor pressure data once T_c is known. In practice, even with vapor pressure data of the highest quality, C_3 is highly correlated with C_5 because the exponent 1.9 is so close to the exponent 2 [Equation (9)]. Fortunately, C_3 can be determined with some reliability from equation of state or C_v data. We have used the careful correlation of equations of state in the critical region by Levelt Sengers et al. (1976). C_3 is approximately equal to $0.7222\ (a)\ (x_o)^{-0.355}$, where a and x_o are parameters that are tabulated in that correlation for fifteen fluids from helium to water. For the fluid C_8H_{18}, we did not find equation of state data in the critical region; therefore, we set C_3 equal to 30.0, a typical value for other fluids. Then, values for C_4, C_5, C_6, and P_c were found by fitting Equation (9) to the vapor pressure data in the same temperature range mentioned above. (C_6 was set equal to zero for C_8H_{18}.) The vapor pressure data were taken from the sources

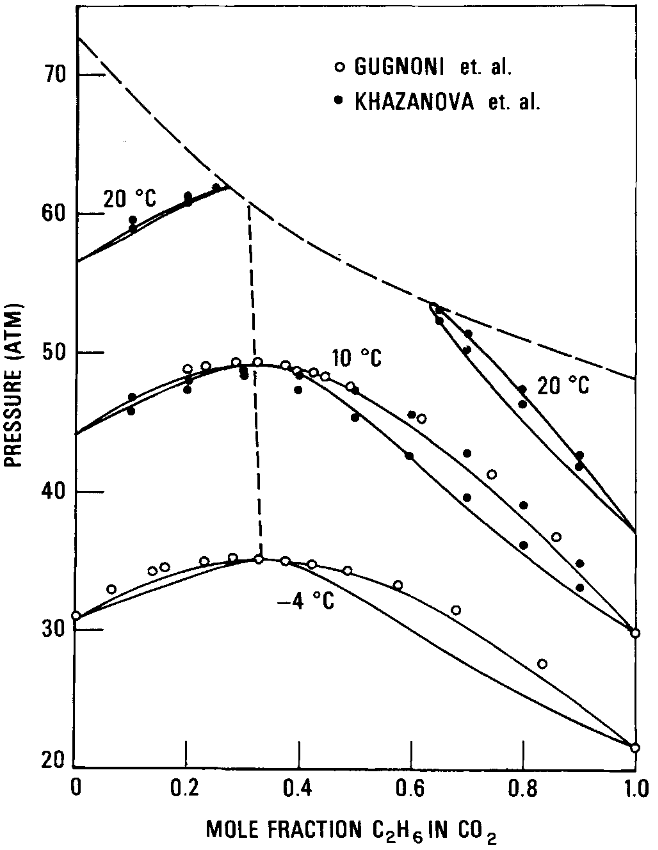

Fig. 3. Vapor-liquid equilibrium in carbon dioxide-ethane. The model is shown by solid curves. The azeotrope and critical locus are shown as dashed curve.

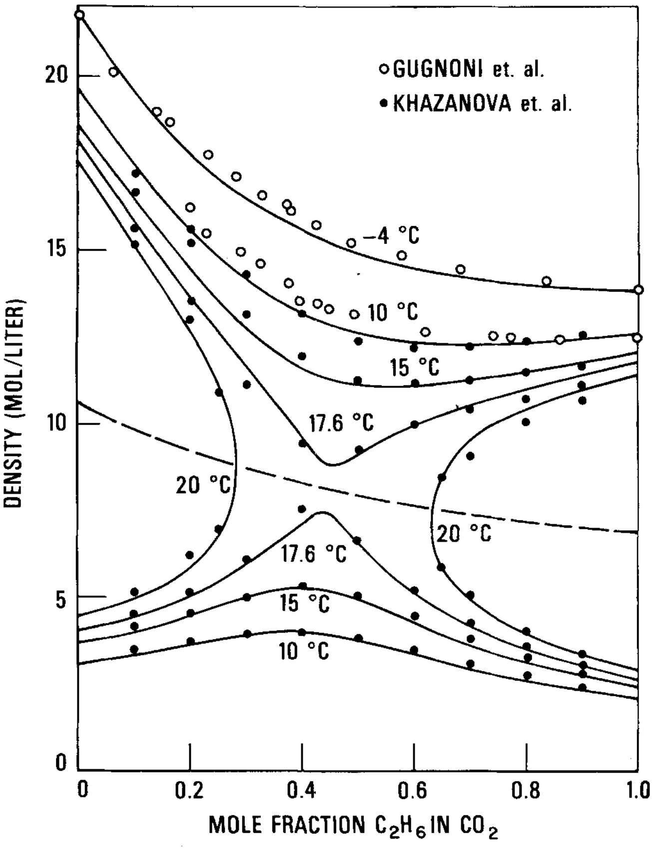

Fig. 4. Vapor-liquid equilibrium in carbon dioxide-ethane. The model is shown by solid curves. The critical locus is the dashed curve.

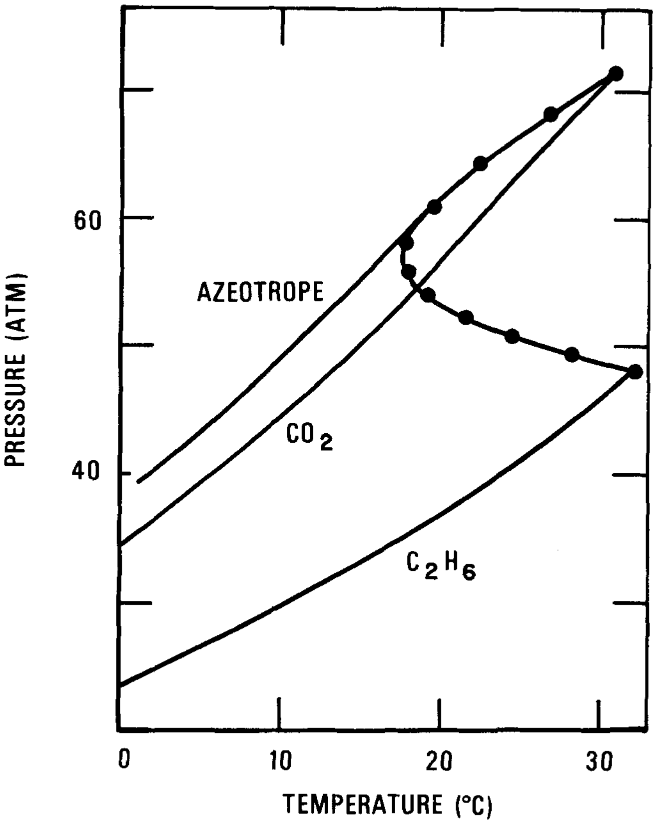

Fig. 5. Pressure-temperature diagram for carbon dioxide-ethane. Dots are placed on the critical locus at intervals of $x = 0.1$. The azeotrope is tangent to the critical locus near $x = 0.3$.

mentioned above with the exception of carbon dioxide which was taken from Levelt Sengers and Chen (1972).

EXPERIENCES IN THE CORRELATION OF MIXTURE DATA

In this section, we will discuss some of the practical problems we encountered in dealing with the mixture data. We will also discuss some of our interesting results. These include the recipe's accurate prediction of critical azeotropy and the significant disagreement between the correlated and experimental values for ρ_c.

In order to represent the mixture data, we used the following convenient representations for the critical loci

$$\frac{1}{RT_c(x)} = \frac{1-x}{RT_{c1}} + \frac{x}{RT_{c2}} + x(1-x)\,[T_1 + (1-2x)\,T_2 + (1-2x)^2\,T_3] \qquad (14)$$

$$\frac{P_c}{RT_c(x)} = \frac{(1-x)P_{c1}}{RT_{c1}} + \frac{xP_{c2}}{RT_{c2}} + x(1-x)\,[P_1 + (1-2x)\,P_2 + (1-2x)^2P_3] \qquad (15)$$

$$\rho_c(x) = (1-x)\rho_{c1} + x\rho_{c2} + x(1-x)\,[\rho_1 + (1-2x)\rho_2 + (1-2x)^2\rho_3] \qquad (16)$$

We used the values in Table 1 for the six pure component critical parameters (T_{c1}, T_{c2}, P_{c1}, P_{x2}, ρ_{c1}, ρ_{c2}) and adjusted T_1, T_2, T_3, P_1, P_2, P_3, ρ_1, ρ_2, and ρ_3 for a satisfactory fit to the mixture data. The parameters we used for the three mixtures are listed in Table 2.

In Figures 3 and 4 we compare the predictions of our thermodynamic model with two sets of data for carbon dioxide-ethane. We adjusted the critical parameter of the model to obtain reasonable agreement with the data of Khazanova et al. (1966). In the range of $PVTx$ displayed, the agreement between the model and the data of Khazanova et al. is better than the agreement between the data of Khazanova et al. and the data of Gugnoni et al (1974). This is particularly evident for the ρ-T-x data at 10°C in the liquid phase. Thus we believe our model is capable of representing such data to an accuracy approaching their absolute accuracy. (To avoid clutter in Figure 3, the 15° and 17.6°C isotherms of Khazanova et al. are not shown. The model agrees with the data on these isotherms as well as it does with the ones shown.)

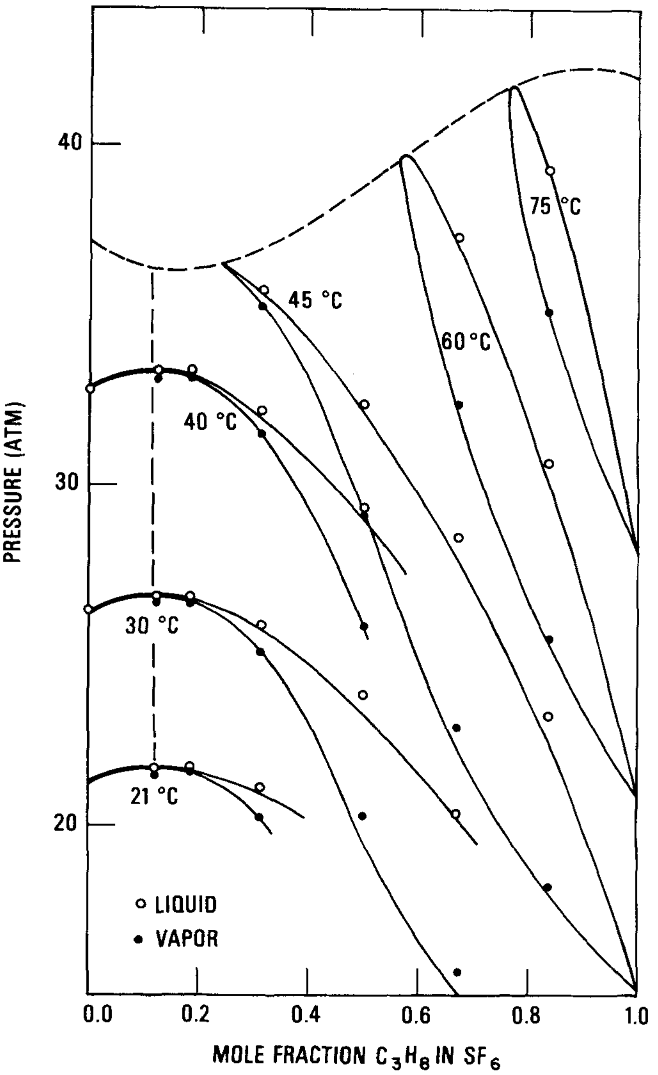

Fig. 6. Vapor-liquid equilibrium in SF_6-C_3H_8. The model (solid curves) is compared to the data of Clegg and Rowlinson. The critical locus and azeotrope are indicated by dashed curves.

We spent a substantial amount of time attempting to find a systematic way of least-squares adjusting the model to the data to find a best fit. This effort was expensive and unfruitful. In the end we proceeded much as one might in fitting data for a pure fluid. The ρ-T-x data were fit to find $\rho_c(x)$ and $T_c(x)$. Then $P_c(x)$ was fit in such a way as to make it consistent with the P-T-x data. This sequence is the mixture counterpart of the procedure we described above for obtaining the critical parameters of the pure fluids.

Khazanova et al. tabulate values for P, T, and ρ on the critical locus. Their tabulated values of ρ_c all fall within 6% of the dashed curve on Figure 4. Their tabulated values of $\rho_c(x)$ show a pronounced kink in the vicinity of

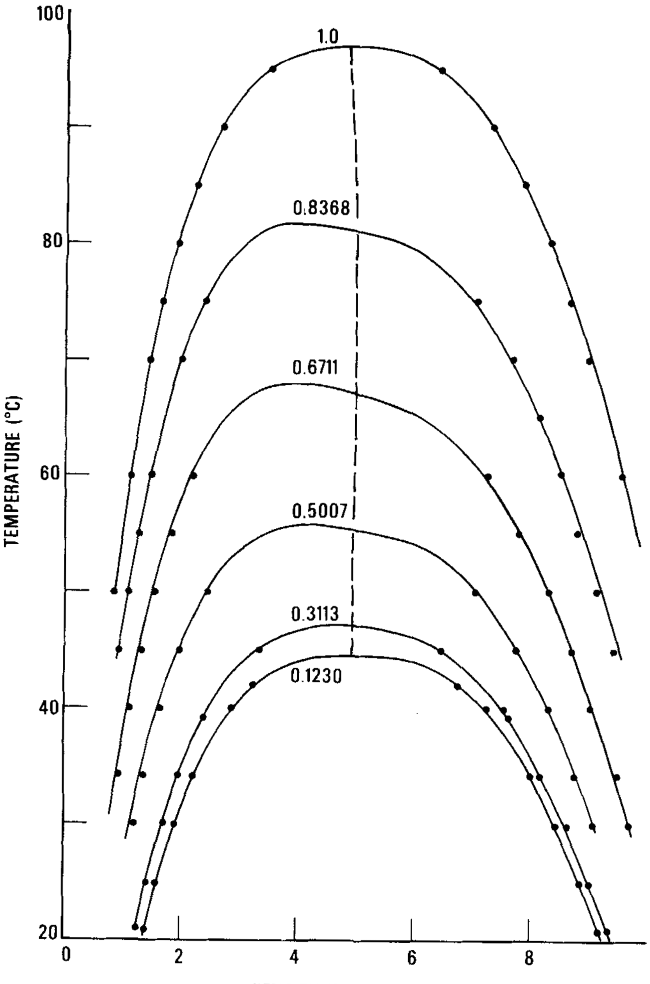

Fig. 7. Vapor-liquid equilibrium in SF_6-C_3H_8. The model (solid curves) is compared to the data of Clegg and Rowlinson. Our critical locus is indicated by a dashed curve. The numerical labels for the curves are the mole fractions of C_3H_8 in the mixtures studied.

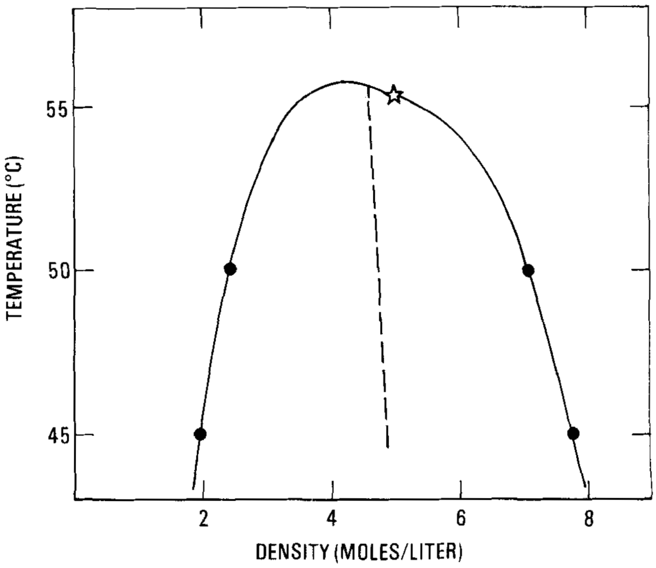

Fig. 8. Vapor-liquid equilibrium in 50.07% SF_6-49.93% C_3H_8. ● data of Clegg and Rowlinson, – – – rectilinear diameter of data, —— model, ☆ model critical point.

the minimium value of $T_c(x)$ ($T_c = 17.6$°C at $x \approx 0.43$). We find no evidence for such a kink in the rest of their tabulated data. Furthermore, simple models of mixtures do not exhibit such a kink. We prefer to interpret the kink as an experimental artifact. (A somewhat analogous situation occurs for SF_6-C_3H_8, but in that case there are enough experimental details published to resolve the differences between the model and the tabulated values.)

The thermodynamic model we use predicts azeotropy in carbon dioxide-ethane mixtures. The condition that both the liquid and the vapor phase have the same composition is simply expressed: $\overline{Q} = 0$ [Equation (12)]. At the critical point this is equivalent to

$$\frac{d(P_c/T_c)}{d(1/T_c)} = -C_4 P_c \tag{17}$$

Equation (17) is the particular expression within our model of the frequently rediscovered thermodynamic result (Rowlinson, 1969) that a critical azeotrope is tangent to the critical locus in the P-T plane. This is illustrated in Figure 5. Our model predicts azeotropic compositions near $x = 0.32$ decreasing slightly as T_c is approached. These azeotropic compositions are in excellent agreement with the data of Gugnoni et al. and with the data of Fredenslund and Mollerup (1974) (not shown). Our values for the azeotropic composition are not in particularly good agreement with the values tabulated by Khazanova et al. ($x \approx 0.23$) in this temperature range.

In Figure 1 (center and right), the P-T-ζ surface for carbon dioxide-ethane is shown. In the center figure the azeotrope is the line of maxima of P-ζ curves at constant T. In the right figure, the temperature axis has been replaced by a $T - T_c(\zeta)$ axis. This is the surface we have assumed to be smooth, and indeed all evidence of the azeotrope has disappeared. These figures suggest that the occurrence of an azeotrope is as accidental as the presence or absence of a ridge in the P-T-ζ surface.

The present model is compared with the data of Clegg and Rowlinson (1955) for SF_6-C_3H_8 in Figures 6 to 9. The model agrees with the ρ-T-x surface to within the accuracy of the data (Figure 7). There are small systematic differences between the model and the experimental P-T-x surface which probably cannot be removed by a better choice of the model critical parameters (Figure 6). In particular, near the azeotropic compositions the model gives much smaller pressure differences between the liquid and vapor phases than the experiment does. Near equimolar mixtures the model yields pressures which are slightly below the experimental ones. We expect nonzero

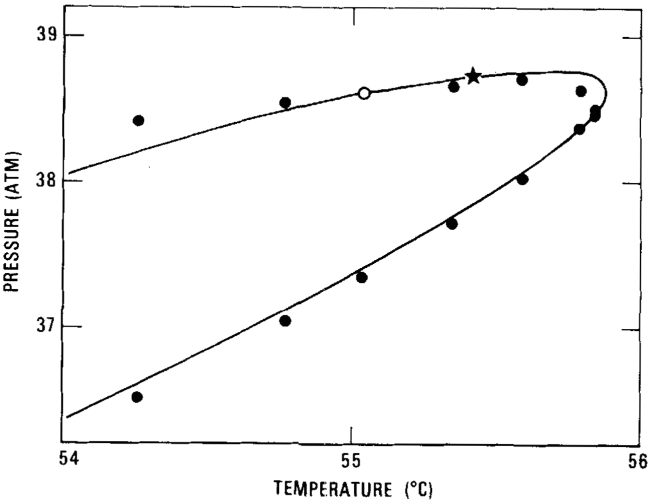

Fig. 9. Vapor-liquid equilibrium in 50.07% SF_6-49.93% C_3H_8. ● data of Clegg and Rowlinson, ○ critical point according to Clegg and Rowlinson, —— model, ☆ critical point of model.

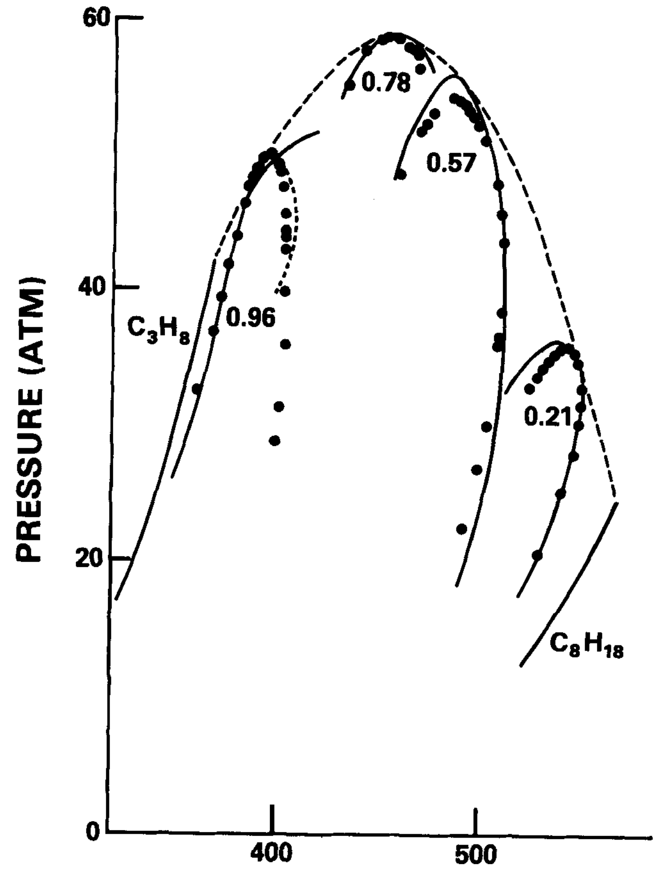

Fig. 10. Vapor-liquid equilibrium in C_8H_{18}-C_3H_8. Our model with $\overline{H} = 0$ (solid curves) is compared with the data of Kay et al. (points). The critical locus is the dashed curve. The dotted curve represents our model with $\overline{H_1} = \overline{H_2} = 0$ and $\overline{H_3} = (25/T_c) \cdot (dT_c/dx)$.

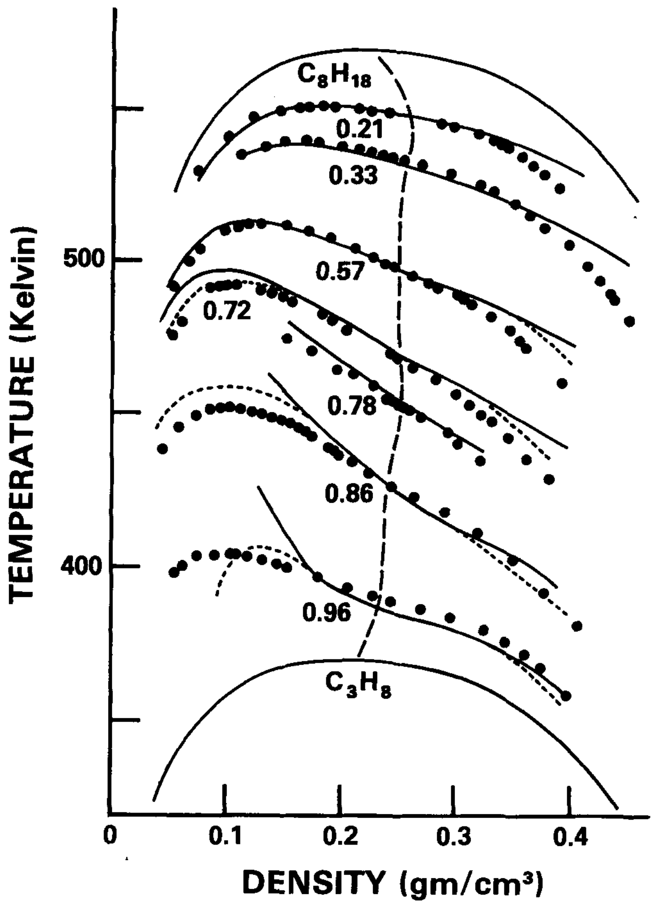

Fig. 11. Vapor-liquid equilibrium in C_8H_{18}-C_3H_8. Our model with $\overline{H} = 0$ (solid curves) is compared with the data of Kay et al. (points). The critical locus is the dashed curve. The dotted curves represent our model with $\overline{H_1} = \overline{H_2} = 0$ and with $\overline{H_3} = (25/T_c) \cdot (dT/dx)$.

values of $\overline{H}$ could improve the agreement between the model and the data.

Clegg and Rowlinson tabulate values of $\rho_c(x)$ which are consistently lower than the dashed curve that best describes the data in Figure 7. The difference between the tabulation and our model is as large as 8% at $x = 0.67$. The tabulated values were obtained by extrapolating the mean of the liquid and vapor densities of each mixture to the observed critical temperature for that mixture. This procedure is illustrated for a nearly equimolar mixture by the dashed curve in Figure 8. The authors knew that such a procedure would not yield the thermodynamic critical density, but they assumed the error would be small because the extent of retrograde condensation in SF_6-C_3H_8 mixtures never becomes much larger than 1°C. Our model, which uses critical parameters consistent with a thermodynamic definition, gives a reasonable estimate for the error they made.

Clegg and Rowlinson do not have density measurement within 5 C of the critical locus. They do have P-T-x measurements quite close to the critical locus. Figure 9 shows the P-T-x data for the same nearly equimolar mixture that we considered in Figure 8. The star denotes the critical point in the model, while the open circle indicates the datum point identified as critical by Clegg and Rowlinson. The fact that the model curve is close to the data at some single point is of course required by our choice of values for T_1, T_2, P_1, and P_2. The fact that the model curve follows the trend of the data so closely gives us confidence in the applicability of the model to this mixture and tends to support our assertion that the critical locus in ρ-T-x lies at densities greater than that given by the rectilinear diameter construction in Figure 8.

In Figures 10 and 11 we compare our model for C_8H_{18}-C_3H_8 with the data of Kay et al. (1974). Even with $\overline{H}$ identically equal to zero, the model provides a very good description of the P-T-x and ρ-T-x surfaces for the mixtures, with mole fractions of propane less than about 0.8. This occurs despite the rather large region of retrograde condensation in some of these mixtures (15°C at $x = 0.57$ and 20°C at $x = 0.71$). The model fails rather badly at densities slightly less than critical for $x > 0.8$. Here the model predicts an unphysically large region of retrograde condensation. We have found that choosing $\overline{H_3} \neq 0$ can greatly improve the representation of the data in this region without degrading the representation elsewhere. The improvement is illustrated by the dotted curves in Figures 10 and 11 for which we have used $\overline{H_3} = (25/T_c)$

$\times\ (dT_c/dx)$. The motivation for this choice is discussed in Appendix B. We expect that nonzero values for $\overline{H}_1$ and $\overline{H}_2$ and/or another choice for $\overline{H}_3$ could further improve the agreement between the present model and Kay's data. Since our intention is to illustrate an approach to correlating data rather than to use the approach to its ultimate accuracy, we have not obtained the optimum values of $\overline{H}_1$, $\overline{H}_2$, and $\overline{H}_3$. From the considerations of Appendix B, we would expect that nonzero values of $\overline{H}_3$ will be required to represent VLE data at least in those cases in which $T_c^{-1}(dT_c/dx)$ is large compared with 1.

We have checked the present thermodynamic model on the VLE data in He^3-He^4 mixtures used by Leung and Griffiths (1973) to test their initial application of field variable concepts. The parameters we used in this test are published elsewhere (Moldover and Gallagher, 1977). Our model fits the VLE data from the critical locus to about two thirds the critical temperature for each composition, a range much wider than one might expect in general. Although the critical temperature of He^4 is 1.5 times that of He^3, this mixture is nearly ideal in the sense that the critical locus is nearly straight, and the VLE data for a mixture of a given x are only slightly different from those for a pure substance.

IMPLICATIONS AND CONCLUSIONS

We have provided a detailed example of the usefulness of the notion of smoothness of the thermodynamic potential as a function of field variable ζ. In this section, we would like to suggest that this general idea has other applications in dealing with phase equilibria in fluids. We would also like to point out the limitations of our particular example.

The usefulness of field variables is illustrated by the observation of Won and Prausnitz that the average density of coexisting phases is a linear function of pressure at constant temperature in many binary mixtures. A constant temperature slice of the ρ-T-ζ surface depicted in Figure 2 will have the same general character as a constant ζ slice, since both T and ζ are field variables in the sense of Griffiths and Wheeler. We would expect that close enough to the critical locus

$$\rho = \rho_c(T)\,[1 \pm C_1(T)\,|P - P_c(T)|^{\beta} + C_2(T)\,(P - P_c(T))] \quad (18)$$

where the exponent β again assumes a value near 0.35 (see below). This does indeed seem to describe some of the data cited by Won and Prausnitz. They also observe that in many mixtures the linearity of the average density is accurate much further from the critical point than the expression for the density difference. The present point of view does not explain this observation but does suggest it is another manifestation of the extraordinary straight rectilinear diameter in pure fluids, which also is not yet explained.

The idea of smoothness of the thermodynamic potential as a function of field variables leads us to expect that an equation analogous to Equations (2) and (18) will describe the temperature dependence of the density at constant pressure. Again, we would expect to find that the density diameter would be fairly straight. Other rules of thumb can easily be generalized to mixtures. For example, a simple power law expression has been proposed by Hall and Eubank (1976) to represent the latent heat as a function of temperature. Their expression could be generalized to mixtures by first writing a thermodynamic potential for a pure fluid from which their expression could be derived and then by making the appropriate coefficients in that potential functions of ζ.

The particular scheme which we have used to correlate binary mixture data has several limitations. They result first from our choice for the form of the thermodynamic potential, second from our choice for the values of the critical exponents, and finally from the rules we used to generate coefficients.

The potential we have chosen is in the form of an expansion about the critical locus and does not reduce to appropriate forms far from the critical locus. It has been chosen to be symmetrical in density about the rectilinear diameter (and the diameter's extension), thus giving accurate representations of the phase equilibria. Unfortunately, in pure fluids above T_c, the μ-ρ isotherms are more symmetrical about ρ_c than about the extension of the diameter. Thus our potential would have to be modified to do a good job of representing single-phase data. Our potential will not be accurate when two critical lines approach each other near a tricritical point. Such a situation occurs in mixtures of carbon dioxide with the n-alkanes near the critical point of pure carbon dioxide in the range $13 < n < 16$.

The exponents we have used were taken from the correlation of Levelt Sengers et al. (1976). Recent theoretical work suggests the expansion for the density difference in all fluid mixtures has the form

$$\rho_{\text{liquid}} - \rho_{\text{vapor}} = C_1(-t)^{\beta}\,[1 + C_7(-t)^{\Delta} + \ldots] \quad (19)$$

Here β and Δ have universal values calculated to be 0.32 ± 0.01 and 0.5 ± 0.1, respectively. C_1 and C_7 vary from fluid to fluid. Recent experiments in pure fluids (within $|t| < 10^{-4}$) and in binary liquid mixtures with miscibility gaps (within $|t| < 0.02$) indicate that close enough to the critical point β is indeed near 0.32 (Hocken and Moldover, 1976; Greer, 1976). Unfortunately, close enough seems to vary somewhat from fluid to fluid. Thus, the value 0.355 which we have used must be viewed as an effective exponent which is approximating the first few terms in Equation (19). The same effective exponent cannot be expected to apply to the same temperature range in all fluid mixtures. Similar considerations apply to the numerical value 1.9 we have used for the other independent critical exponent.

The linear interpolation rule we have used for generating the coefficients $C_i(\zeta)$ obviously cannot be used in mixtures such as carbon dioxide-water, where the critical locus does not extend continuously from one pure fluid to the other.

ACKNOWLEDGMENT

The authors wish to thank Professor R. B. Griffiths for his advice and encouragement throughout this work.

NOTATION

$A^{\pm}$ = coefficients, (4)
B = $1/(RT)$
c = critical point (subscript)
C_i = dimensionless coefficients determined from pure fluid properties
C_i^1, C_i^2 = value of C_i in component 1 or component 2
C_i' = $dC_i/d\zeta$
C_v = constant volume specific heat
D = coefficient in Equation (4)
f_i = fugacity of component i
H = function of fugacities on coexistence surface, (A3)

$\overline{H}$ = function of H and $\overline{Q}$, (A7)
$\overline{H}_i$ = coefficients in expansion of $\overline{H}$, (13)
h = thermodynamic field variable, (A3)
K = coefficient in definition of ζ which depends upon reference states chosen for μ_i
K_T = isothermal compressibility
P = pressure
P_1, P_2, P_3 = critical pressure parameters, (15)
$\overline{Q}$ = derivative of the thermodynamic potential, (A6)
R = gas constant
r = parametric variable
T = thermodynamic temperature
T_1, T_2, T_3 = critical temperature parameters, (14)
t = $(T - T_c)/T_c$
u = energy per unit volume
V = volume
x = mole fraction
α, β, γ = critical exponents
$\Gamma^{\pm}$ = coefficients, (3)
Δ = critical exponent
ζ = fugacity ratio, (6)
θ = parametric variable
μ_i = chemical potential of i^{th} component
ν_i = μ_i/RT
ρ = number density (mole/l)
ρ_1, ρ_2, ρ_3, = critical density parameters, (16)
σ = value on coexistence surface or its smooth extension (superscript)
τ = $1/(RT_c) - 1/(RT)$

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APPENDIX A: THE THERMODYNAMIC POTENTIAL

Here we write down an explicit thermodynamic potential from which Equations (6) to (13) may be derived. We follow the procedure and most of the notation of Leung and Griffiths (1973). Thus, the rather complex thermodynamic expressions they derived for C_{vx} and K_{Tx} may be used directly. Details may be found in their paper.

First, two abbreviations are introduced:

$$B = 1/(RT) \tag{A1}$$

$$\nu_i = \mu_i/(RT)$$

If P/RT is chosen as a thermodynamic potential, the differential form of the fundamental relation is

$$d(P/RT) = \rho_1 d\nu_1 + \rho_2 d\nu_2 - u dB \tag{A2}$$

Here u is an energy per unit volume. The three independent variables ν_1, ν_2, and B are transformed to three new variables defined by

$$\begin{aligned} \zeta &= e^{\nu_1}/(Ke^{\nu_2} + e^{\nu_1}) \\ \tau &= B_c(\zeta) - B \\ h &= \ln(Ke^{\nu_2} + e^{\nu_1}) - \ln(Ke^{\nu_2^\sigma} + e^{\nu_1^\sigma}) \\ &= \ln(Ke^{\nu_2} + e^{\nu_1}) - H(\zeta, \tau) \end{aligned} \tag{A3}$$

(Here $\nu_1{}^\sigma$ denotes the value of ν_1 on the surface of coexisting phases or its smooth extension beyond the critical locus.) The directions of the $-\tau$, ζ, and h axes are shown schematically in Figure 1 (right). The variable ζ has been discussed in the main text of this paper. τ is a temperaturelike variable. It is measured from its value on the critical locus along paths of constant ζ. The variable h vanishes on the coexistence surface and is a measure of the distance of a thermodynamic point away from the coexistence surface in a constant ζ plane and in a constant τ plane. This variable reduces to $\nu - \nu^\sigma(\tau)$ in a pure fluid. Thus it is closely related to the variable $\mu - \mu_c(T)$ frequently used in scaling equations of state.

The total density (in moles per unit volume) and the mole fraction at a point in thermodynamic space may be obtained from differentiating the potential with respect to the transformed variables:

$$\rho = \left(\frac{\partial(P/RT)}{\partial h} \right)_{\tau,\zeta} \tag{A4}$$

$$x = (1-\zeta)\left\{ 1 - \zeta \left(\frac{\overline{Q}(\zeta.\tau)}{\rho} - \frac{\overline{Q}(\zeta,\tau=o)}{\rho_c} - \overline{H}(\zeta,\tau) \right) \right\} \tag{A5}$$

$$\overline{Q}(\zeta,\tau) = \left(\frac{\partial(P/RT)}{\partial \zeta} \right)_{h,\tau} = \frac{\partial(P/RT)}{\partial \zeta} + \frac{dB_c}{d\zeta}\frac{\partial(P/RT)}{\partial \tau} \tag{A6}$$

$$\overline{H}(\zeta,\tau) = \frac{\partial H}{\partial \zeta} + \frac{dB_c}{d\zeta}\frac{\partial H}{\partial \tau} - \frac{\overline{Q}(\zeta,\tau=o)}{\rho_c} \tag{A7}$$

Equations (A1) to (A7) define the variables to be used and the required thermodynamic relations. The particular potential we use is the sum of an analytic part and a part which has singularities (noninteger powers) at the critical locus (where both τ and h equal zero). The singular part of the potential is most conveniently expressed by introducing still two more parametric variables. The parametric variables r and θ are defined by

$$\frac{\tau}{B_c - \tau} = t = \frac{r(1 - 1.39090\theta^2)}{0.3909} \tag{A8}$$

$$h = \frac{P_c}{RT_c}\frac{C_3}{\rho_c C_1(0.1692)} r^{1.545}\,\theta(1-\theta^2) \tag{A9}$$

The singular part of the potential is

$$\frac{P_{\text{sing}}}{RT} = \frac{P_c C_3}{R\,T_c(0.1692)} r^{1.9}\,(0.4753 - 0.7561\theta^2 + 0.4500\theta^4) \tag{A10}$$

The numerical values for the exponents and the coefficients in (A8) to (A10) were taken from the correlation of pure fluid data by Levelt Sengers et al. (1976). In fact our potential would reduce to theirs in a pure fluid if we had defined h such that it reduced to $(\mu - \mu_c)$ in a pure fluid rather than $[\nu - \nu^\sigma(\tau)]$. The analytic part of the potential is given by

$$\frac{P_{\text{an}}}{RT} = \frac{P_c}{R\,T_c}(1 + C_4 t + C_5 t^2 + C_6 t^3) + \rho_c(1 + C_2 t)h \tag{A11}$$

The total potential is given by the sum of (A10) and (A11). The analytic ζ dependence of P_c, T_c, ρ_c, and C_i has not been explicitly shown in these equations.

The variable θ takes on the values ± 1 on the coexistence curve. Thus the total potential (A10) + (A11) evaluated at $\theta = \pm 1$ reduces to the ζ dependent vapor pressure equation which appears as Equation (9) in the text and is sketched in Figure 1, center and right. Similarly, if the total density is obtained by applying (A4) to the potential, and if the result is evaluated at $\theta = \pm 1$, Equation (7) for the coexisting densities will be obtained.

APPENDIX B: THE FUNCTION $\overline{H}(\zeta, \tau)$

The function $\overline{H}(\zeta,\tau)$ defined in Equation (A7) must be specified in any complete thermodynamic model for VLE in mixtures. Ideally, one should model the H-τ-ζ (or H-T-ζ) portion of the coexistence surface much as we have modeled the P-T-ζ and the ρ-T-ζ surfaces. To do this, an intuition about the form of the H-τ-ζ surface would have to be developed. This probably could be done by examining simple, thermodynamically complete, mixture models such as Van der Waals mixtures. Alternatively, one might examine real mixtures for which both P-V-T and entropy information are available in the critical region. Because the H-τ-ζ surface is analytic at the critical locus (at least in the Leung-Griffiths scheme), a simple model probably could be differentiated reliably enough to obtain $\overline{H}(\zeta,\tau)$.

We have not attempted to carry out this program. Instead, we considered the expansion

$$\overline{H}(\zeta,\tau) = \overline{H}(\zeta,o) + \left.\frac{\partial\overline{H}(\zeta,\tau)}{\partial\tau}\right|_{\tau=0}\tau + \ldots$$

$$= \overline{H}(\zeta,o) + \left\{ \frac{\partial^2 H}{\partial\zeta\partial\tau} + \frac{dB_c}{d\zeta}\frac{\partial^2 H}{\partial\tau^2} \right\}\tau + \ldots \tag{B1}$$

Throughout this paper we have chosen $\overline{H}(\zeta, o)$ or, equivalently, $\overline{H}_1$ and $\overline{H}_2$ to be identically zero. Some of the freedom needed to make this choice is available because we have never chosen an explicit value for K in the definition of ζ. This point is discussed in detail by Leung and Griffiths.

One of the coefficients of τ in (B1) may be estimated by observing that in the limit of a pure fluid

$$\frac{\partial^2 H}{\partial\tau^2} \to RT^3\frac{d^2\mu^\sigma}{dT^2} \tag{B2}$$

An estimate for $d^2\mu^\sigma/dT^2$ may be obtained in various ways. Barieau (1966) has shown that for a Van der Waals fluid

$$\lim_{T\to T_c} \frac{T_c}{R}\frac{d^2\mu^\sigma}{dT^2} = -\frac{9}{10} - \frac{C_v^{\text{ideal gas}}}{R} \tag{B3}$$

An alternate route is to combine specific heat and vapor pressure data using the thermodynamic relations

$$\frac{T}{R}\frac{d^2\mu^\sigma}{dT^2} = \frac{T\rho}{R}\frac{d^2P^\sigma}{dT^2} - \frac{C_v^\sigma}{R} \tag{B4}$$

(Here, C_v^σ is the specific heat of a two phase system below T_c.) To follow this route, we used Equation (8) to fit vapor pressure data for steam, carbon dioxide, and argon. We then used the vapor pressure equation with C_v^σ data to find $d^2\mu^\sigma/dT^2$. Our results for these real fluids suggest the constant $-9/10$ in Equation (B3) must be replaced with a number between -2.5 and -4.5. Thus we can now estimate $d^2\mu^\sigma/dT^2$ for C_3H_8 near its critical point using $C_v^{\text{ideal gas}}$. We find

$$\frac{dB_c}{d\zeta}\frac{\partial^2 H}{\partial T^2}\tau \approx -\frac{1}{T_c}\frac{dT_c}{dx}\frac{T_c}{R}\frac{d^2\mu^\sigma}{dT^2}t$$

$$= \frac{1}{T_c}\frac{dT_c}{dx}12t = \overline{H}_3\,t \tag{B5}$$

[Again, we have used $dB_c/d\zeta = -\,dB_c/dx$ which is true only if $\overline{H}(\zeta, o) = 0$.]

From this estimate (B5) we learn that $\overline{H}_3$ will make important contributions to the VLE surface when $(1/T_c)(dT_c/dx)$ is large, a situation we encountered only in the propane rich mixtures of C_8H_{18}-C_3H_8. For these mixtures, the data seem to require a term about twice as large as this estimate (Figures 10 and 11). Thus we have an incentive to make a serious model for $H(\zeta,\tau)$ in future work so that we can estimate the additional contribution to $\overline{H}_3$ from $\partial^2 H/\partial\tau\partial\zeta$.

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