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Calculating Critical Transitions of Fluid Mixtures: Theory vs. Experiment

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The progress in predicting critical transitions in fluid mixtures is reviewed. The critical state provides a valuable insight into the general phase behavior of a fluid and is closely linked with the nature and strength of intermolecular interaction. Calculations of critical equilibria have been confined mainly to binary mixtures. The prediction of binary gas-liquid critical properties was initially limited to empirical correlations. These techniques have been superseded by rigorous calculations of the critical conditions using realistic models of the fluid or equations of state. All of the known types of critical phenomena exhibited by binary mixtures can be, at least, qualitatively calculated. If an optimal combining rule parameter is allowed, continuous gas-liquid properties can be calculated accurately for a wide variety of mixtures. Similarly, the pressure and composition dependence of upper critical solution phenomena can be accurately predicted. Progress has been achieved in predicting discontinuous critical transitions in polar and nonpolar binary mixtures. There is increasing interest in calculating the critical properties of ternary and multicomponent mixtures. Although the techniques applied to binary mixtures often can be directly extended to ternary mixture calculations, calculated critical properties of ternary mixtures indicate that their behavior cannot be considered as a simple extension of binary mixture phenomena. Consequently, ternary critical calculations are likely to provide a superior insight into the phase behavior of multicomponent fluids.

Introduction

A critical transition of a fluid is reached when there is no longer any difference in the physical properties between coexisting phases. In the case of a pure fluid, the pressure, temperature and volume of coexisting gas and liquid phases are identical at the gas-liquid critical point. For binary and other multicomponent fluids, the gas-liquid point is also characterized by an equivalence of composition in both phases. Multicomponent fluids can also exhibit critical equilibria between different coexisting liquid phases. It is this latter aspect that generates most of the variety of critical phenomena between mixtures of different component molecules. At very high pressures, the distinction between what constitutes a liquid and what constitutes a gas is not clear, and many workers (Schneider, 1978; McGlashan, 1985) prefer the term "fluid-fluid equilibria" to embrace both types of phenomena.

There are ample examples of the importance of high-pressure critical transitions in chemical engineering processes. The most commonly cited examples include supercritical extraction, distillation, and the enhancement of oil recovery. The location of the critical point determines whether or not retrograde condensation or evaporation (Hicks and Young, 1975) will occur. The vapor pressure curve of a pure liquid ends at the gas-liquid critical point, whereas in a binary mixture, at any composition, liquid and vapor coexist in equilibrium between the dew and bubble point loci. By definition, these parts of the phase diagram must meet at the critical point. If the temperature of a mixture at constant pressure and composition, and initially on the dew point locus is increased, then a new equilibrium between the vapor and liquid phases will be established until the perimeter of the phase envelope is again encountered.

If the pressure is higher than the critical pressure, then a different region of the dew point locus will be encountered and the fluid condenses to a liquid (retrograde condensation). Alternatively, if the pressure is less than the critical pressure, then the bubble point locus is reached and a vapor phase is formed. Retrograde evaporation occurs when the temperature of a mixture on the bubble point curve is reduced at a pressure which eventually results in the intersection of another part of the bubble point locus.

It is evident that critical transitions are a very important aspect of the high-pressure phase equilibria of fluids. However, the study of critical equilibria is also of considerable practical utility in understanding the phase equilibria of fluids in general. The critical state can be used to determine the "global" nature of the phase behavior of the mixture. This aspect is very well exemplified by the phase behavior classification of van Konynenburg and Scott (1980) for binary mixtures (discussed below), which is based on critical transitions. For example, common questions related to the degree of miscibility and the number and nature of coexisting phases can be answered by examining the type of critical transition. If a mixture of two molecules forms a Type III system, then it can be immediately inferred that there will be limited miscibility with extensive liquid-liquid separation. The associated interruption of vapor-liquid equilibria also indicates the existence of three-phase liquid-liquid-vapor coexistence at low temperatures and pressures. The position of the critical locus also delineates the absolute limit of two-phase coexistence.

Practical applications are rarely confined to mixtures containing either a pure liquid or only two components. The introduction of three or more components greatly increases the variety of observable phase transitions. For example, phase coexistence can, in principle, involve three or more liquid phases, in addition to the vapor phase. It becomes inconceivable to experimentally determine every possible combination in a real multicomponent mixture. It is in this context that an overall phase behavior classification is very desirable. This goal can be most easily achieved by examining the critical state. Either measuring or calculating every possible multiphase coexistence of a ternary mixture that exists over a wide range of temperature, pressure, volume and composition is a daunting undertaking. Furthermore, it would be very difficult to generalize the result for other mixtures. In contrast, it is possible to at least calculate the critical surface from which the existence of multiphase equilibria can be deduced. Critical behavior can be potentially used as a basis for a general classification scheme for multicomponent phase equilibria.

Gibbs (1928) established the thermodynamic criteria for fluid criticality, and van der Waals (Rowlinson, 1988) applied his equation of state to the critical point of a one-component system. Only recently, however, calculations have been successfully attempted for binary and ternary fluid mixtures. Prior to the mid 1970s, the critical conditions of a binary fluid were approximated rather than calculated directly. Grieves and Thodos (1962a,b) and Redlich and Kister (1962) developed correlation procedures, whereas Rowlinson (1969) proposed an approximate solution for gas-liquid properties of binary mixtures. These approaches were valid only for mixtures in which the vapor-liquid critical transition occurred at all compositions between the pure components (Type I or II systems). Even with this limitation, the techniques failed to accurately predict vapor-liquid critical transitions for mixtures of molecules of even moderate dissimilarities in size. Later, van Konynenburg and Scott (1980) demonstrated that even the simple van der Waals equation could be qualitatively used to predict all of the known types of critical transitions with the exception of Type VI behavior.

The work of Spear et al. (1969) represents, possibly, the first attempt to rigorously calculate critical equilibria with realistic equations of state. Hicks and Young (1977) developed a robust algorithm for calculating critical equilibria of binary systems, and Peng and Robinson (1977) solved the conditions for the gas-liquid critical transitions of ternary hydrocarbon mixtures. Until recently, the main focus of critical calculations was to test theory against experimental data. There are ample experimental binary data available for such an analysis, but data for ternary mixtures were confined to a small selection of hydrocarbon mixtures. Sadus and Young (1987) reported the experimental critical temperatures of about 30 new ternary mixtures containing molecules with a considerable diversity of size, shape and polarity. They calculated the critical properties of these systems and found that good agreement between theory and experiment could be obtained using only binary interaction parameters and the critical properties of the constituent components as inputs. Recently, Sadus (1992a) has demonstrated that calculating the critical properties of ternary mixtures can provide a useful insight into the overall phase behavior of the ternary fluid mixture.

Historically, the study of the phase equilibria of either one- or two-component fluid mixtures has been led by experimental measurement. The increase in the complexity and diversity of phase transitions of ternary and other multicomponent equilibria will inevitably require greater reliance on calculation procedures.

This review examines the progress achieved in calculating the critical transitions of both binary and ternary mixtures. The role of critical phenomena in binary mixtures and the relationship between the observed behavior and intermolecular interaction is explored, with focus on the criteria for critical transitions in multicomponent fluids and calculation strategies. Models used to describe molecular fluids are discussed, as well as the role of equations of state and related issues such as mixing rules and combining rules. Quantitative agreement between theory and experiment for both gas-liquid and other critical equilibria in binary mixtures is also described. Results for ternary fluid mixtures indicate that ternary and, by extension, multicomponent fluids, exhibit a great diversity of critical transitions. Finally, some future possibilities for critical calculations are discussed.

Role of Critical Transitions

Classification of binary mixtures by van Konynenburg and Scott

Perhaps, the most important illustration of the role of the critical state is the phase behavior classification proposed by van Konynenburg and Scott (1980). Their classification scheme has been comprehensively examined elsewhere (Scott, 1972; Schneider, 1972, 1991; Streett, 1974, 1989; Rowlinson and Swinton, 1982; Wichterle, 1977a,b; Young, 1986) and therefore, only an outline is presented here. Extensive compilations

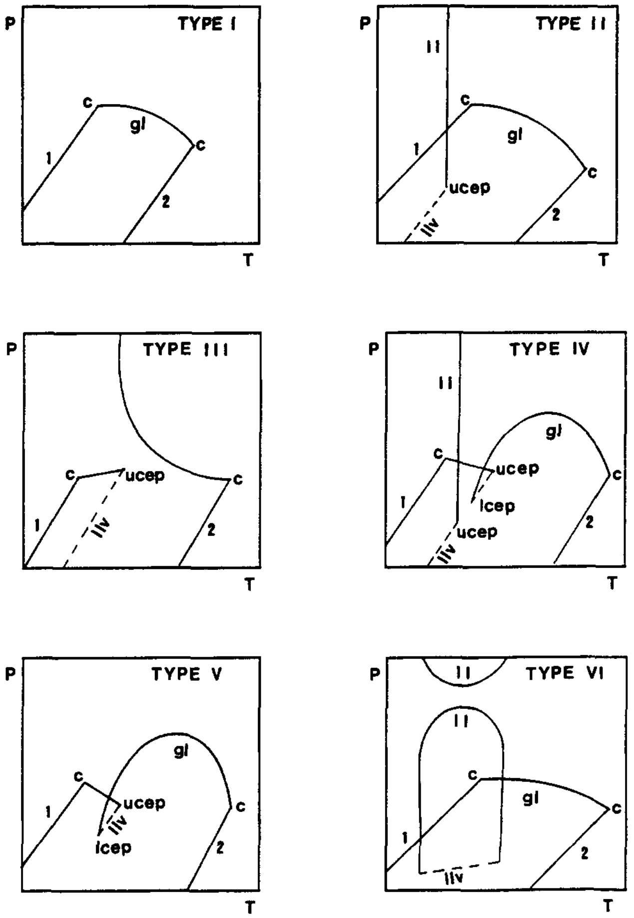

Figure 1. Classification of the phase behavior of binary mixtures with respect to different critical phenomena.

Lines 1 and 2 are vapor pressure curves of the two components which end at a gas-liquid critical point (c). The remaining lines represent critical phenomena except for three-phase equilibria denoted by a broken line.

of experimental critical data can be found in the works of Hicks and Young (1975) and Sadus (1992a).

The six main types of phase behavior, as distinguished by their critical properties, are illustrated in Figure 1. Types I and II behavior are very similar. In both instances, a continuous gas-liquid line is observed linking the critical point of the pure components. At low temperatures, however, Type II mixtures exhibit a liquid-liquid critical line which rapidly rises to high pressures from an upper critical end point (UCEP) on the end of a three-phase liquid-liquid-gas line. The difference between Type I and Type II phenomena is often obscured by solidification at very low temperatures.

The distinction between liquid-liquid and gas-liquid transitions is not straightforward for Type III and higher phenomena. A gas-liquid line from the component with the higher critical temperature usually extends part of the way to the critical point of the other component, but then veers sharply to high pressures. There is effectively a continuous transition between "gas-like" and "liquid-like" properties. A gas-liquid line also extends from the other component until a UCEP is reached on the end of a three-phase line. There are various subclasses of Type III behavior, depending on the position of the main critical locus. Often, so-called "gas-gas immiscibility" is observed when the main critical line extends to temperatures greater than the critical temperature of the least volatile component. The three-phase region can also be located either above or below the vapor pressure curve of the most volatile component.

The critical locus between the pure-component critical points of a Type IV mixture is interrupted by a three-phase liquid-liquid-gas region terminated at either end by a UCEP and a lower critical end point (LCEP), respectively. The critical line from the component with the higher critical temperature ends at the LCEP, whereas a critical line from the other component is terminated by the UCEP. There is also a liquid-liquid critical line at low temperatures which ends at another UCEP. The phase behavior of Type V mixtures is similar, except that the latter phenomenon is absent.

A sixth class of behavior is observed in some aqueous mixtures (such as water + s-butanol) (Schneider, 1978). A liquid-liquid critical line is observed to rise and fall between a LCEP and a UCEP located at either end of a three-phase line. There is also a continuous gas-liquid line linking the critical points of the pure components. In reality, it should be accepted that many mixtures will not fall neatly into one of these categories, particularly for mixtures exhibiting transitional behavior between phase behavior types. Another possible type of phase diagram (Type VII) has been reported (Boshkov, 1987) for Lennard-Jones mixtures of molecules of equal size. It is broadly similar to Type VI behavior with the exception that the critical lines emanating from either pure component are connected by a three-phase line (see Type V behavior). This type of behavior has not been confirmed by experimental measurements.

Intermolecular interaction and classification type

Experimental data can be used to identify a qualitative correspondence between the type and strength of intermolecular interaction and the phase behavior type. Type I behavior is confined to mixtures of simple gases such as argon + methane (Calado et al., 1981) which exhibit strong dispersion force interaction between the dissimilar components. An empirical estimate of the strength of unlike interaction can be obtained by comparing experimental data with optimized calculations using a variable combining rule parameter, ξ, as will be discussed later. Values of $\xi > 1$ indicate strong interaction, whereas weak, unlike intermolecular interaction can be inferred when $\xi < 1$. Of course, this is not an absolute measure of unlike intermolecular interaction. The value of ξ is also influenced by such factors as the accuracy of the combining rule and the suitability of the model of the fluid. A comparison of ξ values obtained from the critical properties of various binary mixtures containing an *n*-alkane is presented in Table 1.

Type I behavior is commonly associated with values of ξ close to or greater than unity. The occurrence of liquid-liquid separation, as evident in Type II equilibria, is associated with appreciably weaker unlike interaction which is reflected by substantially lower ξ values. The component molecules of a Type II mixture typically differ in either molecular type, size or shape, or a combination of properties. The difference in molecular type is the predominating factor. For example, binary mixtures of alkane molecules are formally classified as

Table 1. Comparison of Experimental ξ Values Obtained from the Critical Properties of Binary Mixtures Containing an *n*-Alkane*

	C_6H_6	C_6F_6	CO_2	CF_4	CHF_3	C_2H_5OH
Methane				0.893		
Ethane				0.883	0.860	
Propane				0.855		
Butane			0.90	0.825		
Pentane	0.981	0.940	0.88	0.797		0.906
Hexane	0.980	0.959	0.758	0.766	0.845	0.895
Heptane	0.975	0.952	0.729	0.744	0.738	0.878
Octane	0.972	0.948	0.703			0.866
Nonane	0.968	0.940	0.677			0.876
Decane	0.963	0.938	0.657		0.710	
Undecane			0.635			
Dodecane		0.925	0.565	0.663		
Tridecane	0.957		0.544			

*From Sadus and Young (1985a), Christou et al. (1986, 1991a), and Mainwaring et al. (1988a,b).

Type II systems, but solidification occurs before any liquid-liquid separation occurs. In contrast, liquid-liquid separation is evident for mixtures containing a hydrocarbon and a fluorocarbon (Wirths and Schneider, 1985). Similarly, Type II equilibria are observed for binary mixtures composed of a hydrocarbon and either a chlorocarbon (Christou et al., 1989) or a siloxane partner (Waterson and Young, 1978).

Apart from the influence of specific fluorocarbon-hydrocarbon, siloxane-hydrocarbon or chlorocarbon-hydrocarbon interactions, there is also a large difference in size between the component molecules which also contributes to the weakening of intermolecular interaction. However, molecules of similar size also exhibit Type II behavior if one of the components contains a dipole. The *n*-alkanenitrile + *n*-alkane (McLure et al., 1982) and *n*-alkanol + *n*-alkane (Christou et al., 1991a) mixtures are examples of extensively studied Type II mixtures containing a dipolar component.

A transition between Type II and Type III behavior is commonly observed for a series of mixtures consisting of a relatively small molecule + a systematically changing homologue, such as tetrafluoromethane + *n*-alkane mixtures (Peter et al., 1976; Jeske and Schneider, 1982; Wirths and Schneider, 1985). There is a systematic decrease in the ξ parameter going between Type II and Type III behavior. The component molecules of a binary mixture exhibiting Type III behavior are very dissimilar in size and generally belong to different molecular classes. Type III behavior is also frequently associated with mixtures containing a component with a large permanent dipole moment. The water + hydrocarbon (Brunner, 1990); trifluoromethane + hydrocarbon (Peter et al., 1976; Wirths and Schneider, 1985); ammonia + *n*-alkane (Brunner, 1988a) and ammonia + gas (Brunner, 1988b) mixtures are possibly the most widely studied examples of this type of behavior. Theoretical investigations of the influence of either a quadrupole moment (Gubbins and Twu, 1977) or dipole moment (Twu et al., 1976; Gubbins et al., 1983) on Type III behavior have been made. An increase in either the reduced dipole or quadrupole moment results in a progressive shift in the location of the critical locus to higher temperatures. However, it should be emphasized that having a component with a strong permanent dipole moment is not a necessary prerequisite for Type III behavior. Examples of Type III behavior can be found in the nonpolar sulfur hexafluoride + *n*-alkane (Matzik and Schneider, 1985) and tetrafluoromethane + *n*-alkane (Wirths and Schneider, 1985) series of mixtures. Similarly, mixtures containing a dipolar component and a partner of similar size (such as trifluoromethane + ethane) do not display Type III phenomena. Size difference between component molecules appears to be an important factor governing Type III behavior. Mixtures containing water are anomalous in so far as the available data indicates that Type III equilibria are observed in all cases. Nonetheless, there is usually a substantial size difference between water and the other component of the mixture. The phase behavior of aqueous mixtures has been reviewed by Franck (1985, 1987).

Examples of the remaining categories of phase behavior types are relatively rare, particularly for Type VI equilibria which are confined to a small number of aqueous mixtures (Schneider, 1978, 1991). The distinction between Type IV and Type V behavior is often obscured by solidification at very low temperatures. It is also sometimes difficult to detect the difference between Type II and IV behavior. For example, a second UCEP of carbon dioxide + tridecane has been observed (Fall et al., 1985) close to the gas-liquid line. Due to the close proximity of this point to the gas-liquid line, the mixture was mistakenly classified as Type II, instead of Type IV. Ethane + ethanol (Brunner, 1985a) and methane + hexane (Davenport and Rowlinson, 1963) are other examples of Type IV and Type V behavior, respectively. This behavior has also been identified in mixtures containing a hydrocarbon and either methanol (Brunner, 1985b,c) or pyridine (Brunner, 1987) as the other component. Either Type IV or Type V behavior can be considered as a transition state between either Type I and Type II, or Type II and Type III equilibria. This transition state status is reflected in the narrow range of ξ values which can be used to predict these phenomena. In contrast, both Type II and Type III equilibria are predicted for a broad range of ξ values.

Criteria for Critical Transitions

Criticality criteria for multicomponent mixtures

The classical critical conditions of an *m*-component fluid mixture are due to Gibbs (Gibbs, 1928; Bumstead and van Name, 1906; Donnan and Hass, 1936). A critical transition is observed when the boundary between stable and metastable states (*spinodal curve*) and the coexistence boundary between different stable phases (*binodal curve*) meet. The critical transition can be geometrically interpreted as a point of inflection of the chemical potential with respect to composition. Hence, the first and second derivatives of chemical potential with respect to composition equal zero, whereas a higher derivative must be positive to observe a stable critical transition.

Gibbs showed (Donnan and Hass, 1936) that these critical criteria could be transformed into any thermodynamic function. The nature of this transformation has also been extensively described by other workers (Beegle et al., 1974; Heidemann, 1975; Reid and Beegle, 1977; Modell, 1977; Sadus, 1992a). For practical applications, the critical conditions are most conveniently expressed in terms of the Helmholtz function with temperature and volume as the independent variables:

$$W=\begin{vmatrix} -(\partial^2A/\partial V^2)_T & -(\partial^2A/\partial x_1\partial V)_T & \dots & -(\partial^2A/\partial x_{m-1}\partial V)_T \\ (\partial^2A/\partial x_1\partial V)_T & (\partial^2A/\partial x_1^2)_{T,V} & \dots & (\partial^2A/\partial x_1\partial x_{m-1})_{T,V} \\ \vdots & \vdots & & \vdots \\ (\partial^2A/\partial x_{m-1}\partial V)_T & (\partial^2A/\partial x_{m-1}\partial x_1)_{T,V} & \dots & (\partial^2A/\partial x_2^2)_{T,V} \end{vmatrix}=0 \quad (1)$$

$$X=\begin{vmatrix} (\partial W/\partial V)_T & (\partial W/\partial x_1)_{T,V} & \dots & (\partial W/\partial x_2)_{T,V} \\ (\partial^2A/\partial x_1\partial V)_T & (\partial^2A/\partial x_1^2)_{T,V} & \dots & (\partial^2A/\partial x_1\partial x_2)_{T,V} \\ \vdots & \vdots & & \vdots \\ (\partial^2A/\partial x_2\partial V)_T & (\partial^2A/\partial x_1\partial x_2)_{T,V} & \dots & (\partial^2A/\partial x_2^2)_{T,V} \end{vmatrix}=0 \quad (2)$$

$$Y=\begin{vmatrix} (\partial X/\partial V)_T & (\partial X/\partial x_1)_{T,V} & \dots & (\partial X/\partial x_2)_{T,V} \\ (\partial^2A/\partial x_1\partial V)_T & (\partial^2A/\partial x_1^2)_{T,V} & \dots & (\partial^2A/\partial x_1\partial x_2)_{T,V} \\ \vdots & \vdots & & \vdots \\ (\partial^2A/\partial x_2\partial V)_T & (\partial^2A/\partial x_1\partial x_2)_{T,V} & \dots & (\partial^2A/\partial x_2^2)_{T,V} \end{vmatrix}>0 \quad (3)$$

where A, T, V, and x denote the Helmholtz function, temperature, volume, and mole fraction, respectively. Equations 1 to 3 can be more simply expressed in terms of the Gibbs function using temperature and pressure as independent variables. However, the Helmholtz form is preferred because equations of state commonly used for phase equilibria calculations yield several different volumes for a specified pressure whereas a unique pressure is obtained for a specified volume.

Equations 1 to 3 represent the simplest form of the classical critical criteria in terms of the Helmholtz function. However, they are not unique. A different, but equally valid, form of Eq. 2 is possible depending on which row in determinant 1 is substituted to generate determinant 2. A similar choice determines the nature of Eq. 3. This is discussed in greater detail by Modell (1977) and Sadus (1992a).

When $m=1$, the above equations yield the well known conditions for a critical point of a one-component fluid. There are many examples (Spear et al., 1969; Peng and Robinson, 1977; Hicks and Young, 1977; Sadus et al., 1988) of the application of the above criteria for binary mixtures, but examples of ternary and other multicomponent equilibria are rare. Peng and Robinson (1977) solved the critical conditions for the vapor-liquid equilibria of several ternary and other multicomponent mixtures. Similar calculations were reported by Spear et al. (1971) for ternary hydrocarbon systems. Later, Sadus and Young (1987, 1988) applied the critical conditions to obtain the gas-liquid critical properties of a variety of ternary mixtures containing alkanenitriles, siloxane and fluorocarbon molecules. There are very few calculations of "liquid-liquid" critical equilibria or critical equilibria in general for ternary and other multicomponent systems. Wisniak (1983, 1984a,b) has discussed the thermodynamic criteria for liquid-liquid separation and azeotropy in ternary mixtures. The calculations that are available (Sadus 1992a,b) indicate that ternary fluids exhibit a great diversity of critical phenomena, some of which have no parallel in binary fluids. These are discussed in greater detail later.

Role of stability tests

Calculations for binary mixtures are commonly reported which satisfy Eqs. 1 and 2, but condition 3 is less frequently applied. Condition 3 must be satisfied to guarantee the material stability of the calculated critical point. Equations 1 and 2 are likely to yield solutions which do not always necessarily correspond to real observable phenomena. Omitting condition 3 is not usually a serious oversight for gas-liquid critical properties because physically unrealistic results can usually be detected by "inspection," for example, by observing an anomalous trend in the predicted critical volume. Similarly, there are ample experimental precedents for binary mixtures to confidently identify physically erroneous solutions of Eqs. 1 and 2. However, this prior insight is not available for either ternary mixtures or fluids of more components. In these systems, several solutions of Eqs. 1 and 2 are likely. Many of these potential critical points are likely to be in error, but multiple, physically correct solutions are also possible. Applying Eq. 3 and other stability tests is a necessary procedure for correctly interpreting the outcome of calculations for ternary and multicomponent fluid equilibria.

The complexity of condition 3 has led some workers to develop alternative methods for determining material stability. Hicks and Young (1977) examined the variation of the second derivative of the Gibbs function with respect to composition $(\partial^2G/\partial x^2)$. They identified nine possible variations corresponding to either metastable, unstable or materially stable critical points. However, it is unlikely that such techniques could easily be generalized for multicomponent fluids.

The critical phase must also satisfy the general criteria for phase stability. It is often advantageous to apply these criteria before checking condition 3. If the calculated critical transition fails the general conditions for phase stability, then the solution is unstable and an evaluation of condition 3 is not required. As recently discussed elsewhere (Sadus, 1992a), apart from the requirements that $p>0$ and $(\partial p/\partial V)_T<0$, a phase will be stable

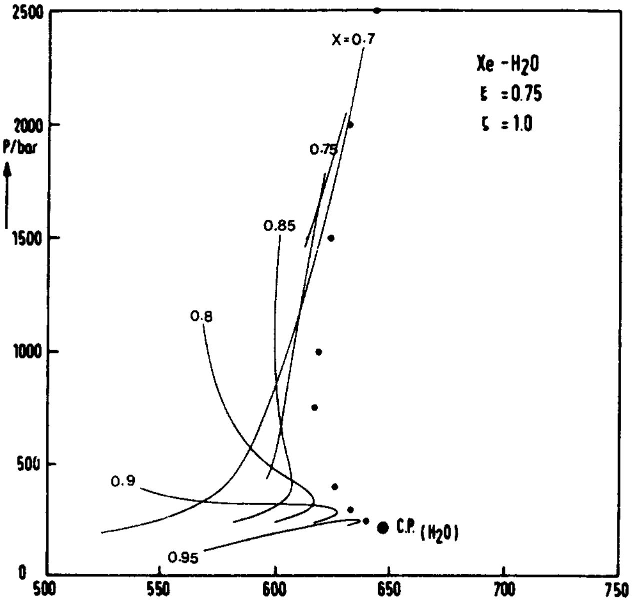

Figure 2. Use of constant-composition pressure-temperature spinodal isopleths to determine the critical curve of the xenon + water binary mixture.

The calculated critical curve is the envelope of the spinodal curves. The experimental critical points (o) are also illustrated (Christoforakos and Franck, 1986).

if all of the minor determinants obtained from the W determinant are negative. For example, a phase containing three components will be stable if the following conditions are satisfied:

$$(\partial p/\partial V)_T < 0 \tag{4}$$

$$(\partial^2 A/\partial x_1^2)_{T,V}(\partial^2 A/\partial V^2)_T - (\partial^2 A/\partial x_1 \partial V)^2 > 0 \tag{5}$$

$$(\partial^2 A/\partial x_1^2)_{T,V} > 0 \tag{6}$$

Although the above criteria are helpful, they will also be satisfied by many materially unstable solutions to Eqs. 1 and 2. Consequently, a mechanism for explicitly determining materially stability is essential for the reliable prediction of multicomponent critical equilibria.

Alternative formulations of the critical point

It is apparent from Eqs. 1 to 3 that there is a very large increase in the complexity of the critical conditions as the number of components in the fluid is increased. Alternative criteria for the critical transition have been proposed to minimize this increase in complexity. For example, Heidemann and Khalil (1980) have adopted a Taylor series expansion at the critical point. At the critical transition, a mixture of total composition N must satisfy the following conditions:

$$Q\Delta N = 0 \tag{7}$$

$$C = \sum_i \sum_j \sum_k \Delta N_i \Delta N_j \Delta N_k (\partial^3 A/\partial N_i \partial N_j \partial N_k)_{T,V} = 0 \tag{8}$$

where Q is a determinant composed of elements of the type,

$$q_{ij} = (\partial^2 A/\partial N_i \partial N_j)_{T,V} \tag{9}$$

and ΔN is a vector. This procedure and refinements by other workers (Michelsen, 1980, 1984; Michelsen and Heidemann, 1981; Billingsley and Lam, 1986; Eaton, 1988) substantially reduces the amount of computation, and it is certainly advantageous for the calculation of multicomponent mixture gas-liquid critical properties.

Indirect methods for determining critical points

The calculation of the binodal curve is considerably more common than critical point calculations. If the binodal curve has been determined, then the critical point can be accurately located by simply determining which point of the binodal curve simultaneously satisfies the condition for spinodal equilibrium (Eq. 1). This has the advantage of avoiding the evaluation of the complicated X determinant. However, the located solution may not be stable because the condition for material stability (inequality 3) has not been evaluated.

The critical curve can also be identified as the envelope of spinodal curves. Christoforakos and Franck (1986) used this approach to identify critical equilibria in Type III binary mixtures. The temperatures and volumes which satisfy the spinodal condition (Eq. 1) are calculated for a fixed value of composition. The pressure is obtained from the equation of state, and the procedure is subsequently repeated for several values of composition. The critical curve is identified as the outer boundary or envelope of the pressure-temperature projections of these different constant composition spinodal curves. An example of this approach is illustrated in Figure 2.

Calculation procedures

An effective method for solving the critical condition is required irrespective of how the critical point is defined. The critical conditions are obviously very mathematically complicated. It is very tempting to employ numerical differentiation procedures rather than obtain the derivatives analytically. Numerical differentiation is not recommended because it often leads to very poor convergence and the loss of arithmetic precision.

If the composition is specified, then Eqs. 1 and 2 represent two simultaneous equations of two variables: temperature and volume. The pressure of the mixture can be determined directly from the equation of state, if composition, temperature, and volume are known. There are many techniques (Henrici, 1964; Traub, 1964) available for solving two simultaneous equations of two variables. They commonly involve successively refining an initial approximate solution until convergence is obtained. The Newton-Raphson method (Henrici, 1964) can be applied to obtain:

$$V^{i+1} = V^i - \{X^i(\partial W/\partial T)^i - W^i(\partial X/\partial T)^i\}/J \tag{10}$$

$$T^{i+1} = T^i - \{W^i(\partial X/\partial V)^i - X^i(\partial W/\partial V)^i\}/J \tag{11}$$

$$J = (\partial W/\partial T)^i(\partial X/\partial V)^i - (\partial W/\partial V)^i(\partial X/\partial T)^i \tag{12}$$

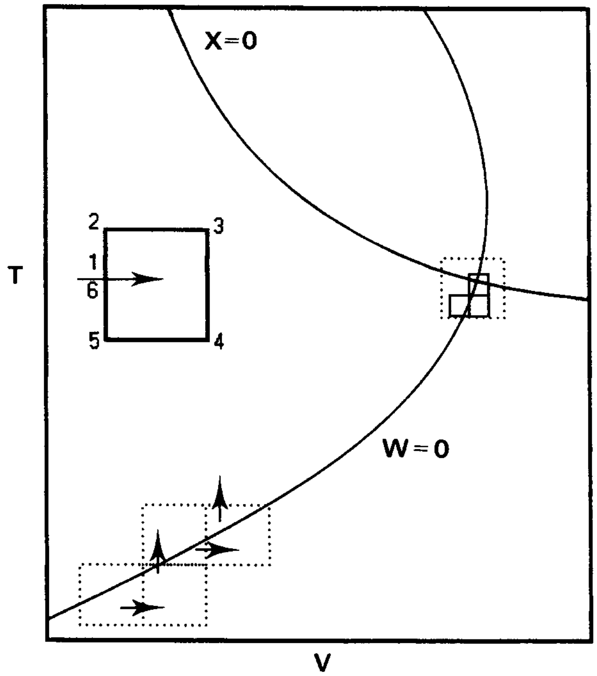

Figure 3. Hicks-Young algorithm for locating the critical point.

Although the Newton-Raphson method has been widely used for critical calculations, its usefulness is largely restricted to calculating gas-liquid critical properties. In common with other iterative procedures, the rapid convergence of the Newton-Raphson method relies on the accuracy of the initial approximation. A reasonable approximation for gas-liquid critical properties can usually be made, but reliable estimates for critical liquid transitions cannot generally be obtained *a priori*. Consequently, the utility of the Newton-Raphson method is restricted to Type I and II phenomena. To predict critical transitions of other types of mixtures, a more general solution is required.

The algorithm developed by Hicks and Young (1977) is useful particularly for locating critical transitions. The algorithm works by carefully tracking either Eq. 1 or 2 while monitoring the sign of the other function in a temperature-volume search plane. It is computationally easier to trace $W=0$ rather than $X=0$ because of the increased complexity of the latter condition. The search procedure is illustrated in Figure 3. Two points (1 and 6) are designated at a small interval on either side of the entry point which lies on one side of a square defined by the points 2, 3, 4 and 5. The sign of W is compared between the adjacent pairs of points: between 1 and 2; 2 and 3; 3 and 4; 4 and 5; and 5 and 6. A change of sign indicates that the condition $W=0$ passes between the point an odd number of times. The sign of X is checked at these points; if it has changed, then an intersection of W and X has been passed. The search procedure is scaled down until the critical point is accurately found. If the sign of X is unchanged, then the new point is used to establish the direction of the $W=0$ line and the next search square is arranged.

The major advantages of the Hicks-Young algorithm are that, in principle, all solutions of the critical conditions are located and that no initial approximations are required. Both these aspects are very important for the *a priori* prediction of critical equilibria. Sadus (1992a) has recently applied the algorithm to the prediction of critical equilibria of ternary mixtures. Three thermodynamically stable critical points, at a particular composition, are commonly encountered in ternary fluid equilibria. Another advantage is that no additional derivatives are required other than those used to obtain Eqs. 1 to 3. However, one disadvantage is that the algorithm is relatively slow compared with traditional iterative procedures such as the Newton-Raphson procedures. However, this slight disadvantage is greatly compensated by its reliability and generality. Van Pelt (1992) has recently proposed improvements to the speed of the algorithm achieved at the cost of an increase in its mathematical complexity. Other techniques, for the calculation of high-pressure phase equilibria in general, are discussed by Heidemann (1983).

Fluid Models

Attempts to predict critical transitions in binary mixtures have either employed *ad hoc* models of the fluid state which utilize an equation of state, or theories such as conformal solution theory or perturbation theory based on the principles of statistical mechanics. Computer simulation (Allen and Tildesley, 1987) is a promising alternative to these approximate theories because the underlying assumptions are solely limited to the nature of the intermolecular potential and the role of multibody interactions. However, no successful applications of computer simulation of the critical state of fluid mixtures have been reported. As discussed below, different methods of approach are to some extent interrelated and often suffer from the same deficiencies. It is not the purpose of this review to provide a comprehensive discussion of the merits of fluid models. Instead, attention will be exclusively focused on those approaches which have been applied to the calculation of critical equilibria. It should be recalled that the modern-day understanding of the critical state indicates that it does not have classical mean field behavior. The issue of the nonclassical nature of the critical state is discussed in greater detail later.

Perturbation models

Considerable emphasis has been placed on the development of perturbation models to represent the fluid state in general. The Helmholtz function is determined from a reference system plus perturbation terms obtained from the radial distribution function of the reference system. The accuracy of the reference term is crucial because it also determines the magnitude of perturbation terms. The underpinning assumption of most perturbation models is that the structure of fluids is determined primarily by strong, short-range repulsive forces, and weaker, long-range forces have only a small effect. The Weeks-Chandler-Andersen model (WCA) (Weeks et al., 1971) is a widely used example of this approach. An alternative suggested by Pople (1954) is to split the intermolecular potential into an angle-averaged isotropic part and an angle-dependent anisotropic component.

Perturbation theories have been applied most widely to pure substances. The most extensive comparison with experiment has involved such small molecules as carbon dioxide and ethane, and the analysis typically only extends to low-pressure equilibria and the thermodynamic functions of mixing. The work of Scalise et al. (1987) is a rare example of the application of a perturbation theory to critical equilibria. In common with most perturbation models they determined the Helmholtz function from:

$$A = A_{\text{iso}} + A_2 + A_3 + \ldots \quad (13)$$

where A_{iso} is the angle-independent isotropic contribution, and the A_2, A_3 terms are the pair and triplet correlation functions, respectively. The above series was obtained by applying the Padé approximation:

$$A = A_{\text{iso}} + A_2/(1 - A_3/A_2) \quad (14)$$

Scalise et al. (1987) specifically calculated critical equilibria of fluids with permanent quadrupole moments. It is clear from their data that the agreement is poor at pressures above 200 MPa. The overall agreement for the nitrogen + hydrogen mixture is better than can probably be obtained from equation of state calculations without quantum corrections. However, the analysis involved using both the depth of the intermolecular potential and the quadrupole moment as adjustable parameters to optimize agreement between theory and experiment. In view of this, the analysis of carbon dioxide + ethane is poor when compared with equation of state calculations which use only one adjustable term. Smith et al. (1989) have demonstrated that an idealized dipole hard-sphere perturbation model can qualitatively reproduce the critical lines exhibited by the six classes of binary mixtures, and Zarragoiocoehea et al. (1989) have successfully compared experiment with perturbation theory for the gas-liquid critical properties of Type I mixtures. Recently, Scalise (1992) has also reported calculations for the Type III critical behavior of water + argon, water + helium and water + hydrogen binary mixtures which were in reasonable agreement with experimental data.

Conformal solution theory

Conformal solution theory (Brown, 1957; Hicks and Young, 1975; Shukla et al., 1986) has been applied frequently to the prediction of critical phenomena of binary mixtures (some examples are found in the works of Hicks and Young, 1975; Christou et al., 1986; Sadus, 1989, 1992a). The theory was originally devised for nonpolar, spherical molecules of similar size, but it has been successfully applied to a much more diverse range of mixtures (Toczylkin and Young, 1980a,b; Sadus and Young, 1985b; Christou et al., 1986). Harismiadis et al. (1991) have concluded that the predictions of conformal solution theory compare very favorably with the results of computer simulation of the phase equilibria of mixtures of molecules which differ vastly in volume. It has also proved useful in the prediction of critical equilibria of ternary mixtures (Sadus and Young, 1987, 1988; Sadus, 1992a,b).

The Helmholtz function of the fluid mixture is obtained from the following relationship:

$$A = f_{es} A_0^* (V/h_{es}, T/f_{es}) - RT \ln h_{es} + RT \sum_i x_i \ln x_i \quad (15)$$

where the f_{es} and h_{es} conformal parameters are related to the energy and intermolecular separation of the intermolecular potential of a hypothetical "equivalent substance" and A_0^* is the configuration Helmholtz function of a reference fluid which can be obtained from an equation of state. The properties of the equivalent substance are typically obtained from a composition-dependent average of the components of the fluid. The conformal parameters of the equivalent substance are defined relative to the reference substance which is usually one of the components of the mixture. Consequently, the correct limiting behavior of the individual components is usually obtained without fitting parameters to the one-component critical point. The other advantage of conformal solution theory is that improvements in either equations of state, mixing rules, or combining rules can be easily incorporated.

Equations of state and critical calculations

The simplest model for the Helmholtz function of a fluid is to directly integrate the equation of state with respect to volume. There is a vast literature on equations of state and their application to phase equilibria. Comprehensive reviews can be found in the works of Martin (1979), Gubbins (1983), Tsonopoulos and Heidman (1985), Han et al. (1988), and Anderko (1990). However, relatively few equations of state have been applied to the study of critical transitions in binary fluid mixtures. Cubic equations are most commonly used in chemical engineering applications although there are advantages in using noncubic equations for critical calculations as discussed below.

Cubic Equations of State. Van Konynenburg and Scott (1980) successfully demonstrated that most of the critical equilibria exhibited by binary mixtures could be qualitatively predicted by the van der Waals equation of state:

$$p = RT/(V - b) - a/V^2 \quad (16)$$

where a and b are adjustable parameters which account for the energy of interaction and covolume occupied by the molecules, respectively. The van der Waals equation (and its various modified forms) can be regarded as a "hard-sphere + attractive" term equation of state composed from the contribution of repulsive and attractive intermolecular interactions, respectively. It represents the simplest "realistic" equation of state, and the successes of van Konynenburg and Scott (1980) in reproducing the critical behavior of binary mixtures clearly established the usefulness of equations of state for critical property calculations.

The van der Waals equation is now rarely used for quantitative calculations having been superseded by many hybrid forms. The equation and its many modified and improved versions represent a category known as cubic equations of state which yield only three values of volume for a specified pressure. Most commonly encountered phase equilibrium calculations, such as vapor-liquid equilibria, involve only two phases for which a cubic equation is suitable. Cubic equations have the advantage that the three values of volume can be obtained analytically without the need for an iterative solution procedure.

Redlich and Kwong (1949) proposed an empirical modification of the van der Waals equation to make the attractive term temperature-dependent:

$$p = RT/(V - b) - a/V(V + b)T^{0.5} \quad (17)$$

Spear et al. (1969) demonstrated that the Redlich-Kwong equation of state could be used to reliably calculate the gas-liquid critical properties of binary mixtures. Later, Spear et al. (1971) reported reasonably accurate calculations of the gas-liquid critical properties of ternary hydrocarbon mixtures. Other workers (Deiters and Schneider, 1976; Baker and Luks, 1980) have also successfully applied the Redlich-Kwong equation to the high-pressure phase equilibria of binary mixtures.

The development of cubic equations of state has been reviewed elsewhere (Martin, 1979; Han et al., 1988; Anderko, 1990). The introduction of a temperature dependence in the van der Waals equation has been a widely used practice in the development of cubic equations of state. Many cubic equations have the following general form:

$$p = RT/(V-b) - a(T)/\{V(V+b) + c(V-b)\} \tag{18}$$

If $c = 0$, then Eq. 18 represents either the Redlich-Kwong (1949) or the Soave (1972) equation. For the Soave equation,

$$a(T) = 0.4274(R^2T^{c2}/p^c)\{1 + m[1 - (T/T^c)^{0.5}]\}^2 \tag{19}$$

$$m = 0.480 + 1.57\omega - 0.176\omega^2 \tag{20}$$

$$b = 0.08664RT^c/p^c \tag{21}$$

where ω is the acentric factor. Elliott and Daubert (1987) have used the Soave equation in conjunction with the critical criteria of Heidemann and Khalil (1980) to calculate the critical locus of a diverse range of binary mixtures. They reported that the agreement obtained was considerably superior than could be otherwise obtained by using empirical estimation methods.

The substitution of $c = b$ into Eq. 18 generates the equation of state proposed by Peng and Robinson (1976) in which $a(T)$ is defined as:

$$a(T) = 0.45724(R^2T^{c2}/p^c)\{1 + k[1 - (T/T^c)^{0.5}]\}^2 \tag{22}$$

$$k = 0.37464 + 1.5422\omega - 0.26992\omega^2 \tag{23}$$

$$b = 0.07780RT^c/p^c \tag{24}$$

Peng and Robinson (1977) successfully demonstrated that their equation of state could be used to predict the critical properties of both binary and multicomponent mixtures.

Palenchar et al. (1986) have reported a rare, direct comparison of the quality of prediction of the critical locus using different cubic equations of state. In addition to the Redlich-Kwong, Peng-Robinson and Soave equations, calculations for equations of state proposed by Teja and Patel (1982) and Adachi et al. (1983) were reported for the carbon dioxide + methane, butane, decane or water; methane + hexane or heptane; and propane + hexane and water + benzene binary mixtures. They concluded that the critical temperatures and pressures of Type I systems could be adequately predicted although there was a substantial discrepancy between theory and experiment for the critical volume. The Peng-Robinson and Soave equations yielded a more accurate representation of mixtures exhibiting a discontinuity in critical equilibria than either the Teja and Patel or Adachi et al. equations.

Noncubic Equations of State. The development of cubic equations of states has been focused on obtaining an improved empirical representation of attractive interactions. It should be emphasized that these improvements have been specifically developed for low-temperature-pressure equilibria. At the high pressures and temperatures typically encountered in critical equilibria, repulsive interactions can be expected to the dominant influence determining the properties of the fluid. Many accurate representations have been developed for the repulsive interactions of hard spheres and incorporated into the equation of state. The use of an accurate model for repulsive interactions invariably results in a noncubic equation of state.

The equation of state proposed by Guggenheim (1965) is an example of a more accurate hard-sphere model which has been extensively used for the calculation of critical equilibria:

$$p = RT/V(1-y)^4 - a/V^2 \tag{25}$$

where $y = b/4V$. Comparison with computer simulation data indicates that the hard-sphere component of the Guggenheim equation is a far superior representation of the repulsive interaction between hard spheres at medium to high densities than the van der Waals model. The equation has been used to predict the critical properties of a diverse range of binary mixtures containing hydrocarbons (Hicks and Young, 1976), perfluorohydrocarbons (Hurle et al., 1977a,b; Hicks et al., 1978; Toczylkin et al., 1980c; Semmens et al., 1980), carbon dioxide (Hicks et al., 1977; Sadus and Young, 1985a), siloxanes (Waterson and Young, 1978), and polar molecules (Toczylkin and Young, 1977, 1980a,b; Sadus and Young, 1985b) as one or more components. Despite the diversity of the systems studied, good results were consistently reported for the gas-liquid critical locus, and the critical liquid-liquid equilibria of Type II mixtures were also adequately represented. Mainwaring et al. (1988a) and Sadus et al. (1988) have reported that a typical standard deviation between experiment and theory for the gas-liquid critical temperature and pressure are 0.5 K and 0.1 MPa, respectively. Generally, calculations involving Type III equilibria are only semiquantitative (Christou et al., 1986). The Guggenheim equation has also recently proved valuable in calculating both the gas-liquid critical properties (Sadus and Young, 1987, 1988) and general critical transitions (Sadus, 1992a,b) of ternary mixtures.

Several other accurate "hard-sphere + attractive term" equations of state have been proposed. Comparison with both computer simulation and the virial expansion of a hard-sphere gas indicates that the hard-sphere representation proposed by Carnahan and Starling (1969) is particularly accurate. Employing the van der Waals attractive term yields the following useful equation of state:

$$p = RT(1 + y + y^2 - y^3)/V(1-y)^3 - a/V^2 \tag{26}$$

Sadus (1993a) has recently demonstrated that the above equation can be used to predict Type III equilibria of nonpolar mixtures with considerable accuracy.

The accuracy of the Carnahan-Starling hard-sphere potential has motivated many attempts to combine it with empirical attractive terms. These equations have the following general form:

$$p = RT(1+y+y^2-y^3)/V(1-y)^3 - a(T)/V[V+\lambda b(T)] \quad (27)$$

Carnahan and Starling (1972) have demonstrated that the use of the Redlich-Kwong attractive term in Eq. 26 improves the prediction of hydrocarbon densities and supercritical phase equilibria.

Christoforakos and Franck (1986) and Heilig and Franck (1989) have developed equations specifically for high-pressure equilibria which also incorporate the Carnahan-Starling hard-sphere term. The Christoforakos-Franck equation introduces a temperature-dependent covolume term $[4\beta = b(T^c/T)^{0.3}]$ into the repulsive term:

$$p = RT(1+\beta/V+\beta^2/V^2-\beta^3/V^3)/V(1-\beta/V)^3 - 4RT\beta(\lambda^3-1)\{\exp(\epsilon/kT)-1\}/V^2 \quad (28)$$

The attractive term was obtained by examining the virial coefficient of gases in terms of a square-well potential. The ϵ parameter reflects the depth of the potential, whereas λ is the relative width of the well. The equation has been successfully applied to the high-pressure phase behavior of some binary aqueous mixtures (Christoforakos and Franck, 1986; Franck, 1987). In particular, Type III critical locus of binary mixtures of water + argon, xenon, nitrogen, methane or carbon dioxide is predicted reasonably accurately.

The Heilig-Franck (1989) equation is similar, except that the attractive term is obtained by applying the Padé approximation of the virial coefficients of a square-well fluid:

$$p = RT(1+\beta/V+\beta^2/V^2-\beta^3/V^3)/V(1-\beta/V)^3 - RTB/V^2(1+C/BV) \quad (29)$$

where B and C are the second and third virial coefficients of a square-well fluid, respectively. Accurate calculations of the critical properties of both binary and ternary mixtures (Heilig and Franck, 1989, 1990) have been reported. Recently, Mather et al. (1993) have demonstrated that Eq. 29 can accurately predict Type III critical loci of either the water + neon or water + krypton mixtures.

Deiters (1981a,b) has adopted a semiempirical approach to construct an equation with three adjustable parameters (a, b, c):

$$p = (RT/\rho)[1+cc_0\{4\eta-2\eta^2/(1-\eta)^3\}] - Ra\rho^2 T_{\text{eff}} I\{\exp(1/T_{\text{eff}})-1\}/b \quad (30)$$

where $\rho = b/V$, $\eta = 0.7404\rho$, $c_0 = 0.6887$, $\lambda = -0.06911c$, $T_{\text{eff}} = (cT/a+\lambda\rho)/y$. I parameter is a hard-sphere constant, and the values of y range from 1 for a dilute gas and between 0.34 and 0.46 for dense fluids. In Eq. 30, the Carnahan-Starling expression for hard spheres has been adjusted to accurately fit the experimental vapor pressure data for argon via c_0 parameter, and deviations from spherical geometry are reflected in values of $c > 1$. The equation can be used to accurately predict the vapor-liquid properties of binary mixtures (Deiters, 1982; Deiters and Swaid, 1984; Calado et al., 1981). Calculations of the gas-liquid critical locus of binary mixtures (Mainwaring et al., 1988a,b) indicate that good results can only be obtained for mixtures of molecules of similar size. The equation has not been extensively tested for noncontinuous critical equilibria, but Type III critical properties of water + benzene and water + hexane can be adequately predicted (Mainwaring et al., 1988a).

Boublik (1981) has generalized the Carnahan-Starling hard-sphere potential for molecules of arbitrary geometry via the introduction of a nonsphericity parameter (α). Svejda and Kohler (1983) have employed the Boublik potential in conjunction with Kihara's (1963) concept of a hard convex body (HCB) to obtain a generalized van der Waals equation of state:

$$p = RT\{1+(3\alpha-2)y+(3\alpha^2-3\alpha+1)y^2-\alpha^2 y^3\}/V(1-y)^3 - a/V^2 \quad (31)$$

Sadus et al. (1988) and Christou et al. (1991b) have used Eq. 31 for the calculation of the gas-liquid critical properties of binary mixtures containing nonspherical molecules. The results obtained were slightly better than could be obtained from similar calculations using the Guggenheim equation of state. Recently, Sadus (1993a) has proposed an alternative procedure for obtaining the equation of state parameters. Equation 31 in conjunction with this modified procedure can be used to predict Type III critical equilibria of nonpolar binary mixtures with a very good degree of accuracy.

There are many other nonspherical or hard-chain equations of state which have not been used for the calculation of critical equilibria. Vimalchand and Donohue (1989) have reviewed several hard-chain equations of state. Recently, van Pelt et al. (van Pelt, 1992; van Pelt et al., 1991) have applied a simplified version of the perturbed hard-chain theory equation of state proposed by Beret and Prausnitz (1975) to binary critical equilibria. For a pure fluid, the equation has the following form:

$$p = (RT/V)(1+c)\{4\eta-2\eta^2/(1-\eta)^3\} - RTzcv^*Y/\{V^2(1+v^*Y/V)\} \quad (32)$$

where $Y = \exp(\epsilon q/2ckT)-1$ and $\eta = 0.7405v^*/V$, where v^* is the molecular volume parameter, ϵ is the intermolecular potential energy per unit area; c is 1/3 of the total degrees of freedom of a molecule; q is the number of external segments per molecule and z is the close-packed coordination number. In common with other equations of state, good results were obtained for the critical pressures and temperatures of many binary mixtures. The calculations cannot be expected to yield accurate critical volumes for binary mixtures because the critical volume of the components was used as an adjustable parameter to optimize the agreement of theory and experiment for the critical pressures and temperatures of the pure components. However, Eq. 32 was successfully employed to qualitatively reproduce a variety of binary mixture phenomena including Type VI behavior.

Choosing an Equation of State for Multicomponent Critical Equilibria. There is obviously a wide selection of equations of state to choose from. What makes an equation of state suitable for critical calculations? It is useful at the outset to consider some inherent limitations of equations of state which are common to most, if not all equations of state. Irrespective

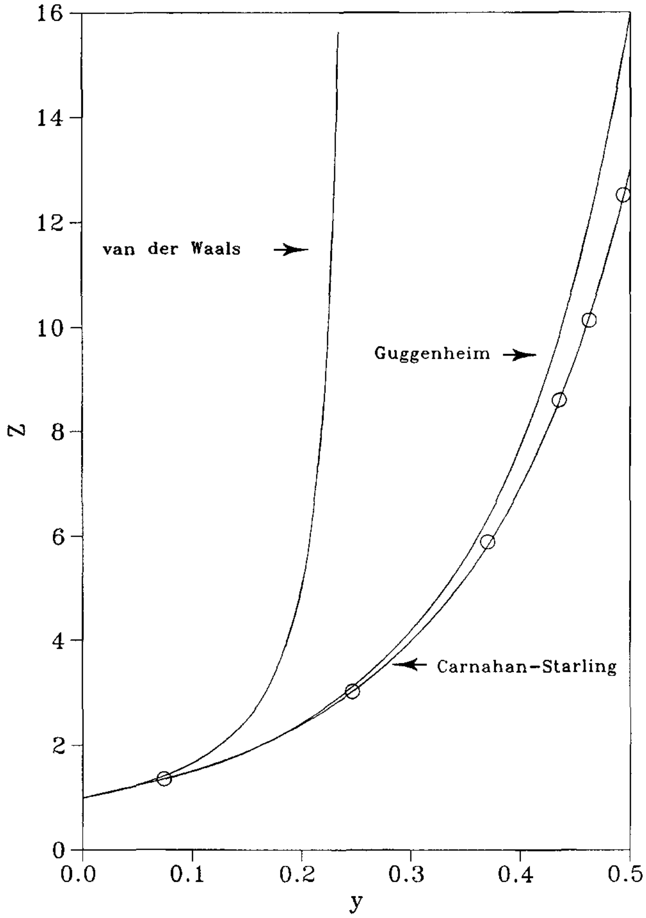

Figure 4. Comparison of the hard-sphere compressibility obtained from different equations of state with molecular simulation data (o) for hard spheres.

of which equation of state is used for critical calculations, the following limitations and features should be borne in mind.

(i) The critical point cannot be described as an analytic function of temperature, pressure, volume and composition. Consequently, any analytic equation of state cannot be expected to be theoretically correct at the critical point.

(ii) No universally applicable equation of state has been developed which can be used to predict fluid properties under different conditions with the same degree of accuracy. For example, an equation of state which is suitable for low densities and pressures may fail to adequately predict phase transitions at higher densities and pressures, and *vice versa.*

(iii) No equation of state is currently capable of predicting all of the physical properties of a fluid (pressure, temperature, volume, and composition) with the same degree of accuracy. Consequently, attempts to optimize the predictive ability of an equation of state for one property typically reduce the quality of agreement between theory and experiment for the other properties.

(iv) It is often very difficult to isolate the influence of the equation of state *per se* from other influences such as mixing rules, combining rules, and adjustable parameters that also contribute to the quality of prediction of multicomponent phase equilibria. The evaluation of equation of state parameters has a profound influence on the agreement between theory and experiment.

(v) The ability of an equation of state to predict the critical point of a one-component fluid is an insufficient criterion for choosing an equation of state for multicomponent critical equilibria because of the limitations outlined in i to iv. The ability to predict the critical point of a pure fluid as accurately as possible is a very desirable feature of any equation of state. However, if this is achieved inappropriately by, for example, the excessive use of adjustable parameters without any real physical justification, then the analysis of multicomponent equilibria will be substantially hindered.

(vi) Most theoretically realistic equations of state which account for both attractive and repulsive intermolecular interactions can be used to at least qualitatively predict most aspects of critical equilibria of binary mixtures.

The main feature which distinguishes cubic equations from noncubic equations of state is a more realistic representation of hard-sphere repulsive interaction. Of course, in reality, representing real molecular repulsion via a hard-sphere or hard-body model is an oversimplification, but it is a useful starting basis which reproduces the characteristic features of intermolecular repulsion. It is well known that the van der Waals hard-sphere term is an inadequate representation of hard-sphere interaction. Consequently, it cannot be expected to be a quantitatively good description of the property of real fluids. The compressibility predicted by the van der Waals, Guggenheim and Carnahan-Starling hard-sphere contributions are compared with molecular simulation data (Alder and Wainwright, 1960) for a one-component hard-sphere fluid in Figure 4. The failure of the van der Waals hard-sphere term is clearly apparent. Despite this, it is well established that most equations of state can be used to calculate the continuous gas-liquid critical equilibria of binary mixtures with a similar degree of accuracy. Why do cubic equations of state which use the inadequate hard-sphere term predict the gas-liquid critical transition with a similar degree of accuracy to theoretically superior noncubic equations of state? This conundrum can be resolved by inspecting Figure 4. The gas-liquid critical transition occurs at a relatively low density corresponding approximately to $y=0.1$. At low density, there is relatively little difference in the hard-sphere compressibility predicted by various hard-sphere equations, although the van der Waals term is still demonstrably inferior. At low densities, however, the relatively small discrepancy between the van der Waals term and the results predicted from molecular simulation can be compensated by the "improved" attractive terms commonly used in cubic equations of state. From a practical point of view, the cubic equation of state is a viable option for the calculation of gas-liquid critical properties offering both a reasonable degree of accuracy and considerable simplicity. However, it cannot represent a theoretically sound basis for the prediction of critical equilibria of multicomponent fluids in general.

The greatest diversity of critical phenomena in binary and multicomponent fluids occurs at very high pressures and moderate ($y=0.1$ to 0.3) densities. At high pressures, repulsive forces are likely to have the most dominant influence on the phase behavior of the fluid. It is also apparent from Figure 4 that a cubic equation of state is not a suitable choice at either moderate or high density. Figure 4 also indicates that, within the density range normally encountered for critical equilibria, the hard-sphere term of the Guggenheim equation is both an accurate and simple alternative to the Carnahan-Starling equation. There is very little quantitative data directly comparing noncubic and cubic equations of state for the prediction of dense fluid critical behavior. Sadus (1992a) has calculated Type III critical locus of some binary mixtures using Redlich-Kwong, Peng-Robinson and Guggenheim equations and compared the results obtained. The calculations for trifluoromethane + octane (Figure 5) are typical of the results obtained for other mixtures. None of the equations of state are capable of accurately predicting the critical curve with the aid of only one adjustable combining rule parameter. However, it is apparent that both Redlich-Kwong and Peng-Robinson equations of state are not even qualitatively reliable at high pressures.

The restriction of cubic equations of state to a maximum of three solutions of volume for a specified temperature, pressure and composition is a limitation which impedes their usefulness for multicomponent critical properties and phase behavior. The phase behavior of binary mixtures involves a maximum of three phases, and only two phases are ever in equilibrium for any critical transition. However, as the number of components increases, the likelihood of multiphase equilibria also increases. Consequently, at some pressures, temperatures and compositions, it is possible to conceive phase equilibria between several different phases at different densities. Therefore, in contrast to binary mixture phenomena, cubic equations of state are unlikely to be capable of predicting the full diversity of critical phase equilibria of ternary and other multicomponent fluid mixtures.

Historically, equations of state have been developed for low-pressure–temperature equilibria and then later applied to high pressure and critical transitions. This development is manifested in the emphasis placed on developing "improved" representations of the contribution attractive intermolecular interactions which are of considerable importance at low temperatures and pressures. The van der Waals attractive term ($p_{att} = -a/V^2$) appears to be an adequate (although far from perfect) representation for the contribution of attractive forces to the pressure of nonpolar fluids at high pressures. However, the van der Waals attractive term is inadequate for the calculations of critical equilibria involving a highly polar or self-associating molecule like water, methanol, or ammonia. There are not enough data available to recommend a general all-purpose replacement. The empirical attractive terms developed in conjunction with cubic equations have been developed for low-temperature–pressure equilibria. The extent to which they genuinely reflect attractive interaction, rather than at least partly compensating for the deficiencies of the van der Waals hard-sphere term, is open to interpretation. Equations 29 and 32 are currently the most promising. A valuable feature of Eq. 32 is its ability to at least qualitatively predict all aspects of critical equilibria of binary mixtures.

Evaluating Equation of State Parameters. The usual starting point for determining the equation of state parameters of the mixture is to determine the appropriate equation of state properties of the individual components and then propose some averaging procedure for the mixture. The conventional procedure for obtaining the equation of state parameters is well known. Two equation-of-state parameters can be evaluated by applying the critical conditions of a one-component fluid to the equation of state. From Eqs. 1 and 2, when $m = 1$:

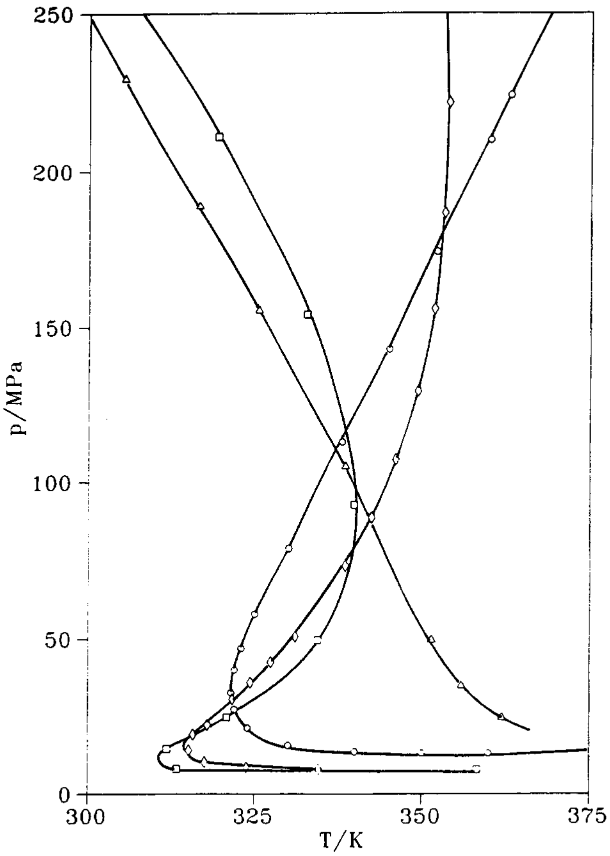

Figure 5. Experiment (○) vs. calculations for octane + trifluoromethane using the Guggenheim (◇, $\xi = 0.738$), Peng-Robinson (□, $\xi = 0.640$), and Redlich-Kwong (△, $\xi = 0.640$) equations.

$$(\partial p/\partial V)_T = 0 \tag{33}$$

$$(\partial^2 p/\partial V^2)_T = 0 \tag{34}$$

To more accurately reproduce the critical pressure, the following condition is also frequently imposed:

$$p(T^c, V^c) = p^c \tag{35}$$

and consequently, the equation-of-state parameters are evaluated from the critical temperature and pressure. In contrast, the equation-of-state parameters evaluated solely from Eqs. 33 and 34 require the critical temperature and critical volume as inputs.

The two alternative sets of equation-of-state parameters will almost invariably fail to coincide, because the critical compressibility predicted by equations of state does not generally coincide with the experimental value. It is commonly stated that equations of state cannot accurately predict the volumetric properties of fluids. The veracity of this statement depends on how the equation-of-state parameters are evaluated. If they are evaluated solely from conditions 33 and 34, then good agreement for the critical volumes will be obtained although the agreement for the critical pressures of the pure fluid will not be optimal. If condition 35 is imposed, then the critical pressures will be more accurately reproduced at the expense of unrealistic values of the critical volume. Most chemical engineering applications are primarily concerned with pressure-temperature, rather than pressure-volume, properties, and as a consequence evaluating the equation-of-state parameters from the critical pressure is preferred. A likely disadvantage of this approach for fluid mixtures is that the accurate prediction of composition is also compromised. For example, liquid-liquid critical equilibria of Type II or III binary mixtures typically occur over a narrow range of composition. Calculations using pressure-defined equation-of-state parameters predict these phenomena over a unrealistically large range of compositions.

The above procedure can only be used to evaluate a maximum of two adjustable parameters independent of each other. Many equations of state have been proposed which contain three or more parameters which must be evaluated from other properties of the fluid. The acentric factor and vapor-liquid equilibrium data are commonly chosen for this purpose. If only three parameters are involved, then a viable alternative is to evaluate two of the terms from the critical properties at a fixed value of the third parameter. The procedure can be repeated for different third-parameter values, and an empirical relationship between the parameters can be deduced. This procedure has recently been successfully employed by Sadus (1993a) to obtain relationships between α, a and y for Eq. 31. The critical conditions were applied to obtain the values of a and y for different values of α. These data were then used to obtain a and y in terms of a polynomial equation in α.

Mixing Rules. The equation-of-state parameters of the fluid mixture are typically obtained from a composition-dependent average of the equation-of-state parameters of pure components. The discussion here will be limited to mixing rules for the a and b equation of state parameters. These two parameters have a real physical significance and are common to many realistic equations of state.

The simplest possible mixing rule is a linear average of the equation-of-state parameters:

$$a=\sum_i x_i a_i \tag{36}$$

$$b=\sum_i x_i b_i \tag{37}$$

Although Eq. 37 is sometimes employed to simplify the calculation, Eq. 36 is rarely used because it does not account for the important role of unlike interaction in binary fluids. Consequently, employing both Eqs. 36 and 37 would typically result in poor agreement of theory with experiment.

The van der Waals one-fluid prescriptions are the most widely used mixing rules for a and b parameters.

$$a=\sum_i \sum_j x_i x_j a_{ij} \tag{38}$$

$$b=\sum_i \sum_j x_i x_j b_{ij} \tag{39}$$

They are based on the implicit assumption that the radial distribution function of the component molecules are identical, and they both explicitly contain a contribution from interactions between dissimilar molecules. The results obtained from the van der Waals mixing rules compare well with computer simulation data, if the size difference between the component molecules is not too great. Recently, Harismiadis et al. (1991) compared the results of the one-fluid model with computer simulation data. They concluded that the one-fluid model was valid for mixtures of hard spheres with up to an eightfold difference in size. The quadratic nature of the van der Waals prescriptions is also consistent with the quadratic dependence of the second virial coefficient.

Equations 38 and 39 are independent of density. There have been many proposals for density-dependent mixing rules (Deiters, 1987; Ely, 1986). Other workers have modified the van der Waals prescriptions to include composition-dependent parameters (Panagiotopoulos and Reid, 1986; Adachi and Sugie, 1986; Sandoval et al., 1989; Schwartzentruber et al., 1989). The mixture prescriptions have also been related to the excess thermodynamic properties of mixing (Huron and Vidal, 1979; Mollerup, 1986; Wong and Sandler, 1992). These modified approaches have not been widely applied to the calculation of critical equilibria. It is unlikely that the calculation of gas-liquid critical properties would be substantially improved, although the use of a density-dependent mixing rule may benefit the calculation of the critical liquid-liquid equilibria of fluid mixtures containing polar or highly associating components. Recently, Shibata and Sandler (1989) concluded that the van der Waals mixing rules were superior to the density-dependent Panagiotopoulos-Reid and Huron-Vidal mixing rules for calculating the vapor-liquid equilibrium properties of the asymmetric nitrogen + butane mixture. Mansoori (1986) effectively compare mixing rules for cubic equations of state. Boublik (1970) and Mansoori et al. (1971) proposed an alternative procedure whereby the Carnahan-Starling hard-sphere term is directly adapted for mixture properties. However, the effect of this procedure for the calculation of critical properties has not been widely examined.

Sadus (1989) has used conformal solution theory to derive an alternative to the conventional procedure for obtaining the a equation-of-state parameter. Instead of proposing an average of the pure-component parameter data, a parameter for the mixture is calculated directly. Consequently, a is a function of composition only via the conformal parameters (f, h) and the contribution from the combinatorial entropy of mixing. The a parameter is obtained by taking the positive root of the following quadratic equation:

$$\begin{gathered}a^2\theta^6[-2f''/f+(f'/f)^2-2h''/h-2f'h'/fh+(h'/h)^2)]\\+aRTV[\phi_B\theta^2\{-h''/h-f''/f\}]+2\phi_A\theta^3\{h''/h+f'h'/fh\\-(\mathrm{h}'/\mathrm{h})^2\}+2\theta^6\{-h''/h+(h'/h)^2+1/x(1-x)\}]\\-(RTV)^2[\phi_A^2\{(f'/f)^2-(h'/h)^2\}\\+\phi_B\theta^2\{h''/h-(h'/h)^2-1/x(1-x)\}-\phi_A\phi_B h''/h\theta]=0\end{gathered} \tag{40}$$

where superscripts ′ and ″ denote successive differentiation of the conformal parameters, and θ and ϕ are characteristic of the equation of state. The main advantage of Eq. 40 is that a equation-of-state parameter can be calculated directly from the critical properties of pure components without using combining rules for the contribution of unlike interactions. Sadus (1992a,c) has applied the above equation to the calculation of the gas-liquid critical properties of a wide range of binary mixtures. The agreement is generally very good in view of the fact that no adjustable parameters were used to arbitrarily optimize the agreement between theory and experiment.

Combining Rules. Any realistic mixture prescriptions will invariably contain contributions from interactions between unlike molecules. The unlike contributions to the equation-of-state parameters are obtained by applying suitable combining rules. The most widely used combining rule for the a_{ij} term was first proposed by van der Waals:

$$a_{ij} = \xi_{ij}(a_{ii}a_{jj})^{0.5} \tag{41}$$

Alternatively, many workers prefer to use the following combining rule for critical calculations:

$$a_{ij} = \xi_{ij}b_{ij}(a_{ii}a_{jj}/b_{ii}b_{jj})^{0.5} \tag{42}$$

The ξ_{ij} term (also commonly defined as $1-k_{ij}$) is frequently introduced into combining rules to optimize the agreement between theory and experiment. The ξ_{ij} parameter is frequently interpreted as reflecting the strength of intermolecular interaction. This interpretation is supported by the fact that values of ξ_{ij} obtained from the analysis of the critical properties of many binary mixtures consistently decline with increasing size difference between the component molecules. Mixtures of molecules of similar size, but different molecular interactions, are associated with different interaction parameters. Nonetheless, the requirement for ξ_{ij} values to optimize agreement between theory and experiment is also testimony to the inadequacy of the combining rule, mixture prescriptions and the equation of state. It has been frequently documented that different ξ_{ij} values are required to obtain optimal agreement between theory and experiment for gas-liquid and liquid-liquid critical equilibria, respectively. A similar conclusion has also been reached for molecular simulation studies of binary mixture phase equilibria. In both cases, the underlying cause of this so-called "density dependence" is probably the adequacy of the assumptions made regarding the nature of intermolecular interactions in the fluid. For example, equation-of-state models often fail to take adequate account of interactions induced by a permanent dipole, and the Lennard-Jones potential frequently used in molecular simulation studies is known to be inadequate even for the simple case of the noble gases.

The most widely used combining rules for b_{ij} are the simple arithmetic rule:

$$b_{ij} = \zeta_{ij}(b_{ii}+b_{jj})/2 \tag{43}$$

and the Lorentz combining rule:

$$b_{ij} = 0.125\zeta_{ij}(b_{ii}^{1/3}+b_{jj}^{1/3})^3 \tag{44}$$

The two combining rules yield nearly identical results for mixtures of molecules of similar size, but the discrepancy increases substantially for mixtures of molecules of very dissimilar size.

The ζ_{ij} parameter is used to optimize the agreement between theory and experiment. It is generally found that the ζ_{ij} parameter is not required for the accurate prediction of gas-liquid critical properties. Similarly, good agreement between theory and experiment for Type II liquid-liquid equilibria can usually be obtained by solely adjusting the ξ_{ij} term and setting $\zeta_{ij}=1$. However, obtaining an optimal ζ_{ij} parameter is essential for the accurate representation of Type III behavior. It is found (Sadus, 1993a) that the arithmetic rule substantially overestimates the two-phase region, whereas the Lorentz rule is more accurate but it extends the one-phase region. Sadus (1993a) has examined Type III behavior of nonpolar mixtures using both arithmetic and Lorentz combining rules. Good agreement between theory and experiment could be obtained by determining both the optimal ξ_{ij} and ζ_{ij} parameters. An alternative combining rule was deduced from this analysis which could be used to accurately calculate Type III equilibria without the ζ_{ij} parameter:

$$b_{ij} = \{1/4(2^{1/3})\}(b_{ii}^{1/3}+b_{jj}^{1/3})^2(b_{ii}+b_{jj})^{1/3} \tag{45}$$

The remaining types of critical equilibria exhibited by binary mixtures have not been extensively calculated. However, it can be anticipated that optimal values of both ξ_{ij} and ζ_{ij} will be required to obtain accurate agreement between theory and experiment. Equation 45 may also be beneficial for calculations involving these types of mixtures.

Recent Calculations for Binary Mixtures

Gas-liquid critical properties

Mainwaring et al. (1988a) have applied both the Guggenheim equation and the Deiters equation of state in conjunction with conformal solution theory, the van der Waals one-fluid mixing rules and the Lorentz combining rule to the prediction of the gas-liquid critical properties of 46 binary mixtures. The mixtures ranged in diversity from mixtures of simple permanent gases to *n*-alkane + *n*-alkanes, hydrocarbons + *n*-alkanes, perfluorobenzene + *n*-alkanes, and acetone + *n*-alkanes. The agreement between theory and experiment was optimized by using the value of ξ_{12}. The standard deviation between the experimental and calculated critical temperature was typically between 0.1 to 1 K for the Guggenheim equation. Calculations with the Deiters equation of state were of similar accuracy for molecules of similar size, but standard deviations between 1 to 12 K were obtained for binary mixtures with a moderate to large-size difference between the component molecules. The Guggenheim equation yielded a standard deviation of between 0.1 and 0.6 MPa for the critical pressure, whereas the range in uncertainty was between 0.04 and 1.81 MPa for the Deiters equation of state. Vidal (1984) and Elliot and Daubert (1987) have also reported that the Soave equation of state can also adequately predict the gas-liquid critical properties of binary mixtures containing hydrocarbons.

Sadus et al. (1988) reported a similar analysis of the gas-liquid critical properties of 61 binary mixtures using the Guggenheim equation and the hard convex body (HCB) equation of state of Svejda and Kohler (1983). They extended the analysis of Mainwaring et al. (1988a) to also include additional perfluorobenzene + hydrocarbons, perfluoroheptane + *n*-alkanes, perfluoromethylcyclohexane + linear siloxanes, and hexamethyldisiloxane + linear siloxane mixtures. Incorporating the shape of the molecule explicitly in the HCB equation

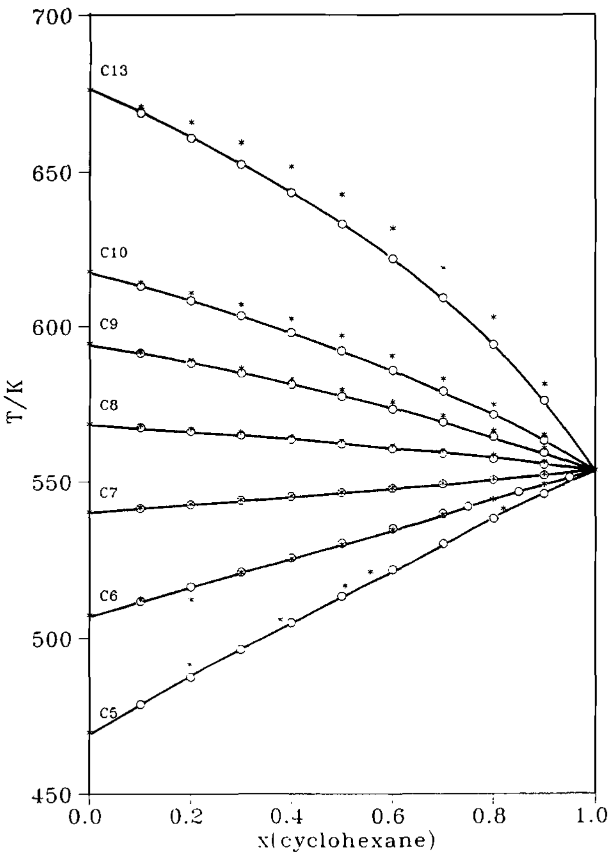

Figure 6. Experiment (*) vs. theory (o) for the critical temperatures of cyclohexane + *n*-alkane mixtures.

The contribution of the attractive equation of state parameter was obtained from Eq. 40.

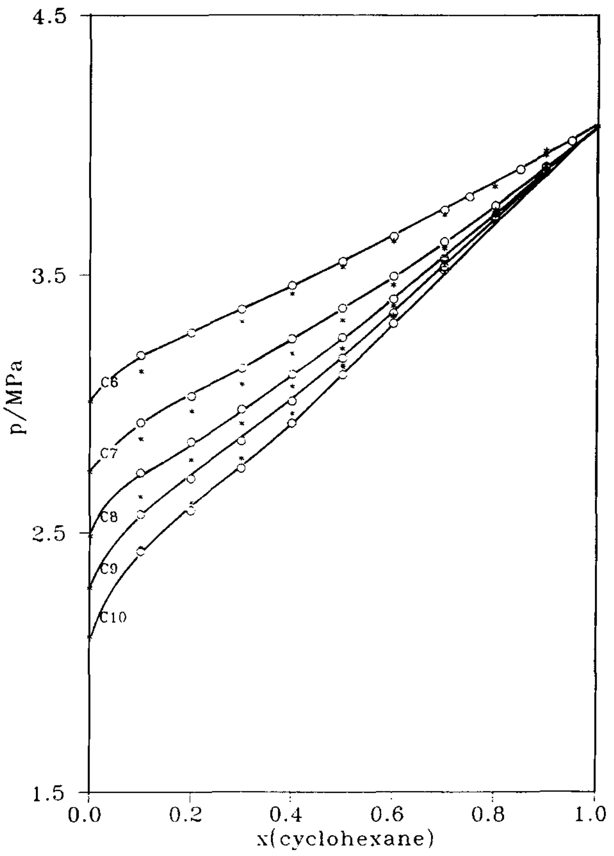

Figure 7. Experiment (*) vs. theory (o) for the critical pressure of cyclohexane + *n*-alkane mixtures.

The contribution of the attractive equation of state parameter was obtained from Eq. 40.

of state generally improved the standard deviation between theory and experiment by 0.1-0.5 K and 0.01-0.1 MPa compared with the results obtained from the Guggenheim equation of state.

Christou et al. (1989, 1991b) calculated the gas-liquid critical temperatures of weakly polar halocarbons + hydrocarbon mixtures and compared the results with experiment. The optimal agreement of theory with experiment is typically within a standard deviation of 1 to 2 K, which reflects the greater uncertainty introduced by the permanent dipole. Christou et al. (1991a) have reported a similar analysis for the gas-liquid critical temperatures of 26 1-alkanol + *n*-alkane mixtures. The alkanol molecule has a substantial reduced dipole and is highly self-associating. Consequently, the variation of the critical temperature with respect to composition is highly nonlinear and exhibits a very pronounced temperature minimum. The calculations using only ξ_{12} as an adjustable parameter qualitatively reproduce this nonideal behavior. The standard deviation between theory and experiment is typically between 0.5 and 3.0 K.

Sadus (1989) demonstrated that Eq. 40 can be used to accurately obtain the *a* equation-of-state parameter for a binary mixture. Christou et al. (1991c) also successfully applied Eq. 40 to the critical temperatures of binary mixtures containing a siloxane component. Sadus (1992c) used Eq. 40 to calculate both the critical temperature and pressures of hydrocarbon + *n*-alkanes, hexamethyldisiloxane + cycloalkanes and chlorocarbons + *n*-alkanes. The agreement between theory and experiment is often similar in accuracy to calculations which rely on the arbitrary use of ξ_{12} to optimize the agreement of theory with experiment. An example of the agreement between theory and experiment using the Guggenheim equation and Eq. 40 is illustrated in Figures 6 and 7. The significance of these calculations is that they represent genuinely *a priori* calculations. However, Eq. 40 is not appropriate for binary mixtures containing a highly dipolar component (Sadus, 1992d).

From a practical point of view, it is apparent that existing theoretical methods can be used to more than adequately calculate the gas-liquid critical properties of an extensive range of binary mixtures containing either nonpolar or slightly polar components. The properties of mixtures containing a component with a larger permanent dipole moment are less accurately calculated although the reduction in accuracy is often not as great as would be intuitively expected.

Upper critical solution temperature phenomena

Type II mixtures exhibit upper critical solution temperature phenomena (UCST) transitions over a very large range of pressures, but a very narrow range of both composition and temperature. Mixtures that exhibit UCST behavior either contain components from different molecular families or a component with a permanent dipole moment. This is not generally an impediment to accurate calculations. However, in some cases, the existence of critical equilibria will be wrongly predicted in regions where solidification can be expected to occur.

Toczylkin and Young (1980a,b) accurately calculated the UCST of binary mixtures containing electron donors such as ether molecules and amides. Sadus and Young (1985b) reported an analysis of the UCSTs of *n*-alkanenitrile + *n*-alkane and nitromethane + alkane mixtures. A similar analysis has also been reported for carbon dioxide and hydrocarbon mixtures (Sadus and Young, 1985a). In common with the calculations of gas-liquid critical properties, the accurate predictions of UCST require only one adjustable parameter (ξ_{12}) to be optimized. A typical error in the predicted UCST is approximately 0.5 K. ξ_{12} values required to obtain optimal agreement for gas-liquid and UCST behavior do not generally coincide. The UCST ξ_{12} values are substantially less than the gas-liquid values. The size of this discrepancy depends on the nature of the components of the binary mixture. A discrepancy of 5% is typical for nonpolar mixtures, whereas a difference of 8–10% is common for polar mixtures. UCST phenomena are considerably more sensitive to the ξ_{12} value than gas-liquid properties. A change of 0.01 in the ξ_{12} value frequently alters the gas-liquid critical temperature by 1 K, whereas a 10 K shift can be typically expected for the UCST.

The ability of theory to accurately reproduce the pressure dependence of UCST behavior is illustrated by calculations reported by Christou et al. (1986) and Mainwaring et al. (1988b). Christou et al. (1986) reported the UCST locus of mixtures of tetrafluoromethane + methane, ethane, propane, *i*-butane or *n*-butane over a pressure range extending from the UCEP to 250 MPa. Mainwaring et al. (1988b) were also able to reproduce the UCST locus over a similar range of pressure for mixtures of trifluoromethane + methane and trifluoromethane + propane. Both these sets of calculations used only the ξ_{12} parameter to optimize the agreement of experiment with theory.

Type III mixtures

The critical properties of Type III binary mixtures represent a considerable challenge to theory. Theory must be able to accurately reproduce the continuous transition between low-density gas-liquid equilibria and medium-density liquid-liquid critical equilibria. Simple cubic equations of state qualitatively predict the main features of Type III behavior; but, as illustrated in Figure 5 and demonstrated elsewhere (Sadus, 1992a), good agreement between theory and experiment cannot generally be expected. Palenchar et al. (1986) calculated the critical properties of water + benzene and water + carbon dioxide with the Redlich-Kwong and Soave equations of state. The agreement of theory with experiments was poor for the water + benzene mixture, but the calculations for the water + carbon dioxide system using the Soave equation agreed well with experimental data.

Calculations for tetrafluoromethane + hydrocarbon (Christou et al., 1986) and sulfur hexafluoride + *n*-alkane (Mainwaring et al., 1988b) mixtures have been reported using the Guggenheim equation. The agreement of theory with experiment is at best semiquantitative. However, it should be noted that only one optimizing parameter (ξ_{12}) was used. A similar analysis was also undertaken (Mainwaring et al., 1988b) for trifluoromethane + hydrocarbon mixtures. These calculations were considerably less accurate which can be attributed to the inability of theory to adequately take account of the influences of the permanent dipole of trifluoromethane.

Many factors, such as molecular shape, size and polarity, contribute to the observation of Type III behavior in binary mixtures. Consequently, it is sometimes difficult to isolate the relative importance of various contributions to the success or otherwise of the theoretical model. Recently Sadus (1993a) has attempted to isolate the relative contribution of molecular shape and the b_{12} combining rule to the prediction of Type III behavior of nonpolar mixtures. Equation 26 and an equation similar to Eq. 31 for nonspherical molecules was used to calculate the critical properties of tetrafluoromethane + *n*-alkane and sulfur hexafluoride + *n*-alkane mixtures. Very good agreement between theory and experiment could be obtained for either equation of state if optimal values of both ξ_{12} and ζ_{12} were employed. The shape of the *n*-alkanes was modeled as a spherocylinder. Accounting more realistically for the shape of the alkanes in this manner improved the accuracy of the calculations, particularly at the region close to the pressure-temperature minimum which coincides with the transition between "gas-liquid" and "liquid-liquid" equilibria. However, obtaining optimal a_{12} and b_{12} parameters is the overriding factor governing the quality of agreement between theory and experiment. It appears likely that demonstrably nonspherical molecules like moderately sized alkanes (such as undecane) can be legitimately modeled as hard spheres without substantially affecting the prediction of Type III behavior. Hard-sphere equations of state may be valid for a wider range of binary mixtures than would otherwise be intuitively expected. Figure 8 illustrates the quality of agreement between theory and experiment for the critical properties of sulfur hexafluoride + *n*-octane.

An investigation has also been reported (Sadus, 1992e) on the influence of quantum effects on the critical properties of binary mixtures containing hydrogen. The quantization of translational motion substantially influences the occurrence of critical equilibria. However, a simple, theoretically based correction to the equation of state can be used to dramatically improve the agreement of theory with experiment for this class of binary mixture.

Binary mixtures containing water represent a technologically important class of mixtures which exhibits Type III behavior. Christoforakos and Franck (1986) applied their equation of state to the prediction of the critical curve of binary mixtures containing water and a permanent gas molecule. The pressure-temperature behavior of water + nitrogen, carbon dioxide or methane was accurately calculated, whereas there was a slightly greater degree of uncertainty in the agreement of theory with experiment for the water + xenon system. Identical optimal adjustable parameters ($\zeta = 1$, $\xi = 0.75$, $\lambda = 2.5$, $m = 10$) were employed for the mixtures containing nitrogen, methane and xenon, whereas a different set of values ($\zeta = 0.99$, $\xi = 0.94$, $\lambda = 1.5$, $m = 10$) were required for the water + carbon dioxide system.

Heilig and Franck (1989) employed several equations of state to calculate critical properties of the water + *n*-hexane binary mixture (Figure 9). Neither the HCB equation of state (Eq. 31) nor the approach of Mansoori et al. (1971) could accurately

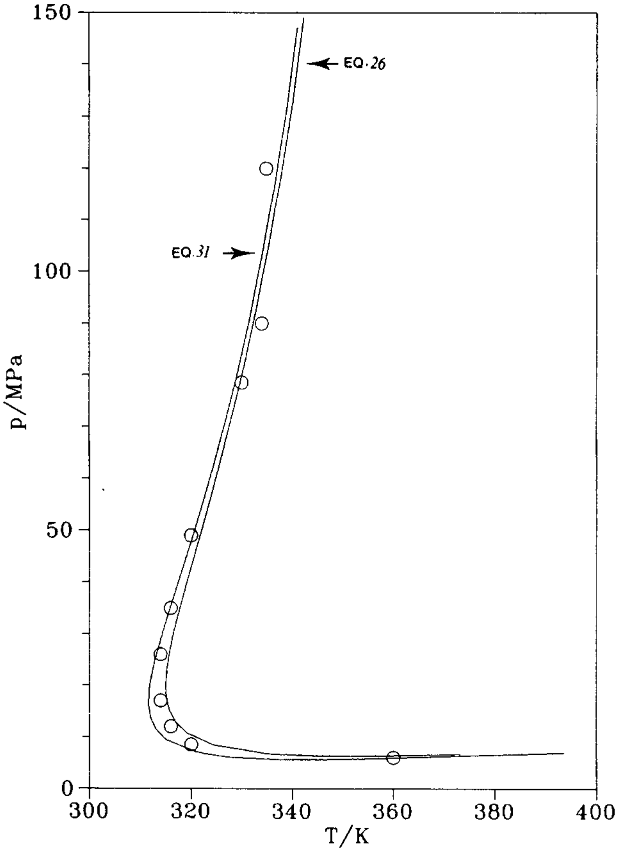

Figure 8. Experiment (o) vs. theory for the critical locus of sulfur hexafluoride + nonane using the Carnahan-Starling (Eq. 26, $\xi = 0.823$, $\zeta = 0.945$) and arbitrary shape (Eq. 31, $\xi = 0.928$, $\zeta = 0.945$) equations of state.

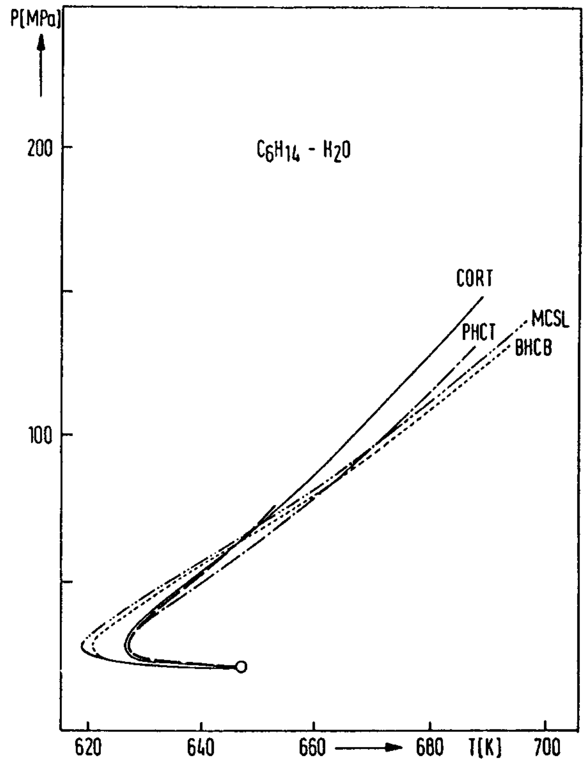

Figure 9. Experiment (- - -) vs. theory for the critical locus of hexane + water using the chain-of-rotators (CORT), perturbed hard-chain theory (PHCT), hard convex body (BHCB), and Mansori et al. (MCSL) equations of state (Heilig and Franck, 1989).

predict the occurrence of the pressure-temperature minimum. The quality of agreement between theory and experiment with these equations was similar to that achieved by Mainwaring et al. (1988a) with the Deiters equation of state. Calculations using the chain-of-rotators theory equation of state (Chien et al., 1983) and the perturbed hard-chain theory (Donohue and Prausnitz, 1978) accurately predicted the pressure-temperature minimum with a similar degree of uncertainty. Heilig and Franck (1989) also demonstrated that their equation of state could also accurately predict the critical properties of water + hexane, nitrogen and carbon dioxide.

Experimental data are available for binary mixtures containing water + all the noble gases with the exception of radon. These mixtures are of interest because a transition occurs between different types of so-called "gas-gas" immiscibility. The critical curve of water + helium or neon commencing at the critical point of water extends directly to higher temperatures and pressures without passing through a pressure-temperature minimum. This behavior is so-called "gas-gas" immiscibility of the first kind. The critical locus of the remaining water + noble gas mixtures pass through a pressure-temperature minimum before returning to pressures and temperatures above the critical point of water ("gas-gas" immiscibility of the second kind). The occurrence of the first kind of "gas-gas" immiscibility can be predicted on the basis of the relative critical temperatures and volumes of the pure components (Temkin, 1952; Mather et al., 1993). Wu et al. (1990) demonstrated that the Heilig-Franck equation could be used to predict the critical properties of water + argon. Similarly, good agreement using the Heilig-Franck equation of state has also been recently reported (Mather et al., 1993) for the water + krypton or neon systems. Scalise (1992) has employed perturbation calculations to predict the critical locus of water + helium or hydrogen with a reasonable degree of accuracy. Stretenskja et al. (1994) applied the Guggenheim, Heilig-Franck and van der Waals equations of state to predict the critical properties of water + helium. Despite using two adjustable parameters, neither the Guggenheim nor Heilig-Franck equations of state calculations yielded quantitative agreement with the experimental data (Figure 10). In contrast, the simple van der Waals equation with only one optimizing parameter could be used to predict the critical curve to within experimental accuracy (Figure 11).

Other phenomena

Examples of a quantitative comparison of theory with experiment for the remaining types of critical transitions exhibited by binary mixtures are rare. The Type IV system methane + *n*-hexane is possibly the most widely studied, particularly in connection with hypothetical tricritical points in quasi-binary mixtures. Type IV or V behavior can be consid-

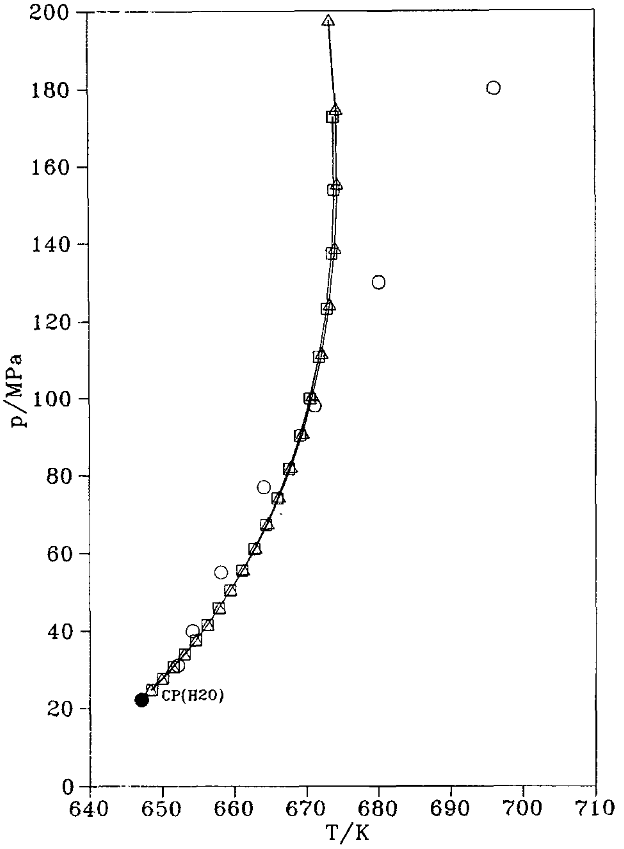

Figure 10. Experiment (○) vs. calculations using the Guggenheim (△, $\xi = 1.0$, $\zeta = 0.68$) and Heilig-Franck (□, $\xi = 1$, $\zeta = 0.65$) equations for the critical curve of water + helium.

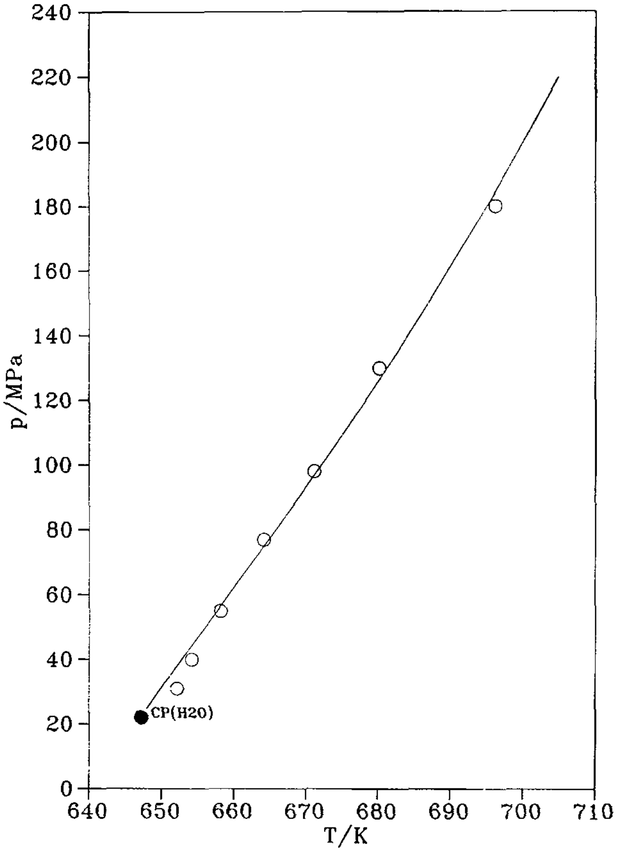

Figure 11. Theory (- -) vs. experiment (○) for the critical curve of water + helium, using the van der Waals equation ($\xi = 0.95$, $\zeta = 1.0$).

ered as a transition state between Types I/II and VI behavior. This transitional status is reflected in the sensitivity of the adjustable parameters required to predict the appropriate critical properties.

Boshkov (1987), Deiters and Pegg (1990), van Pelt et al. (1991), and Smith et al. (1989) demonstrated that all of the known phase behavior types exhibited by binary mixtures can be qualitatively reproduced if a suitable model is used. For example, Boshkov (1987) used an equation of state for a Lennard-Jones fluid, whereas van Pelt et al. (1991) used a simplified version of the perturbed hard-chain equation of state. It is probable that many noncubic equations of state can be used for such calculations. However, no comparisons of theory and experiment have been reported for either Type V or VI behavior which can be used to judge the accuracy of these models. Examples of these types of behavior are confined to either aqueous mixtures or highly polar or self-associating molecules. Consequently, they represent the severest test possible for a theoretical model.

Calculations of Ternary Mixture Properties

Critical surfaces

The critical properties of binary mixtures are commonly referred to as critical "points." The "point" terminology is valid strictly only for the gas-liquid point of a one-component fluid or invariant properties such as the UCEP or LCEP of a binary fluid. The so-called critical "point" of a binary fluid is commonly part of a critical *line*. Similarly, the additional degree of freedom generated by the introduction of a third component commonly generates a critical *surface*. In a ternary mixture, a critical *line* is formed at the junction of two surfaces, whereas a tricritical point is an invariant property of the fluid. Consequently, a two-dimensional representation of the critical properties of a ternary fluid should be generally interpreted as a cross-sectional profile of the critical surface. Failure to observe these distinctions can result in considerable confusion in interpreting ternary and multicomponent equilibria.

Gas-liquid critical properties

Spear et al. (1971) and Peng and Robinson (1977) calculated the gas-liquid critical properties of several ternary mixtures using the Redlich-Kwong and Peng-Robinson equations of state, respectively. Peng and Robinson also reported calculations of some other multicomponent mixtures. These early works are significant; they showed that techniques used to predict binary mixture critical properties could be extended to the prediction of ternary mixtures without a reduction in accuracy. Spear et al. (1971) used the van der Waals mixing rules for both equation-of-state parameters, whereas Peng and Robinson used the van der Waals prescription for *a* and a linear rule for *b*. The interaction parameters were obtained from the analysis of binary mixtures. The accuracy of the ternary cal-

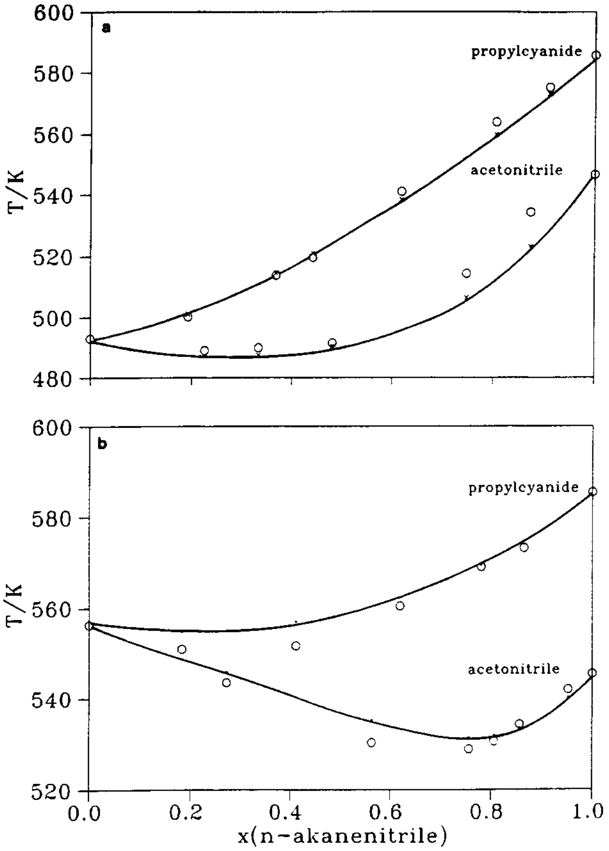

Figure 12. Experiment (o) vs. theory (-) for: a. ternary alkanenitrile + pentane + hexane; b. alkanenitrile + heptane + octane mixtures.

culations reflected the error associated with the analysis of the three constituent binary mixtures.

Sadus and Young (1987, 1988) and Sadus (1992a) reported calculations for the critical temperatures of 30 ternary mixtures using the Guggenheim equation of state in conjunction with the van der Waals mixing rules and the interaction parameters obtained from the calculation of the appropriate binary gas-liquid critical properties. The mixtures studied involved combinations of hydrocarbon, siloxane, perfluorohydrocarbon and alkanenitrile molecules. The calculations correctly reproduced the variation of critical temperature with respect to composition. Generally, the accuracy of calculated critical temperatures were within the limitations imposed by the accuracy of the binary interaction parameters. The agreement of theory with experiment for the critical temperatures of ternary mixtures containing an alkanenitrile as one component is illustrated in Figure 12.

The above studies indicate the feasibility of employing binary mixture parameters and the van der Waals mixing rules to calculate ternary mixtures. However, it can be anticipated that for some mixtures, three-body interactions may be important. This can be expected to be particularly important for liquid-liquid equilibria.

Types of critical transitions of ternary mixtures

The critical transition of a one-component fluid involves only two phases: vapor phase and liquid phase. In contrast, phase separation between different liquid phases is possible in binary mixtures. Nonetheless, the critical transition is commonly between two phases only. In rare cases, a critical transition between two different two-phase equilibria has been detected. For example, such a transition occurs in some aqueous binary mixtures when a LCST (lower critical solution temperature) curve and a UCST (upper critical solution temperature) meet. Behavior of this kind has been variously described as unsymmetrical tricritical points, double critical points, or hypercritical points. The lack of uniformity of nomenclature is likely to lead to misunderstanding in the interpretation of ternary and other multicomponent mixtures in which this type of transition is very common. In addition, a genuine tricritical point involving the simultaneous disappearance of three distinct phases is possible for the first time in a ternary mixture. Sadus (1992a,b, 1993b) has identified the following distinct *classes* of critical transition:

Class 1. Multiphase critical points (such as tricritical and tetracritical) involving three or more phases undergoing a simultaneous transition to produce a single homogeneous phase. In the case of a tricritical point, the two menisci signifying the phase boundaries disappear simultaneously.

Class 2. Lower critical solution phenomena and gas-liquid critical transition meet at relatively low temperature. A critical transition occurs transforming the two-phase liquid-liquid equilibrium into a two-phase gas-liquid equilibrium. That is, the meniscus between the two liquid phases becomes critical simultaneously with the formation of a gas-liquid meniscus.

Class 3a. A region of LCST and UCST phenomena meets. The resulting critical transition is between the different two-phase liquid-liquid equilibria. That is, the lower solution meniscus disappears with the simultaneous formation of an upper critical solution meniscus.

Class 3b. There is a transition between two different two-phase upper critical solution menisci.

The above classifications were based on the interpretation of ternary critical calculations using the Guggenheim equation of state. They are consistent with phenomena which have been observed experimentally, and they offer a new insight into the high-pressure phase behavior of multicomponent fluids. The variation of critical temperature, pressure and volume with respect to composition near the transition point is shown in Figure 13 as a cross-sectional profile of the ternary surface. The upper or lower branches of the profile represent different LCST, UCST or gas-liquid equilibria.

One of the earliest postulations of multiphase critical phenomena can be attributed to van der Waals (Rowlinson, 1988), and the first substantial experimental studies are found in the Russian literature (Radyshevskaya et al., 1962; Krichevskii et al., 1963; Efremova and Shvarts, 1966, 1969; Myasnikova, 1969). Knobler and Scott (1984) summarized the data for several ternary systems and the coordinates for a tricritical line in the quaternary carbon dioxide + water + methanol + ethanol mixture. Some workers have postulated a hypothetical tricritical point in binary mixtures exhibiting transitional Type III mixtures (Brunner, 1990) and between Types II and IV systems (Scott, 1987). These works are discussed in greater detail elsewhere (Sadus, 1992a).

Many investigations of tricritical equilibria have described an unsymmetric tricritical point corresponding to a class 2

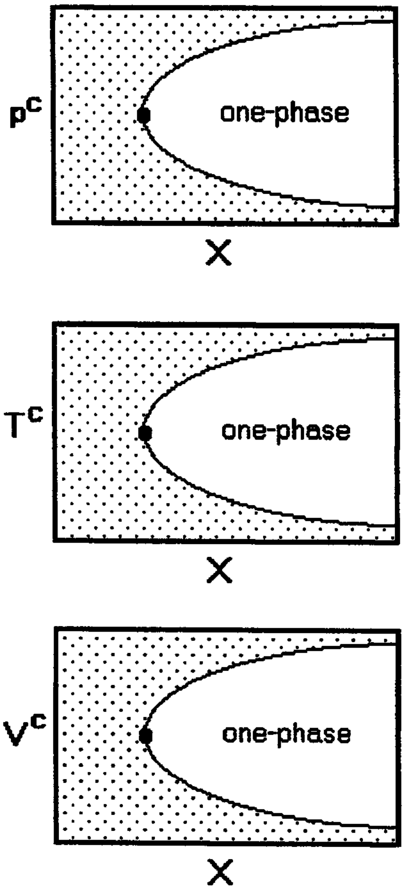

Figure 13. Variation of the critical profile of a ternary fluid in the proximity of class 2 or 3 transition (●).

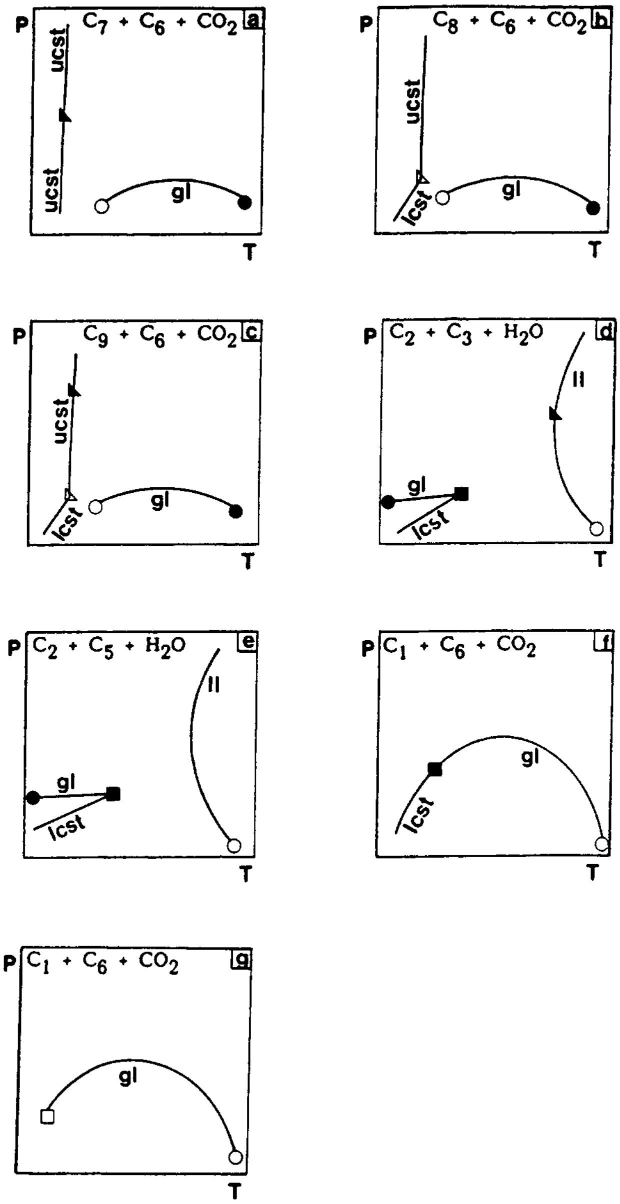

Figure 14. Cross-sectional pressure-temperature profiles of the critical surface of ternary mixtures indicating the position of class 1 (□), class 2 (■), class 3a (◺) and class 3b (◣) transitions.

The position of the critical point of component 3 (○) and the binary component 1 + component 2 critical transition (●) is also indicated. An example of a ternary mixture exhibiting these types of equilibria is given.

transition. In one investigation of the carbon dioxide + methanol + water mixture, Efremova and Shvarts (1966) had reported a possible tricritical point, although they later (1969) detected a class 2 transition in the same mixture. In some mixtures, a line of class 2 critical transitions can be envisaged along the edge formed by the gas-liquid critical surface and the LCST surface. A unique point on this curve may correspond to a tricritical point. Similarly, it is also probable that some experimental investigations of tricritical transitions in quasi-binary mixtures (Creek et al., 1981; Specovius et al., 1981; Lindh et al., 1984; Goh et al., 1987, 1988; Fernandez-Fassnacht et al., 1987) may have identified a class 2 transition rather than a genuine tricritical point. Tricritical equilibria had been analyzed by the theory proposed by Griffiths (1974) and later extended by Scott (1987). There is some evidence (Pegg et al., 1983) that a phenomenon of this type behaves classically, in contrast to the nonclassical behavior of conventional critical equilibria. Kohse and Heidemann (1992) have recently successfully calculated tricritical lines in quaternary mixtures using cubic equations of state.

The critical properties of 22 ternary mixtures have been extensively calculated (Sadus, 1992a). One or more of the above classes of critical transitions have been identified in mixtures in which at least two of the three constituent binary mixtures display a limited degree of miscibility. The cross-sectional critical pressure-temperature profile of a selection of mixtures exhibiting one or more of the above transitions is qualitatively illustrated in Figure 14. Heilig and Franck (1990) have calculated the critical surface of water + nitrogen + hexane near the critical point of water. Their results are consistent with calculations for other aqueous mixtures (Sadus, 1992a). Class 2 transitions can be expected in these systems at relatively low temperatures and pressures.

In some instances, three distinct portions of the critical surface can be identified corresponding to two different upper critical solution equilibria and lower critical solution behavior. The changeover between these different equilibria can be identified by a line of class 3a and 3b transitions. The characteristic cross-sectional profile of mixtures exhibiting dual transitions is shown in Figure 15.

Future Directions

Global phase behavior classification of multicomponent mixtures

The phase behavior of binary mixtures has been extensively measured and, as outlined above, there are ample examples of the calculation of critical properties. There is also sufficient evidence to indicate that these calculations can be successfully used for critical equilibria in ternary and other multicomponent fluids. Part of the motivation for studying binary mixture phenomena is to gain an insight into the phase behavior of multicomponent equilibria. There are certainly some similarities between binary mixture phenomena and the behavior of ternary fluid systems. However, it is also apparent that the addition of a third component introduces a considerable increase in the diversity of phase transitions. Consequently, with the exception of relatively simple, highly miscible ternary mixtures, the phase behavior of ternary mixtures cannot be regarded as a simple extension of the phenomena exhibited by the constituent binary mixtures.

It is probable that the phase behavior of ternary mixtures is generally a good indication of the phase behavior of multicomponent fluids in general. It definitely provides a superior insight than binary mixture equilibria. Calculation of the critical equilibria of ternary mixtures provides a potentially useful mechanism for defining the "global" nature of phase equilibria of ternary and possibly multicomponent equilibria. Calculations are also likely to play a valuable role in supplementing and directing experimental work. The available experimental data are extremely limited. There is not a single example of a ternary system for which even the continuous gas-liquid critical surface has been fully investigated. The available gas-liquid critical properties for any ternary system only cover a minute region of composition. The increased complexity and scope of ternary phase equilibria impose considerable difficulties for experimental measurements. It is in this context that systematic calculations of ternary equilibria will prove valuable in supplementing experimental data and discovering interesting phenomena.

Nonclassical improvement of the prediction of near-critical phase equilibria

From a practical point of view, it has been demonstrated that mean field theories and equations of state, in general, can be used to adequately calculate critical equilibria in binary and ternary mixtures. However, it is well known (Levelt Sengers et al., 1986) that the critical state cannot be treated analytically. It is increasingly apparent that the nonclassical nature of the critical state must be taken into account to genuinely improve the prediction of critical or near-critical equilibria. It can be argued that the use of optimizing parameters is at least, partly due to an inadequate description of the critical state. On the other hand, the predictive capabilities of current nonclassical models of the critical state is very restricted.

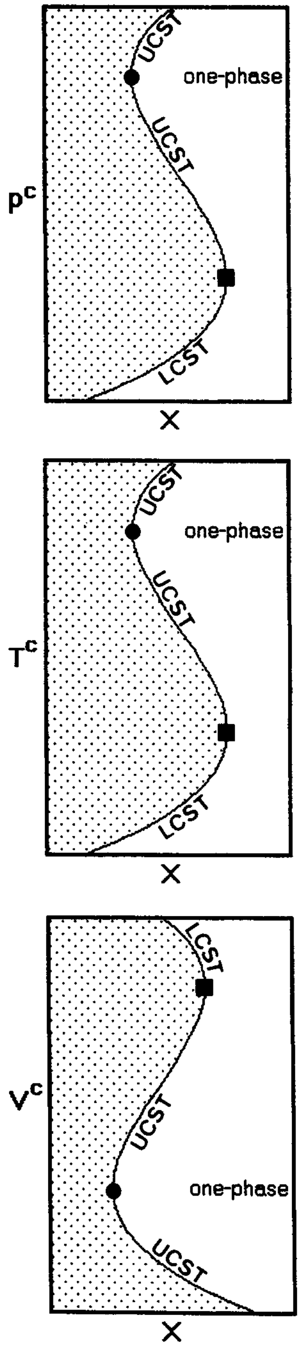

Figure 15. Critical profile of a ternary mixture exhibiting both a class 3a (■) and class 3b (●) transition on the same critical surface.

These transitions divide the critical surface into three distinct regions (the x axis is exaggerated to clearly show the transition points).

The variation of the physical properties of fluids (for example, specific heat and isothermal compressibility) approaching the critical point has been extensively investigated (Stanley, 1971; Levelt Sengers, 1983; Levelt Sengers et al., 1983). These studies can be used to define critical exponents which provide an insight into the nature of the critical transition. Consider a function $f(\epsilon)$ where $\epsilon \approx T - T^c/T$ is a dimensionless variable

Table 2. Definition of Critical Exponents for One-Component Fluids

Exponent	Definition	Property
α	$C_v \sim \lvert T-T^c \rvert^{-\alpha}$	isochoric heat capacity
β	$(\rho' - \rho'') \sim (T^c - T)^{\beta}$	saturation densities
γ	$K_T \sim \lvert T-T^c \rvert^{-\gamma}$	isothermal compressibility
δ	$\lvert p-p^c \rvert \sim \lvert \rho-\rho^c \rvert^{\delta}$	pressure

that reflects the difference in temperature from the critical temperature. It is assumed that $f(\epsilon)$ is both positive and continuous for sufficiently small positive values of ϵ and that the following limit exists:

$$\lambda \approx \lim_{\epsilon \to 0} [\ln f(\epsilon)/\ln \epsilon] \tag{46}$$

The limit λ is the critical point exponent associated with the $f(\epsilon)$ function. Four of the most common critical exponents of a pure substance are defined in Table 2.

If the van der Waals equation of state or other mean field theories are used to obtain these critical exponents, then the values of $\alpha = 0$, $\beta = 0.5$, $\delta = 3$ and $\gamma = 1$ are typically obtained. These values compare with experimental values of $\alpha = 0.08$-0.15, $\beta = 0.32$-0.36, $\delta = 4.3$-5.1, and $\gamma = 0.96$-1.28 (Wagner et al., 1992). The discrepancy between theory and experiment indicates that the critical state cannot be treated analytically. Analogous critical exponents can also be defined for binary mixtures (Scott, 1972; Rowlinson and Swinton, 1982).

Griffiths and Wheeler (1970) developed an alternative to the conventional description of fluid properties based on a division of variables into fields (such as T, $-p$, μ, which must be equal in phases at equilibrium) and densities (such as, S, V, n, which may differ). This formalism has been applied to the detection of tricritical points in quasi-binary mixtures (Pegg et al., 1983). A "scaling" approach is frequently employed to incorporate the effects of nonclassical behavior. Leung and Griffiths (1973) constructed a scaled thermodynamic potential for gas-liquid equilibria in binary mixtures by splitting the potential into a regular and scaled part. Rainwater and Moldover (1983) proposed a modified version of the Leung-Griffiths equation. The modified equation has been successfully used to reproduce the critical curve and predict the dew-bubble curves of binary mixtures. The methodology has been recently extended (Lynch et al., 1992) to predict vapor-liquid transitions in ternary mixtures. However, the requirement for a large number of adjustable parameters severely restricts the model's predictive ability. The approach is also confined to the prediction of continuous gas-liquid critical properties.

A procedure for transforming the coordinates of a classical equation of state to nonclassical coordinates has been proposed (Fox, 1979, 1983). First, the Helmholtz-density of the fluid ($\psi = A/V$) is expressed in terms of a regular background term (ψ_r) and a singular (ψ_s) contribution:

$$\psi = \psi_r + \psi_s \tag{47}$$

Classically,

$$\psi_s(a_1, a_2) = \lambda^{-4}\psi_s(\lambda^3 a_1, \lambda^2 a_2) \tag{48}$$

where λ is a positive constant, and a_1, a_2 are field variables. Fox (1979) replaced Eq. 48 with

$$\psi_s(a_1, a_2) = \lambda^{-4}\psi_s(\lambda^{3+\phi} a_1, \lambda^{2+\theta} a_2) \tag{49}$$

where the θ and ϕ terms are related to the α and β critical exponents:

$$\alpha = (\theta - 2)/(\theta + 2) + 1 \tag{50}$$

$$\beta = (1 - \phi)/(2 + \theta) \tag{51}$$

This rescaling technique enables the transformation from classical to nonclassical coordinates via the following relationships:

$$a_1 = \lambda\phi a_1 = [g(\Psi)]\phi a_1 \tag{52}$$

$$a_2 = \lambda\theta a_2 = [g(\Psi)]\theta a_2 \tag{53}$$

where g is a positive-valued homogeneous function, and Ψ represents the distance from the critical point.

De Pablo and Prausnitz (1989) have applied some of these concepts to the liquid-liquid equilibria of binary and ternary mixtures. They reported a good representation of liquid-liquid equilibria including the critical region. Vine and Wormald (1993) used this method to adapt the Patel-Teja equation of state to improve the agreement between theory and experiment for the near-critical isothermal properties of pure substances. It has been demonstrated that classical equations of state can be at least fitted accurately to the binary gas-liquid or liquid-liquid critical point. The addition of an accurate nonclassical correction to the equation of state can conceivably improve the prediction of normal-phase coexistence. If this can be achieved, then critical calculations may form a useful starting basis for the prediction of phase separation in general.

Ionic fluids

The calculation of critical equilibria of fluids containing an electrolyte is in its infancy. Nonetheless, there are ample experimental data to indicate that electrolyte fluids are likely to exhibit a rich diversity of critical transitions. Some of these critical transitions, such as gas-liquid equilibria close to the critical point of the electrolyte, occur at conditions which are currently experimentally inaccessible and which provide a useful role for reliable and accurate calculations.

Pitzer (1990) has recently reviewed the critical properties of ionic fluids, and a review of the statistical mechanics and thermodynamics of ionic fluids is also available (Pitzer, 1984). The NaCl system has been widely investigated due to its importance in geological processes and as a prototype model for other electrolyte systems. Sourirajan and Kennedy (1962) reported the critical curve of NaCl + water to a temperature and pressure of 700°C and 1,237 bar (123.7 MPa), respectively. The mixture is believed to represent a Type I system with a continuous critical curve extending from the critical point of water to the critical point of NaCl estimated by Bischoff and Pitzer (1989) to be at 3,600°C and 260 bar (26 MPa). They estimated that the critical curve has a maximum at 2,000°C and 2,500 bar (250 MPa). It is believed that Type I behavior is common for mixtures of water + a 1:1 electrolyte like NaCl and KCl. Weingärtner (1989) proposed that 1:1 electrolytes exhibit liquid-liquid separation if the second virial coefficient is large and negative, and the third and higher virial coefficients are positive. Limited miscibility (Type IV behavior) is commonly associated with 2:2 electrolytes such as SiO_2 (Sourirajan and Kennedy, 1962) or UO_2SO_4 (Bischoff and Pitzer, 1989). Upper critical solution equilibria (and possibly lower critical solution behavior) has been reported for aqueous mixtures containing tetraalkylammonium salts (Glasbrenner and Weingärtner, 1989; Weingärtner et al., 1991; Weingärtner and Steinle, 1992). An interesting outcome of the analysis of the coexistence curve of electrolyte systems is that the critical exponent β equals 0.5 as predicted by classical mean field theories.

Krader and Franck (1987) examined the coexistence equilibria of ternary water + methane + NaCl and water + methane + $CaCl_2$ mixtures. Michelberger and Franck (1990) reported similar measurements for water + alkane + NaCl and methanol + methane + NaBr systems. All of these systems contain a nonelectrolyte binary mixture which displays Type III behavior. The introduction of even a small amount of salt results in a substantial increase in the temperature required for one-phase coexistence (Figure 16).

Ionic fluids represent a considerable challenge to theory. Apart from normal dispersion forces and dipolar forces, ion-ion interactions and ion-induced dipole interaction must also be considered. Questions of charge distribution and the extent of ionic dissociation must also be addressed. No quantitative calculations of the critical properties of ionic fluids have been reported. However, Harvey (1991) used the mean spherical approximation (MSA) theory to qualitatively calculate critical equilibria in water + salt mixtures. It was demonstrated that a phase transition between Types III and II and either Type IV or V was encountered depending on the relative magnitude of the critical temperatures of the components. The MSA theory is not very accurate for phase equilibrium calculations, and it assumes that the molecules are of equal size. This latter point is particularly important because a key feature of, for example, the water + NaCl system (Sourirajan and Kennedy, 1962), is that there is a continuity in critical equilibria despite a very large difference in the size of the component molecules. Limited miscibility would be normally expected for nonelectrolyte binary mixtures with a correspondingly large disparity in molecular size. Recently, Blum et al. (1992) have extended the MSA model for molecules of different size.

Polymer fluids

Historically, the phase behavior of polymer mixtures has been treated in terms of variations of the Flory lattice model or simple equations of state (Flory, 1953; Kamide, 1990). The simplicity of these models is appealing, although comparison of experiment with theory indicates that the concept is probably not suitable for accurate quantitative predictions. More recently (Beret and Prausnitz, 1975; Cottermann et al., 1986; Chien et al., 1983), considerable emphasis has been placed on developing equations of state for long-chain molecules. The validity of existing long-chain equations of state is probably limited to the higher-molecular-weight *n*-alkanes ($n < 20$), and as such, they are unsuited to polymer mixtures. Chiew (1990) has recently presented a plausible theoretical model for obtaining an equation of state appropriate for polymer molecules. Song and Prausnitz (1993) have used this approach to formulate a generalized equation for polymer systems in terms of bonded and nonbonded interaction. Developments of this kind offer the opportunity to extend the investigation of critical equilibria to mixtures containing a large macromolecule.

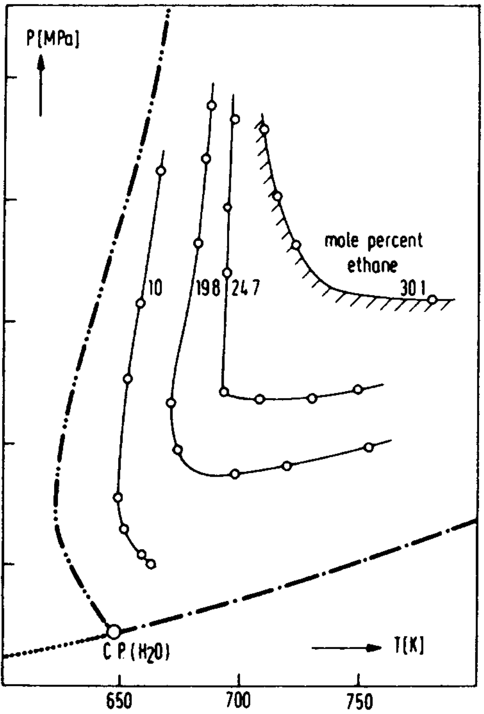

Figure 16. Pressure-temperature behavior of the experimental isopleths of the water + ethane + NaCl with 1.7 wt. % NaCl relative to water.

The vapor pressure curve of water (. . .) and the critical curves of water + NaCl (- • • • -) and water + ethane (— · · —) are also illustrated (Michelberger and Franck, 1990).

Why calculate the critical properties of polymer mixtures? The critical equilibria of mixtures containing a polymer or large macromolecule have not been comprehensively calculated. It is evident from experimental data that mixtures of polymers have a diverse range of phase transition which are rarely evident in nonpolymeric mixtures. For example, the existence of lower and upper critical solution temperature equilibria is quite commonly reported. Examining the binary and ternary critical properties of polymer-polymer or polymer-solvent mixtures is useful in identifying the "global" nature of the phase behavior of the system which has important consequences for optimizing polymer-related commercial processes.

Conclusion

The experimental gas-liquid critical properties of a diverse range of binary mixtures can be accurately calculated with a wide variety of equations of state. The size, shape, polarity or other molecular characteristics of the components of the binary mixture do not substantially affect the agreement between theory and experiment. However, a distinction must be made between *a priori* calculations and calculations which use combining rules to fit theory to experiment. Genuinely, *a priori* calculations using conventional mixing rules and combining rules can only be accurately made for relatively simple mixtures of nonpolar molecules of similar size. Typically, only one adjustable combining rule parameter (ξ) is required for optimal agreement between theory and experiment. The values of ξ are of similar magnitude irrespective of which equation of state is employed. This indicates that the deficiency is primarily in the choice of mixture prescriptions used to extend equations-of-state calculations to mixtures. This problem is not intractable, and it is likely that new approaches can be developed to improve *a priori* prediction of mixture properties. For example, it has been demonstrated that Eq. 40 can be used in conjunction with an equation of state to accurately predict *a priori* the critical properties of a diverse range of nonpolar or slightly polar binary mixtures.

Theory can at least predict qualitatively all the known types of critical equilibria of binary mixtures. In some instances, new types of critical behavior have been predicted which have hitherto not been confirmed by experimental measurement. The calculation of "transitional" Type IV or V behavior is very sensitive to the value of the interaction parameters. Similarly, Type VI behavior is associated with mixtures containing molecules with interactions which are difficult to accurately model. However, Type II UCST behavior and Type III behavior can be adequately calculated. The pressure and composition dependence of UCST phenomena can be accurately reproduced by using the ξ term as an adjustable parameter. In contrast, optimal values of both the ξ and ζ combining rule parameters must be evaluated to obtain good agreement of theory with experiment for Type III behavior. Nonetheless, the agreement of theory and experiment is very good for nonpolar mixtures, and good agreement can also be obtained for some polar mixtures including aqueous systems. It is probable that improvements in the b_{12} combining rule, as exemplified by Eq. 45, will substantially reduce the dependence on the ζ term for good quantitative agreement.

The investigation of critical equilibria of ternary and other multicomponent equilibria is in its infancy; however, some definite observations can be made for ternary mixtures. Comparison of theory with experiment for the gas-liquid properties of ternary mixtures indicates that good agreement can be obtained by utilizing the interaction parameters obtained from the analysis of the constituent binary mixtures. If this conclusion is generally valid, then reasonably reliable *a priori* calculations of ternary mixtures can be undertaken. Such calculations could have a valuable role in discovering new phenomena and directing experimental work. The available calculations clearly indicate that critical equilibria and the phase behavior of ternary mixtures, in general, are not simple extensions of phenomena exhibited in binary mixtures. It is highly probable that the phase behavior of ternary mixtures provides a superior insight into the phase behavior of multicomponent fluids than could otherwise be obtained by solely examining the behavior of binary mixtures.

The challenge for the future is to improve our ability to predict the phase behavior of ternary and multicomponent fluids. The ability to accurately model multicomponent fluids is important because of the increase in experimental difficulty in comprehensively measuring multicomponent phase equilibria. To maximize the benefits of calculations of this kind, attention must also be focused on reducing the deficiencies in the analysis of binary mixtures. Although the properties of mixtures of conventional molecular fluids can be adequately calculated, the same techniques cannot be successfully applied to either ionic fluids or polymer mixtures. Calculations should also increasingly take account of the nonclassical nature of the critical state. Conventional calculation procedures can adequately reproduce the critical properties of many mixtures, but the prediction of near critical equilibria is compromised by the nonclassical nature of critical equilibria. It would be very useful to incorporate nonclassical effects into a conventional equation of state and then use critical calculations as the starting basis for the accurate prediction of phase equilibria in general.

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