Phase equilibria in fluid mixtures at high pressures

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Abstract The six types of phase behaviour observed in binary mixtures are described briefly. Liquid-liquid immiscibility in Type II and Type III phase behaviour is discussed in terms of pressure-temperature-composition diagrams. The conditions for the coexistence of two phases and the conditions for a critical point in both binary and ternary mixtures are presented. The criticality conditions are given in terms of both the Gibbs and Helmholtz functions. Methods for calculating high pressure equilibrium in fluid mixtures using these conditions together with a one fluid model are discussed. The use of empirical and theoretically based equations of state to calculate the Helmholtz function are briefly reviewed and the need for caution when using this approach is pointed out. Finally the need for a classification for the phase behaviour of ternary mixtures and for liquid-liquid equilibrium data of higher accuracy are considered.

INTRODUCTION

Although there have been a very large number, literally thousands, of studies on liquid-liquid and gas-liquid solubility at or near atmospheric pressure our knowledge of solubility at pressures of more than a few atmospheres is rather sketchy. In this article some recent advances in the study of such systems are described. The term "fluid equilibria" has been deliberately used in the title but, in some instances, "gas" or "liquid" will be used where appropriate. Over a century ago Andrews (ref. 1) showed that there is a continuity of state around the critical point. Normally liquid-liquid and gas-liquid equilibria are discussed separately but during the last two decades it has become apparent that the limits between liquid-liquid, gas-liquid and gas-gas equilibria are not well defined and that continuous transitions occur. This point has been discussed in several instances by Schneider and coworkers (ref. 2-5 and also references therein). It is the purpose here to deal briefly with theoretical approaches and discuss some recent advances. The rapidly developing area of ternary mixtures is discussed. It is not possible to deal with even most of the important aspects of phase equilibria here. There are a number of reviews which deal with most topics to which the reader is referred (ref. 6-12).

BINARY MIXTURES

In order to discuss fluid phase equilibria of binary mixtures it is useful to use the phase behaviour classification of Scott and van Konynenburg (ref. 13-15). They proposed that the phase behaviour of binary mixtures could be classified into six broad groups. They found that five groups could be predicted using the van der Waals equation of state. The sixth class, which could not be predicted by the van der Waals equation, arises only in aqueous mixtures. The pressure-temperature projection of the pressure-temperature composition diagram of the six types of phase behaviour are represented schematically in Fig. 1.

Type I. The phase diagram has a simple continuous gas-liquid critical locus with or without azeotropy.

Type II. The phase diagram is as for Type I but with the addition of a three phase (liquid-liquid gas) line ending at an upper critical end point, UCEP, and a (liquid-liquid) critical line starting from the UCEP and rapidly approaching high pressures. This type can occur with or without azeotropy.

Type III. This phase diagram has two distinct critical lines, one starts at the critical point of the component with the higher critical temperature but never approaches the critical point of the other component.
moving rapidly to high pressures. The other line starts at the critical point of the component with the lower critical temperature and meets a three phase (liquid-liquid-gas) line in an UCEP. The three phase line may be between the vapor pressure curves of the two components or may be above the vapor pressure curves of both components. There are several subgroups of Type III behaviour depending on whether there is a heteroazeotrope and on the shape of the critical line starting at the critical point with the higher temperature.

Type IV. This phase diagram has three distinct critical loci, one of which (the liquid-liquid critical line) starts at an UCEP on a three phase (liquid-liquid-gas) line and moves to higher pressures. The second line starts at the critical point of the component with the lower critical temperature and ends at an UCEP on a three phase line. The third line starting at the critical point of the other component and ends in a lower critical end point, LCEP, on the same three phase line as the second critical line.

Type V. This type is as Type IV but without the liquid-liquid critical line and three phase line at lower temperatures.

Type VI. This type of phase behaviour is characterised by a continuous critical locus between the critical point of the two pure components. However, at lower temperatures there is a three phase line which is bounded above and below by critical end points. A liquid-liquid critical line joins these two critical end points. There are several known configurations of the line joining the ends of the three phase line. In the example illustrated the liquid-liquid critical line has two branches with a region of complete liquid miscibility between them.

Type II and Type III phase behaviour have been the most widely studied and they are discussed in more detail. Only the "general" characteristics of the type of phase behaviour can be understood from the diagram given above. In practice solid phases often complicate the diagrams. The pressure-temperature-composition diagram for Type II phase behaviour is illustrated in Fig. 2A. It can be seen that the three phase line on the pressure-temperature projection is derived from three lines on the pressure-

Fig. 1. Pressure-temperature projections for the six types of phase equilibria in binary mixtures. A - Type I; B - Type II; C - Type III; D - Type IV; E - Type V; F - Type VI. Lines labelled 1 and 2 are the vapor pressures of the two components; lines labelled LLG, GL and LL are three phase lines, gas-liquid critical loci and liquid-liquid critical loci respectively; points denoted X C are critical points of the pure components.
Fig. 2. Pressure-temperature-composition diagrams for Type II (Fig. 2A) and Type III (Fig. 2B) phase behaviour. The three phase line is denoted LL.

The temperature-composition diagram representing the composition of gas, liquid 1 and liquid 2. At pressures above this three phase line a maximum of two phases can coexist. Although four different phases are possible at pressures and temperatures between the three phase line and the vapor pressure curve of the more volatile component, it is impossible to have more than two in equilibrium at any one composition. At temperatures below the upper critical end point and pressures above the vapor pressure of the more volatile component, depending on the overall composition it is possible to have two coexisting (liquid) phases. These liquids can continue to coexist even at very high pressures, the mutual solubility of the liquids often changes little even with very large changes in pressure. However, near the critical end point, i.e. the point on the three phase line at which the two liquid phases become identical the effect of pressure can change the composition of coexisting phases dramatically. A typical pressure-temperature-composition diagram for Type III phase behaviour is illustrated in Fig. 2B. As in Type II phase behaviour it can be seen that the three phase line on the pressure-temperature projection is the result of three separate lines on the p, T, x diagram representing the composition of liquid 1, liquid 2 and vapor.

There are many sub-types of Type III phase behaviour. Let us consider the portion of the phase diagram in the region of the upper critical end point and the critical point of component with the lower critical temperature. There are four possibilities. The three phase line could be at higher or lower pressures than the vapor pressure curve of the pure component. Each of these two cases could have the upper critical end point at a higher (or lower) temperature than the critical point. These four possibilities are illustrated in Fig. 3. Consider Fig. 3A, the three phase line is at lower pressures than the vapor pressure of the pure component (1). At a temperature, T1, the pressure composition diagram is shown in Fig. 3B. It can be seen that depending on the pressure and overall composition it is possible to have one or two phases present. At high pressures we have a fluid-fluid equilibrium which if T1 is sufficiently low, it is reasonable to refer to the equilibrium as liquid-liquid. Although a line parallel to the composition axis at pressures between the three phase line and the vapor-pressure of component (1) cuts the boundary lines in four places, only two phases can be in equilibrium. The two phases in equilibrium will depend on the overall composition. At temperature, T2 a different situation exists in that at pressures above the three phase line it is possible to have two phases present which on increasing the pressure can pass through a critical point as is illustrated in Fig. 3C. Again, although at pressures between that of the three phase line and the critical point of the mixture at constant pressure
four phases of different composition can exist, only two phases can exist in equilibrium. The particular two phases in any instance will depend on the overall composition. It should be pointed out that for a pressure between that of the three phase line and the critical point of the mixture at

Fig. 3. The four possibilities for the relative position of the three phase line and vapor pressure curves of pure components for Type III phase behaviour. Figures A, D, G and J are pressure-temperature projections of the four classes. Figures B, E, H and K are the constant temperature, $T_1$ sections of the $p, T, x$ diagrams; Fig. C, F, I and L are analogous sections at temperature $T_2$. 
temperature $T_2$ as the composition is increased from pure 1 to pure 2, the phases in equilibrium change from one fluid to two fluids (gas & liquid), to one fluid to two fluids (liquid & liquid) and finally back to one fluid. Now consider Fig. 3D; the pressure composition diagrams at constant temperatures, $T_1$ and $T_2$ are shown in Figs. 3E and 3F respectively. Figures 3G-3L represent the corresponding diagrams for the systems in which the three phase line is above the vapor pressure curve of pure component 1.

It is now convenient to consider the effect of pressure on liquid-liquid immiscibility in a more general phenomenological manner. Consider Fig. 4A, in this case an increase in pressure causes the liquids to become more miscible. We now combine this condition together with the four types of known temperature composition diagrams:

(a) systems with an upper critical solution temperature (Fig. 4D),
(b) systems with a lower critical solution temperature (Fig. 4H),
(c) systems with both and a closed loop on the temperature composition diagram (Fig. 4L), and
(d) systems with an upper critical solution temperature and a lower critical solution temperature at higher temperatures (Fig. 4P).

The corresponding pressure, temperature, composition diagrams for these four classes are shown in Figs. 4E, 4I, 4M and 4Q. Figure 4B illustrates the situation where an increase in pressure causes the liquids to become less

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Fig. 4. Pressure effects on immiscibility phenomena in liquid binary systems. Figures A,B and C are constant temperature sections of the $p,T,x$ diagrams and Figs. D,H,L and P are constant pressure sections of the $p,T,x$ diagrams.
miscible and Figs. 4F, 4J, 4N and 4R represent the p, T, x diagrams corresponding to the combining of the behaviour illustrate in Fig. 4B with that of Figs. 4D, 4H, 4L and 4P. Figure 4C illustrates the situation in which the mutual solubilities of liquids passes through a minimum on increasing the pressure and Figs. 4G, 4K and 4R illustrate the p, T, x behaviour corresponding to the combination of the behaviour of Fig. 4C with that of Figs. 4D, 4H and 4L. Schneider has given examples of phase behaviour for all the types illustrated in Fig. 4.

**THERMODYNAMIC CONDITIONS FOR HIGH-PRESSURE EQUILIBRIA IN FLUID MIXTURES**

The conditions for the coexistence of two phases, denoted ' and ' in equilibrium are

\[
\begin{align*}
\frac{\partial G}{\partial x_2}(T, p, x_1=x_1') &= \frac{\partial G}{\partial x_2}(T, p, x_1=x_1'') \\
G(T, p, x_1=x_1') + x_1'(\frac{\partial G}{\partial x_2}(T, p, x_1=x_1')) &= G(T, p, x_1=x_1'') + x_1'(\frac{\partial G}{\partial x_2}(T, p, x_1=x_1''))
\end{align*}
\]

(1)

(2)

and

\[
G(T, p, x_1=x_1') + x_1'(\frac{\partial G}{\partial x_2}(T, p, x_1=x_1')) = G(T, p, x_1=x_1'') + x_1'(\frac{\partial G}{\partial x_2}(T, p, x_1=x_1''))
\]

(3)

(4)

The conditions for a critical point of a binary are (ref. 11)

\[
\begin{align*}
(3G/\partial x_1^2)_{T,P} &= 0 \\
(3G/\partial x_1^3)_{T,P} &= 0 \\
(4G/\partial x_1^4)_{T,P} &> 0
\end{align*}
\]

(5)

(6)

(7)

Similarly for a ternary mixture the conditions for a critical point are (refs. 16, 17)

\[
\begin{align*}
(3G/\partial x_1^2)_{T,P}(3G/\partial x_2^2)_{T,P} - (3G/\partial x_1^3)_{T,P} &= 0 \\
(3G/\partial x_1^3)_{T,P} + (3G/\partial x_1^3)_{T,P} + (3G/\partial x_2^3)_{T,P} &= 0 \\
(3G/\partial x_1^3)_{T,P} + (3G/\partial x_2^3)_{T,P} &> 0
\end{align*}
\]

(8)

(9)

Equations of state which describe the coexistence of phases give several values of volume for some pressures and temperatures but a unique value of volume at a given pressure. Therefore, it is more convenient to use T and V as the independent variables rather than T and p and express the critical conditions in terms of the Helmholtz function.

For a binary mixture we have

\[
\begin{align*}
-(2A/\partial V^2)_T(2A/\partial x_1^2)_T, V + (2A/\partial V^2)_T &= 0 \\
-(2A/\partial x_1^2)_T, V(3A/\partial x_1^3)_T - (2A/\partial x_1^2)_T, V(3A/\partial x_1^3)_T &= 0 \\
+ 3(2A/\partial x_1^2)_T, V(2A/\partial x_1^3)_T - 2(2A/\partial x_1^3)_T(3A/\partial x_1^3)_T &= 0 \\
+ (2A/\partial x_1^3)_T, V(3A/\partial x_1^3)_T &= 0
\end{align*}
\]

(10)

(11)

The increase in complexity becomes even more apparent when we consider ternary mixtures. The critical conditions for a ternary mixture become (ref. 16)

\[
\begin{align*}
-(2A/\partial V^2)_T D_1 + (2A/\partial V^2)_T D_2 - (2A/\partial V^2)_T D_3 &= 0 \\
(3W/\partial V)_T D_1 - (3W/\partial V)_T D_2 + (3W/\partial V)_T D_3 &= 0
\end{align*}
\]

(12)

(13)

where

\[
D_1 = (2A/\partial x_1^2)_T, V(2A/\partial x_2^2)_T, V - (2A/\partial x_1^2)_T, V
\]

(14)
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\[ D_2 = (\begin{vmatrix} a^2 & a_{11} \end{vmatrix} T_1 \begin{vmatrix} a_{11} \end{vmatrix} T_2) - (\begin{vmatrix} a^2 & a_{22} \end{vmatrix} T_1 (a^2 T_2) - (\begin{vmatrix} a^2 & a_{22} \end{vmatrix} T_1 (a^2 T_2) - (\begin{vmatrix} a^2 & a_{12} \end{vmatrix} T_1 (a^2 T_2) \) \] 

\[ D_3 = (\begin{vmatrix} a^2 & a_{11} \end{vmatrix} T_1 (a^2 T_2) - (\begin{vmatrix} a^2 & a_{22} \end{vmatrix} T_1 (a^2 T_2) - (\begin{vmatrix} a^2 & a_{12} \end{vmatrix} T_1 (a^2 T_2) \) \] 

and 

\[ W = \begin{vmatrix} a^2 & a_{11} & a_{12} & a_{22} \\ T_1 & T_2 & T_1 T_2 & T_1 T_2 \end{vmatrix} \]

SOLUTION OF THE CRITICALITY CONDITIONS

Several approaches for the calculation of fluid phase equilibria at high pressures and critical loci have been used (refs. 18-24). A detailed discussion is outside the scope of the present paper, however, we shall briefly discuss methods based on equations of state particularly with reference to the prediction of critical loci.

Approximate solutions. Several workers have proposed methods for obtaining the critical properties of a binary mixture by an averaging of the pure component properties. For example, Kay (ref. 25) proposed the averaging rules

\[ T^C = x_1 T_1^C + x_2 T_2^C + 2x_1 x_2 T_{12} \]
\[ V^C = x_1 V_1 + x_2 V_2 + 2x_1 x_2 V_{12} \]

where the cross terms \( V_{ij} \) and \( T_{ij} \) are obtained by a combining rule. Similar equations have been proposed for the volume and pressure of the mixture. The usefulness of these equations is limited to mixtures of simple molecules. They cannot be used to predict liquid-liquid critical phenomena and they have no sound theoretical justification. Redlich and Kister (ref. 26) have proposed an approximate solution based on the critical conditions of a binary mixture. The most unsatisfactory aspect of this approach is the assumption that the variation of critical temperature and critical pressure with composition near the pure component properties can be interpolated over all compositions. This assumption is only approximately valid when the critical locus is a simple continuous function (Type I or Type II phase behaviour). This method does not enable liquid-liquid critical loci to be predicted. An alternative solution, based on the criticality conditions have been given by Rowlinson (ref. 27). Rowlinson's solution assumes conformal solutions and an ideal Gibbs function of mixing. The usefulness of this approach is again limited to relatively simple systems and it cannot be used for liquid-liquid critical phenomenon or in any situations where the critical locus is discontinuous (Type III, IV or V phase behaviour).

Iterative techniques. Several workers have proposed iterative solutions of the criticality conditions. Most are based on a Newton-Raphson iteration. While these techniques are to be preferred to the approximate solution techniques. They have only been used to obtain critical properties for the gas-liquid critical lines in Type I and Type II phase behaviour. Iterative techniques have the advantage over the more general solution techniques that they require only a fraction of the computer time. These techniques have been applied both to binary and ternary mixtures (ref. 11 and 28).

General solution techniques. There are several general solution techniques which have been proposed. Hicks and Young (ref. 19) have proposed a technique which uses the one-fluid model and is, in principle, applicable to any equation of state. Details of the computer technique are outside the scope of this paper. To predict the phase behaviour of a mixture using an equation of state together with the one fluid model it is necessary to make three major assumptions. Firstly it is necessary to have a "prescription" or "recipe" for calculating the properties of the hypothetical fluid (the equivalent substance) which has the same configurational property as the mixture. The prescription is a function of composition, energy and volume parameters characterizing interactions between like and unlike molecules. The most widely used prescription is that referred to as the van der Waals model (ref. 11)

\[ a_{es} = a_{11} + a_{22} + 2a_{12} \]
\[ b_{es} = b_{11} + b_{22} + 2b_{12} \]
Several other prescriptions have been proposed (ref. 11). Secondly it is necessary to have some form of combining rule which enables the unlike energy and volume parameters to be calculated from the energy and volume parameters characterizing interactions between like molecules. Numerous combining rules have been proposed and have been written in terms of the equation of state constants $a$, and $b$, energy and volume reducing parameters $f$ and $h$ or in terms of critical properties (ref. 11). The most widely used combining rule, in terms of $a$ and $b$ are

$$a_{12} = \xi b_{12}(a_{11}a_{22})^{0.5}$$  \hspace{1cm} (22)

$$b_{12} = 0.125(b_{11}^{1/3} + b_{22}^{1/3})^{3}$$ \hspace{1cm} (23)

which in the case of the van der Waals, Guggenheim (ref. 29) or Carnahan and Starling (ref. 30) equation of states are identical to

$$T_{12}^c = \xi(T_{11}^cT_{22}^c)^{0.5}$$ \hspace{1cm} (24)

$$V_{12}^c = 0.125(V_{11}^c + V_{22}^c)^{1/3}$$ \hspace{1cm} (25)

Equations (22 and 23) and (24 and 25) are not equivalent to each other in the case of all equations of state. Thirdly, of course, an equation of state is necessary for prediction using this approach. There have been numerous equations of state used for the prediction of phase behaviour at high pressures. Two general comments are in order here before discussing individual equations of state in more detail. First, the van der Waals equation of state is inaccurate but is capable of qualitatively predicting phase behaviour. Second, most hard sphere and attractive term equations of state tend to give very similar results for critical loci if the attractive term is of the $-a/V^2$ and is temperature independent.

Equations of State. The Helmholtz function can be calculated from an equation of state by using the standard thermodynamic relationship

$$p = -(\partial A/\partial V)_{T,x}$$ \hspace{1cm} (26)

Perhaps the most commonly used equation of state apart from the van der Waals equation is that proposed by Redlich and Kwong which has a temperature dependent attractive term

$$p = RT/(V-b) - a/V^{0.5}(V+b)$$ \hspace{1cm} (27)

The Redlich-Kwong equation (ref. 31) has been widely used by chemical engineers and has also been used to predict phase behaviour of mixtures (ref 32). While it can be argued that polar molecule mixtures will have temperature dependent attractive forces the justification for the use of this equation is that it gives, in general, better agreement with experiment than does van der Waals equation (as judged by comparison with the vapour pressure data of pure substances). There have been several attempts to modify the Redlich-Kwong equation. Two equations of this type which are worthy of note are those of Soave (ref. 32) and Gibbons and Laughton (ref. 33). Both have additional parameters and predict the pure component data better than the Redlich-Kwong equation. Their usefulness for mixture properties have not been adequately tested although they show some promise. The Soave equation is:

$$P = RT/(V-b) - a(T)/(V+b)$$ \hspace{1cm} (28)

where

$$a(T) = 0.4274(R^2T_c^2/p_c)(1 + m(1-(T/T_c)^{0.5}))^2$$ \hspace{1cm} (29)

$$m = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$ \hspace{1cm} (30)

$$b = 0.008864RT_c/p_c$$ \hspace{1cm} (31)

and $\omega$ is the acentric factor defined by

$$\omega = -\log(p_s/p_c) - 1.00$$ \hspace{1cm} (32)

The equation proposed by Gibbons and Laughton is similar to that of Soave but uses experimental vapor pressure data to calculate the temperature dependence of the a term.
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\[ p = \frac{RT}{V-b} - a(T)/V(V+b) \]  \hspace{1cm} (33)

where \[ a = 1 + X(T/T_C) + Y((T/T_C)^{0.5}-1) \]  \hspace{1cm} (34)

and X and Y are obtained by fitting the equation to vapor pressure data over a wide range of temperature. The Soave and Gibbons and Laughton equations are formally identical if

\[ X = m^2 \quad Y = -2m(m+1) \]  \hspace{1cm} (35)

Since these equations contain more adjustable parameters their extension to mixtures is less straightforward and more uncertain than for equations with a more fundamental basis. These equations have the advantage that they predict a more realistic compressibility factor than the van der Waals equation. Although these equations have been used to predict phase behaviour of mixtures their long term usefulness is limited by their lack of a fundamental basis. Peng and Robinson (ref. 34) have proposed an equation of state

\[ p = \frac{RT}{V-b} - a(T)/(V(V+b) + b(V-b)) \]  \hspace{1cm} (36).

It gives a value of the compressibility factor, \( Z_c = pV/RT \), of 0.307. These workers have used this equation to predict the gas-liquid critical properties of binary and multicomponent mixtures with good accuracy. However, their analysis was somewhat limited to relatively simple hydrocarbon mixtures. Furthermore the form of the equation makes manipulation to obtain all the necessary derivatives for the prediction of critical properties for mixtures difficult.

A number of equations of state are based on modifications to the molecular size term by replacement of \((V-b)\) by a term derived from an approximation for a hard sphere equation of state. The most widely used equation of this type is that due to Guggenheim (ref. 29):

\[ P = \frac{RT}{(1-y)^4} + a/V^2 \]  \hspace{1cm} (37)

where \( y = b/4V \) \hspace{1cm} (38).

This equation is relatively easy to manipulate to obtain all the necessary derivatives for the prediction of critical properties for mixtures. Guggenheim’s equation has been used to predict the phase behaviour at elevated pressures of a wide range of binary and some ternary mixtures (ref. 11 and 28). Most of the comparison between theory and experiment have concentrated on the critical temperatures of mixtures. The equation cannot be expected to give good results (a) at low pressures (the equation does not predict second virial coefficients of pure gases correctly) nor (b) for volumetric properties. The critical compressibility given by this equation is 0.36 instead of approximately 0.29 for the inert gases.

Several other hard sphere and attractive force term equations of state have been proposed. The hard sphere term \( \phi(y) \) for several equations is as below:

\[ \phi(y) = 1/(1-4y) \quad \text{van der Waals} \]

\[ = 1 + 4y + 16y^2 + 64y^3 + 256y^4 + 1024y^5 + 4096y^6 + \]  \hspace{1cm} (39)

\[ \phi(y) = 1/(1-y)^4 \quad \text{Guggenheim} \]

\[ = 1 + 4y + 10y^2 + 20y^3 + 35y^4 + 56y^5 + 84y^6 + \]  \hspace{1cm} (40)

\[ \phi(y) = (1+2y)/(1-2y) \quad \text{Scott V (ref. 12)} \]

\[ = 1 + 4y + 8y^2 + 16y^3 + 32y^4 + 64y^5 + 128y^6 + \]  \hspace{1cm} (41)

\[ \phi(y) = (1+3y+4y^2)/(1-2y)(1+y) \quad \text{Scott VI (ref. 12)} \]

\[ = 1 + 4y + 10y^2 + 18y^3 + 38y^4 + 74y^5 + 150y^6 + \]  \hspace{1cm} (41)

\[ \phi(y) = (1 + y + y^2/(1-y))^{-3} \quad \text{Frisch et al. (ref. 34)} \]

\[ = 1 + 4y + 10y^2 + 19y^3 + 31y^4 + 46y^5 + 64y^6 + \]  \hspace{1cm} (42)
\[ \psi(y) = (1 + 2y + 3y^2)(1-y)^{-2} \quad \text{Thiele (ref. 35)} \]
\[ = 1 + 4y + 10y^2 + 16y^3 + 22y^4 + 28y^5 + 34y^6 + \quad (43) \]

The usefulness of these approximations to the true hard sphere equation of state can be gauged by comparing the expansions of these equations with the exact virial expansion for a hard-sphere gas (ref. 12) which up to the seventh virial coefficient is:

\[ \psi(y) = 1 + 4y + 10y^2 + 18.3y^3 + 28.24y^4 + 39.53y^5 + 43.52y^6 + (44) \]

There have been several equations of state which have been suggested which use a temperature dependent attractive term together with a hard sphere term. Such equations may be expected to lead to better agreement between theory and experiment for mixtures containing a polar component. McElroy (ref. 36) has proposed an equation which combined the Guggenheim hard sphere term with the Redlich Kwong attractive term.

There have been several attempts to extend the "hard-sphere" term of the equation of state to allow for non-spherical molecules. While such approaches offer a sound extension of theory to non-spherical molecules without resorting to arbitrary parameters often the final hard body term becomes considerably more complex. Such complexity can be serious in the application to mixtures in the critical region.

Kohlen, Kohler and Svejda (ref. 37) have proposed a generalized van der Waals equation of state which may be written

\[ p = Z_h(RT/V) + Z_{corr}(RT/V) - a/V^2 \quad (45) \]

or

\[ pV/RT = Z_h - a_0y/(V^*RT) + Z_{corr} \quad (46) \]

where \( Z_h \) is the compressibility factor for an assembly of hard particles

\[ Z_{corr} \] is the correction term for the non-linear density dependence of the attractive term at medium and low densities.

\[ a_0/V^2 \] is the uncorrected attractive term

\[ * \]

and \( y \) is the "reduced" density and equal to \( V/V^* \)

where \( V^* \) is the volume of one mole of hard particles.

It is convenient to take \( Z_h \) as given by the Boublik Nezbeda equation (ref. 38)

\[ Z_h = [1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - f(\alpha)y_3]/(1-y)^3 \quad (47) \]

where \( \alpha \) is the parameter for anisotropic molecular shape

and \( f(\alpha) = \alpha^2 \) (for hard fused spheres)

or \( f(\alpha) = \alpha(6\alpha - 5) \).

If \( \alpha = 1 \) eqn. (47) reduces to the eqn. (42) which is a form of the equation for hard spheres proposed by Frisch et al. (ref. 35).

A slightly different approach has been used by Deiters (ref. 39) who developed a semi-empirical equation of state for non-polar and weakly polar fluids and fluid mixtures from the square well model of the intermolecular pair potential. The equation of state has three adjustable parameters and contains "corrections" for non-spherical molecular shape, "soft" repulsive potential and three-body effects. Deiters equation may be written

\[ p = (RT/b)pZ_h(\rho) - (Ra/b)p^2(T/y)(\exp(y/T)-1)I(\rho) \quad (48) \]

where \( b \) is the covolume (i.e. the volume of 1 mole of particles in the cubic close packed arrangement) and can be calculated from the molecular diameter

\( \rho \) is the reduced density equal to \( b/V_m \) where \( V_m \) is the molar volume

\( a \) is the characteristic temperature equal to \( c/Vk \) where \( c \) is the depth of the potential well and \( k \) is Boltzmann's constant.

\( T \) is the reduced temperature equal to \( T/a = kT/c \)

and \( I(\rho) \) is a function related to the square well potential.

Both the equations of Kohlen et al. and Deiters have been used to predict critical loci of a limited range of mixtures.
Criteria for Using a Particular Equation of State. There is often considerable confusion over what is and what is not an acceptable equation of state. In general when using equations of state for mixture properties it is necessary to introduce mixture prescriptions (or models) and combining rules. There is necessarily some additional uncertainty introduced by these prescriptions and combining rules. Unfortunately the uncertainty introduced for some of the more complicated equations of state are considerable and the uncertainty may override the advantage gained by the use of a more accurate equation of state. Finally, perhaps it is necessary to have in mind that when applied to phase behaviour of mixtures at high temperatures and pressures it is necessary to obtain various differentials of the Helmholtz function. Some of the more complicated equations of state lead to a great increase in complexity with little or no improvement in agreement between theory and experiment. Several of the more complicated equations, which are superior in predicting the properties of pure substances and appear to have promise when applied to phase behaviour of mixtures at elevated pressures and temperatures have not been extensively tested.

CONCLUDING REMARKS

In 1983 Schneider (ref. 2) listed several applications in which he claimed "fluid mixtures, especially in the critical and supercritical region, are becoming increasingly important." Since that time there have been both theoretical and experimental developments in the subject. A discussion of the experimental study of liquid-liquid equilibrium has been omitted from this paper. Perhaps the most pressing requirement in this area is for more accurate data. The pioneering work of Francis (ref. 40) has added much to our knowledge of liquid-liquid equilibrium in binary and ternary mixture at or near atmospheric pressure. Several groups have more recently added to our knowledge of the effect of pressure on liquid-liquid equilibrium. However, there are still very significant discrepancies between the data of various workers for liquid-liquid equilibrium both near and above atmospheric pressure for many systems. The work of the liquid-liquid group of the IUPAC Commission V8 has revealed the seriousness of these discrepancies even for systems such as hydrocarbon + water mixtures.

The state of our theoretical development can be summarized by saying we can now predict the critical loci of simple binary systems, such as mixtures of inert gases or mixtures of similar size hydrocarbons with good accuracy (within a few kelvin and a few tenths of a megapascal) using one adjustable parameter. Theoretical description of binary mixtures showing Type III or Type IV behaviour is semi-quantitative at present. However it can be expected that development of equations of state which allow for shape factors and additional non-dispersion forces will lead to a more accurate description of the critical loci and liquid-liquid equilibrium at elevated pressures. This will also require development work on combining rules and equivalent substance prescriptions with a more fundamental basis. The extension of the one fluid model to critical loci of ternary and multicomponent mixtures is in its infancy. At present, even the general phase behaviour type for ternary mixtures (analogous to the six binary types) are not known. As the phase behaviour of ternary mixtures is likely to be much more difficult to study experimentally it would be especially useful to be able to predict the behaviour even if only in a semi-quantitative manner.

REFERENCES


