9 MIXING AND COMBINING RULES

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Equations of state (EOS) are powerful tools in chemical engineering practice since they can be used to correlate and/or predict the thermodynamic properties and phase behavior of pure fluids and mixtures over large ranges of temperature and pressure. However, since there is no exact statistical-mechanical solution relating the properties of dense fluids to their intermolecular potentials, or detailed information available on intermolecular potential functions, all equations of state are, at least partially, empirical in nature. The equations in common use can be classified as being of the van der Waals family of cubic equations, of the extended virial family of equations, or equations based more closely on results from statistical mechanics and computer simulations. Such equations are discussed elsewhere in this book. Here we are concerned with mixing and combining rules that extend the use of equations of state developed for pure fluids to mixtures. There have been many such models proposed in recent years, and we have had to pick and choose among them. We have decided to discuss only those which have stood the test of time, or are reasonably new and appear to be important advances.

One of the exact results we do have from statistical mechanics is the virial equation of state

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + ...$$

(9.1)

where Z is the compressibility factor, P is the pressure, R is the gas constant, T is the temperature, v is the molar volume, and B and C are second and third virial coefficients. The virial coefficients are related to the intermolecular potential between molecules, and for pure fluids they are functions of temperature only. Also, for mixtures the only composition dependence of the virial coefficients is given by

$$B = \sum_i \sum_j x_i x_j B_{ij}(T)$$

(9.2)

$$C = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk}(T), \;\; etc.$$

(9.3)

Since Equations (9.2) and (9.3) are exact results, these equations can be considered low-density boundary conditions that should be satisfied for mixtures by other equations of state when expanded into the virial form.

At present, there is no exact high-density-mixture boundary condition for mixture equations of state. However, there is the observation that, at liquid densities, empirical activity-coefficient models, such as those of van Laar, Wilson, NRTL, UNIQUAC, *etc.* provide a good representation of the excess, or nonideal, part of the energy of mixing. Therefore, another boundary condition that could be imposed is

excess free energy of mixing calculated from an equation of state	=	excess free energy of mixing calculated from an activity-coefficient model	(9.4)

In what follows, we will consider mixing rules for each of the classes of equations of state mentioned above. As we shall see, Equation (9.2) has frequently been used in the formulation of mixing rules for equations of state, Equation (9.3) is used as the basis for mixing rules with extended virial equations of state, and Equation (9.4) has been used to develop equation-of-state mixing rules in recent years.

9.1 MIXING RULES FOR CUBIC AND RELATED EQUATIONS OF STATE

The van der Waals equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{9.5}$$

was the first equation of state that could describe, at least qualitatively, both the vapor and liquid phases, and therefore phase transitions. In this equation the parameter b is a volume-exclusion parameter accounting for the fact that molecules cannot overlap, and the parameter a results from the attraction between molecules. The van der Waals equation has been used as the basis for many other, more accurate equations of state that are also cubic in volume, such as the Peng-Robinson equation (1)

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v-b) + b(v+b)} \tag{9.6}$$

which, because of its volume dependence and the fact that the attraction parameter has been made a function of temperature, provides a more accurate representation of fluid behavior and is widely used in the chemical industry, as is the almost equivalent Soave-Redlich-Kwong (2) equation. The important question that arises is how does one extend these equations (and others) to mixtures.

9.1.1 The Van der Waals One-Fluid Mixing Model

One method of generalizing a pure-fluid equation of state to mixtures is the one-fluid model proposed by van der Waals. The underlying assumption of the van der Waals one-fluid model is that the same equation of state used for pure fluids can be used for mixtures, if a satisfactory way can be found to obtain the EOS parameters for mixtures. The common method for doing this is based on expanding the equation of state in powers of (b/v); for the van der Waals equation one obtains

$$\frac{Pv}{RT} = \sum_{n=0}^{\infty} \left(\frac{b}{v}\right)^n - \frac{a}{RTv} \tag{9.7}$$

To satisfy the boundary condition of Equation (9.2), the composition dependence of a two-parameter cubic equation of state of the van der Waals family must conform to the relation

$$B(T,x) = \sum_i \sum_j x_i x_j B_{ij}(T) = b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \tag{9.8}$$

It should also be noted that

$$C(T,x) = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk}(T) = b^2 \tag{9.9}$$

It is not possible to set a composition dependence of the b parameter to simultaneously satisfy both Equations (9.2) and (9.3).

Until recently, the most common way of choosing mixture parameters was to use the so-called van der Waals one-fluid mixing rules to satisfy only Equation (9.8) with the mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{9.10}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{9.11}$$

The following combining rules are frequently used to obtain the cross coefficients a_{ij} and b_{ij} from the corresponding pure-component parameters:

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \tag{9.12}$$

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj})(1 - \delta_{ij}) \tag{9.13}$$

where k_{ij} and δ_{ij} are the binary-interaction parameters obtained by fitting equation of state predictions to measured phase-equilibrium and volumetric data. Generally δ_{ij} is set to zero, in which case Equation (9.11) reduces to

$$b = \sum_i x_i b_i \tag{9.14}$$

where b_i is the volume parameter for component i (subscript ii and i are used interchangeably in this chapter for pure component parameters depending upon the number of summations in an equation). When fitting vapor-liquid equilibrium (VLE) data, it is found that k_{ij} is approximately zero for relatively ideal mixtures, such as alkane mixtures, whereas for other mixtures, it is not only nonzero but will also change in value with temperature.

There is only a qualitative justification for Equations (9.12) and (9.13). The a parameter is related to attractive forces and, from intermolecular potential theory (3), the parameter in the attractive part of the intermolecular potential for a mixed interaction is given by a relation like Equation (9.12). Similarly, the excluded-volume parameter b would be given by Equation (9.13) if the molecules were hard spheres. However, in general, there is no direct relation between the attractive part of the intermolecular potential and the a parameter in a cubic EOS, and real molecules are not hard spheres. Further, it could be argued that even for the case of

hard spheres it is really the collision diameters that are additive, so that if σ_{ii} is the hard-sphere diameter for species i, then

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right) \quad \text{which implies} \quad b_{ij} = \left(b_{ii}^{1/3} + b_{jj}^{1/3}\right)^3 \tag{9.14b}$$

since the volume is proportional to the third power of the diameter. Conformal solution theory and other molecular-based theories have led to other mixing and/or combining rules for intermolecular-potential parameters and, by analogy, for equation-of-state parameters. But as there is no direct relationship between these two parameter sets, except for the van der Waals equation, there is only a tenuous basis for such mixing rules, and little evidence that they are superior to the van der Waals one-fluid rules.

The shortcoming of the van der Waals one-fluid mixing rules is that they are only applicable to mixtures which exhibit relatively moderate solution nonidealities as seen in Figures 9.1 and 9.2. In Figure 9.1, the Peng-Robinson equation of state, as modified by Stryjek and Vera (4), is shown to represent the vapor-liquid equilibrium behavior of the CO_2 + n-butane system (5) very accurately with a single binary-interaction parameter; but, as seen in Figure 9.2, the VLE data for the acetone + water binary system at 200°C (6) cannot be adequately correlated with a single binary parameter and the van der Waals mixing rule. Why the van der Waals one-fluid mixing rule cannot describe highly nonideal mixtures can be understood by starting with the relation between the molar excess Gibbs energy of mixing, G^{ex}, and fugacity coefficients obtained from an equation of state:

$$G^{ex} = RT\left[\ln\varphi - \sum_i x_i \ln\varphi_i\right] \tag{9.15}$$

where φ and φ_i are the fugacity coefficients of the solution and of the pure component i calculated, using the mixture and pure component parameters, respectively, from the equation

$$\ln\varphi = \ln\left(\frac{f(T,P)}{P}\right) = \frac{1}{RT}\int_{\infty}^{v}\left(\frac{RT}{v} - P\right)dv - \ln Z + (Z-1) \tag{9.16}$$

For the van der Waals cubic EOS this leads to the following expression for the excess Gibbs energy of a binary mixture:

$$\frac{G^{ex}}{RT} = \ln\left(\frac{P}{RT}\prod_{i=1}^{2}\frac{\left(\frac{RT}{P} - b_{ii}\right)^{x_i}}{\left(\frac{RT}{P} - b\right)}\right) - \frac{x_1 x_2}{RT\left(x_1 b_{11} + x_2 b_{22}\right)}\left(\sqrt{\frac{a_{11}b_{22}}{b_{11}}} - \sqrt{\frac{a_{22}b_{11}}{b_{22}}}\right)^2 \tag{9.17}$$

$$+ \frac{2x_1 x_2 \sqrt{a_{11}a_{22}}\left(1 - k_{12}\right)}{x_1 b_{11} + x_2 b_{22}}$$

This equation shows that the excess Gibbs energy, computed from a van der Waals-family cubic EOS and one-fluid mixing rules, contains three contributions. The first, which is the Flory free-volume term, comes from the hard-core repulsion terms and is completely entropic in nature. The second term is very similar to the excess Gibbs-energy term in regular-solution theory, and the third term is similar to a term that appears in augmented regular-solution theory (7). As a result the combination of a cubic EOS with the van der Waals mixing rules can only represent those mixtures that have a moderate degree of solution nonideality describable by augmented regular-solution theory. Many mixtures of industrial interest have a much greater
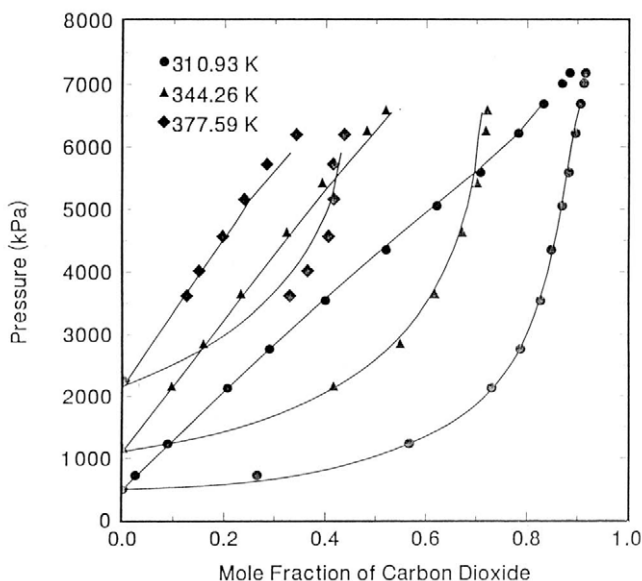

Figure 9.1 Correlation of carbon dioxide + n-butane vapor-liquid equilibrium data of reference 5 (points) with the modified Peng-Robinson equation of state [see reference 4] and with the van der Waals one-fluid mixing rules with a single binary-interaction parameter.

degree of solution nonideality and therefore require different mixing rules.

One misconception that has occurred in the use of the van der Waals one-fluid mixing rule is that setting the binary-interaction parameter k_{12} equal to zero results in an ideal solution. Equation (9.17) clearly shows that this is not the case since, even with $k_{12}=0$, G^{ex} is not equal to zero; indeed none of the three terms in the equation vanish. Also, as shown in Figure 9.2, setting $k_{12}=0$ for a mixture of very different components such as acetone and water not only does not produce an ideal solution, but can lead to unrealistic phase-behavior predictions. Therefore, a value of zero is not always the best choice of a default guess for k_{12} in the absence of experimental data.
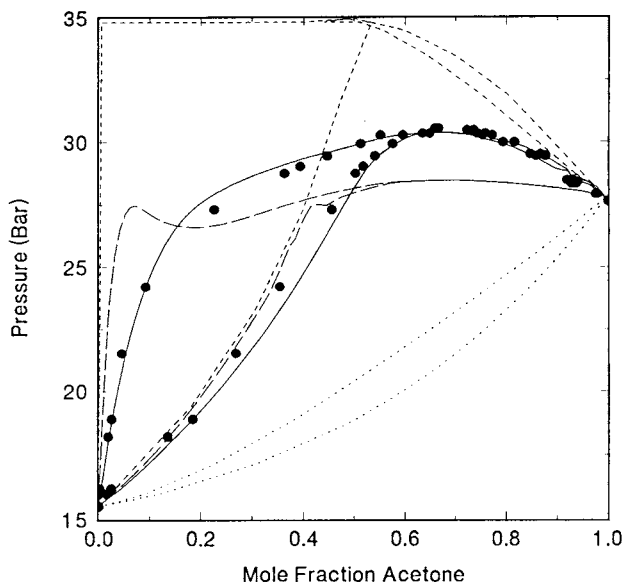
Figure 9.2 Correlation of acetone + water vapor-liquid equilibrium data of reference 6 (points) at 200°C with the modified Peng-Robinson equation of state. The solid lines are correlations with the Huron-Vidal mixing rule, the long and short dashed lines are correlations with the van der Waals one-fluid mixing rule with a single binary interaction parameter fit to experimental data, and set to zero, respectively. The dotted lines result from the Wong-Sandler mixing rule with all model parameters set to zero (see last paragraph of Section 9.1.3.2 for explanation).

9.1.2 Non-Quadratic Combining Rules for Van der Waals One-Fluid Model

One empirical approach to eliminate the shortcomings of the van der Waals one-fluid model for a cubic EOS has been to provide additional composition dependence by adding parameters to the combining rule for the a parameter, generally leaving the b-parameter rule unchanged. Some examples are the combining rules of Panagiotopoulos and Reid (8)

$$k_{ij} = K_{ij} - \left(K_{ij} - K_{ji} \right) x_i \tag{9.18}$$

Adachi and Sugie (9)

$$k_{ij} = K_{ij} + l_{ij} \left(x_i - x_j \right) \tag{9.19}$$

Sandoval *et al.* (10),

$$k_{ij} = K_{ij} x_i + K_{ji} x_i + 0.5 \left(K_{ij} + K_{ji} \right) \left(1 - x_i - x_j \right) \tag{9.20}$$

and Schwartzentruber and Renon (11,12)

$$k_{ij} = K_{ij} + l_{ij} \frac{m_{ij}x_i - m_{ji}x_j}{m_{ij}x_i + m_{ji}x_j}\left(x_i + x_j\right)$$ (9.21)

where in the last equation $K_{ij} = K_{ji}$, $l_{ji} = l_{ij}$, $m_{ji} = 1\text{-}m_{ij}$ and $K_{ii} = l_{ii} = 0$. It should be pointed out that these combining rules do not satisfy any of the boundary conditions given by Equations (9.2) to (9.4). By an appropriate choice of parameters, these combining rules reduce to one another, and to Equation (9.12), and they have been shown to provide good correlations of vapor-liquid equilibrium data for complex binary mixtures, including highly nonideal systems that previously could be correlated only with activity-coefficient models. An example is given in Figure 9.3, where it is seen that the VLE for the ethanol + heptane system at 60°C (5) can be correlated with the two-parameter Adachi-Sugie combining rule much better than with the single-parameter van der Waals mixing rule.

The relationship between an activity coefficient and the fugacity coefficients from an EOS is

$$\gamma_i = \left[\hat{\varphi}_i(T,P,\pmb{x})/\varphi_i(T,P)\right]$$ (9.22)

where $\hat{\varphi}_i(T,P,\pmb{x})$ is the fugacity coefficient of species i in a mixture and $\varphi_i(T,P)$ is the pure-component fugacity coefficient, both obtained from the EOS. Consequently, the two interaction parameters per binary system, in the class of combining rules being considered here, can be related to activity coefficients over the whole composition range or to the values at a specified composition, such as the two infinite-dilution activity coefficients of a mixture, (12,13,14) thus eliminating the need for VLE data over the whole composition range. In this latter case one writes Equation (9.22) at the two infinite-dilution limits, obtaining two equations for the two parameters in Equations (9.18) to (9.21), in terms of the pure-component EOS parameters and infinite-dilution activity coefficients. In this case it is possible to predict the phase behavior of some highly nonideal systems successfully using only infinite-dilution activity-coefficient information.

However, there are several problems associated with these multiparameter combining rules that limit their use. One is that, due to added composition dependence in the a parameter, this group of combining rules fails to satisfy the theoretical quadratic composition dependence of the second virial coefficient given in Equation (9.2). This fact is usually ignored on the grounds that pure-component second virial coefficients calculated from a cubic EOS are in poor agreement with experimental data. However, the equation for the fugacity coefficient of a species in a mixture,

$$\ln\hat{\varphi}_i = \frac{1}{RT}\int_{V=\infty}^{V}\left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right]dV - \ln Z$$ (9.23)

where N_i is the mole number of species i in the mixture and V is the total volume, shows that the evaluation of the fugacity coefficient from the equation of state involves an integral of a
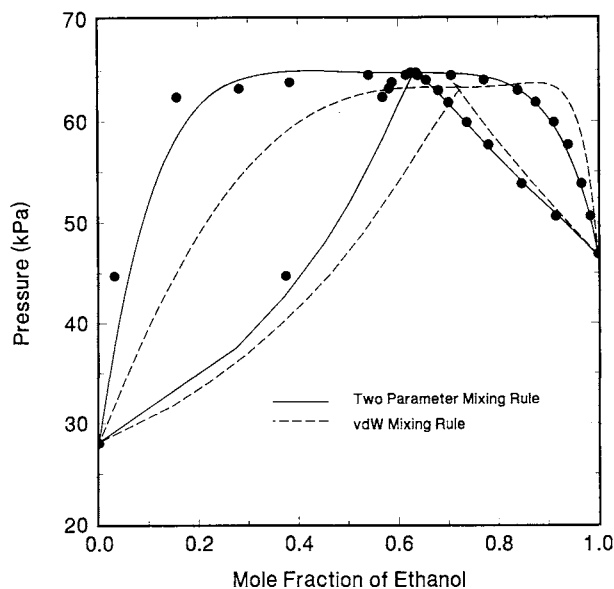
Figure 9.3 Correlation of ethanol + n-heptane vapor-liquid equilibrium data of reference 5 (points) at 60°C with the modified Peng-Robinson equation of state. The solid lines are correlations with the two parameter Adachi-Sugie (9) mixing rule and the dashed lines are correlations with van der Waals one-fluid mixing rule with a single binary-interaction parameter.

term that includes a partial derivative with respect to composition from zero density to the density of interest. Therefore, an error in the composition dependence of the equation of state at low densities will affect the fugacity coefficient calculated from Equation (9.23) at all densities. It should be stressed that the correct composition dependence of the mixture second virial coefficient and accurate values of pure-component second virial coefficients are two different problems, and both will affect the computed fugacity coefficient. Models that have the correct second-virial composition dependence eliminate one of these sources of error.

A second difficulty associated with mixing rules in this category, as pointed out by Michelsen and Kistenmacher (15), is that they do not result in the correct treatment of multicomponent mixtures containing two or more very similar components. To see this, consider a mixture of three components, and for the sake of demonstration allow two of these components, such as 2 and 3, to become identical. (This is not a trivial thought experiment, as there are multicomponent mixtures of industrial interest in which two or more components have very similar EOS parameters, for example, the isomers 1-methyl-naphthalene and 2-methyl-naphthalene.) In this case, to be internally consistent, the mixing rule for the parameter a should reduce to that for a binary mixture with the composition (x_2+x_3) for the new component 2+3. The one-fluid mixing/combining rule of van der Waals satisfies this test, whereas the group of combining rules being considered here does not.

Yet another problem with Equations (9.18) to (9.21) is the so-called dilution effect, which refers to the fact that as the number of components in a mixture increases, mole fractions of individual components in the system become smaller. This leads to smaller contributions from the terms with the higher-order composition dependence and the added parameter(s), thus effectively reducing the mixing rule to the quadratic one-fluid mixing rule of van der Waals as the number of components in the mixture increases.

9.1.3 Mixing Rules that Combine an Equation of State with an Activity-Coefficient Model

Many mixtures of interest in the chemical industry exhibit strong nonideality, greater nonideality than results from regular-solution theory, and have traditionally been described by activity-coefficient (or excess Gibbs energy) models for the liquid phase, and an equation of state model for the vapor phase. However, there are numerous problems with the activity-coefficient description. For example, there are difficulties in defining standard states especially for supercritical components, the parameters in these models are very temperature dependent, and since a different model is used for the vapor and liquid phases critical phenomena are not predicted. Also other thermodynamic properties (densities, enthalpies, entropies, etc.) cannot be obtained from the same model. Therefore, there has been interest in mixture equation-of-state models that are capable of describing greater degrees of nonideality than is possible with the van der Waals one-fluid model.

9.1.3.1 The Huron-Vidal Model

Vidal (16) and later Huron and Vidal (17) proposed the first successful combination of equations of state and activity-coefficient models by using Equation (9.4) in the following form

$$G_\gamma^{ex}\left(T, P=\infty, x\right) = G_{EOS}^{ex}\left(T, P=\infty, x\right) \tag{9.24}$$

where $G_\gamma^{ex}(T, P=\infty, x)$ and $G_{EOS}^{ex}(T, P=\infty, x)$ are the excess Gibbs energies at infinite pressure (i.e., at liquid-like densities) calculated from an activity-coefficient model and the equation of state, respectively. Since $G^{ex}=A^{ex}+Pv^{ex}$, A^{ex} in the liquid state is almost independent of pressure, and at infinite pressure from an equation of state, $v_i=b_i$, in order to use Equation (9.24) it is necessary that

$$v^{ex} = v - \sum_i x_i v_i = b - \sum_i x_i b_i = 0 \tag{9.25}$$

That is, to use Equation (9.24), Equation (9.14) must also be used. This provides the two equations necessary to determine the two EOS parameters. The resulting mixing rule for the a parameter, then, is

$$a = b\left[\sum_i x_i\left(\frac{a_i}{b_i}\right) - CG^{ex}\right] \tag{9.26}$$
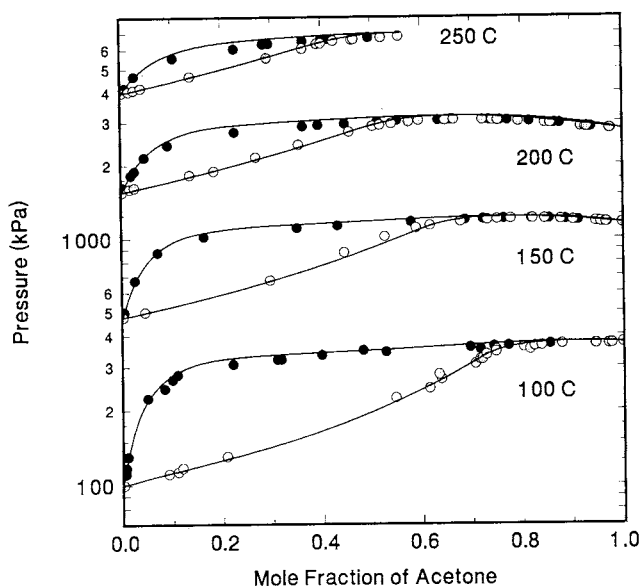
Figure 9.4 Correlation of acetone + water vapor-liquid equilibrium data of reference 6 (points) with the modified Peng-Robinson equation of state. The solid lines are correlations with the Huron-Vidal mixing rule and the NRTL excess energy model. Note that different parameters are used for each isotherm.

where C is a numerical constant that depends on the particular EOS used, and G^{ex} is an excess Gibbs energy of mixing expression appropriate for the mixture of interest.

This mixing model has been successful for describing the VLE of highly nonideal systems. An example is shown in Figure 9.4 for the VLE of the acetone + water system (6) in which the three-parameter NRTL activity-coefficient model was used for G^{ex}. However, each of the isotherms in this figure were calculated with a different set of parameters (i.e. three parameters have been fit to each isotherm). Also, none of the parameter sets are the same as those reported in the DECHEMA Chemistry Data Series (5) where this same activity-coefficient model is used to correlate the data directly.

However, there are several theoretical and computational difficulties associated with the Huron-Vidal mixing rule. For example, this mixing rule has not been successful in describing nonpolar hydrocarbon mixtures. Also this mixing rule does not satisfy the quadratic composition dependence required by the boundary condition of Equation (9.2). Further, as already mentioned, even though the Huron-Vidal approach allows the use of G^{ex} models with an EOS, the parameters are not the same as those obtained when correlating data directly with the activity-coefficient model. Consequently, one cannot use parameter tables (for example, the DECHEMA Chemistry Data Series) developed for excess Gibbs-energy models at low pressure with this equation of state model. The reason for this is that the excess Gibbs energy of mixing, both from experiment and as calculated with an equation of state, is very pressure dependent as seen in Figure 9.5 for the methanol + benzene system at 373 K. Therefore, the
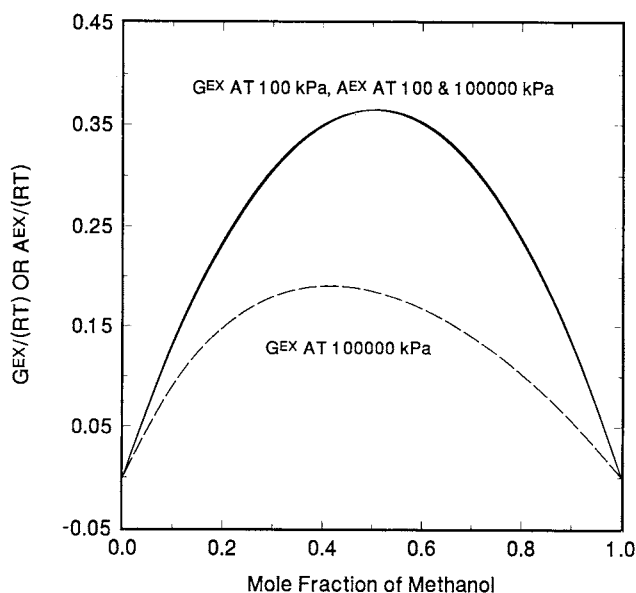
Figure 9.5 The excess Gibbs and Helmholtz energies of mixing for the methanol + benzene mixture at 1 bar and 1000 bar calculated from the modified Peng-Robinson equation of state and the Wong-Sandler mixing rule.

excess Gibbs energies at infinite pressure and at the pressure at which experimental data were obtained can be very different. Finally, the G^{ex} parameters in this model are very temperature dependent, so that while the model can be useful for correlation, it has little extrapolative or predictive capability.

9.1.3.2 Wong-Sandler Model

Wong and Sandler (18) have developed a mixing rule that combines an equation of state with an excess Gibbs energy model but produces the desired EOS behavior at both low and high densities without being density dependent, uses existing G^{ex} tables, allows extrapolation over wide ranges of temperature and pressure, and provides a conceptually simple method of accurately extending UNIFAC or other low-pressure VLE prediction methods to high temperature and pressure. This mixing rule is based on several observations. First, while Equations (9.10) and (9.11) are sufficient conditions to ensure the proper composition dependence of the second virial coefficient, they are not unique. In particular, the van der Waals one-fluid mixing rules of Equations (9.10) and (9.11) place constraints on the two functions a and b to satisfy the single relation

$$B(x_i, T) = \sum \sum x_i x_j B_{ij}(T) = \sum \sum x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right) = b - \frac{a}{RT} \tag{9.27}$$

The original version of the Wong-Sandler mixing rule uses the last equality above as one of the restrictions on the parameters, together with the combining rule

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_{ii} - \frac{a_{ii}}{RT} \right) + \left(b_{jj} - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij}) \tag{9.28}$$

which introduces a second-virial-coefficient binary-interaction parameter k_{ij}. Note that Equation (9.27) does not provide relations for the parameters a and b separately, but only for the sum $b-a/RT$, so that an additional equation is needed. Also, by using Equation (9.27) as one of the relations to determine the equation of state parameters, the proper composition dependence of the second virial coefficient is assured, regardless of which additional equation is used.

The second equation in their mixing rule is based on the observation that the excess Helmholtz energy of mixing is relatively insensitive to pressure as can be seen in Figure 9.5. Consequently to an excellent approximation:

$$G^{ex}(T, P = 1\,\text{bar}, x) = A^{ex}(T, P = 1\,\text{bar}, x) = A^{ex}(T, \text{high pressure}, x) \tag{9.29}$$

The first of these equalities follows from the fact that $G^{ex}=A^{ex} + Pv^{ex}$, and that the Pv^{ex} term is very small at low pressures. The second of these equalities is a result of the essential pressure independence of A^{ex} at liquid densities. Therefore, the second equation for the a and b parameters comes from Equation (9.4) in the form of

$$A_{EOS}^{ex}(T, P = \infty, x) = A_\gamma^{ex}(T, P = \infty, x) = A_\gamma^{ex}(T, \text{low } P, x) = G_\gamma^{ex}(T, \text{low } P, x) \tag{9.30}$$

where subscript γ refers to a property obtained from an excess-energy model. Combining Equations (9.27) and (9.30) gives the following mixing rules

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \tag{9.31}$$

and

$$\frac{G_\gamma^{ex}}{CRT} = \frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT} \tag{9.32}$$

where the cross term in Equation (9.31) is obtained from Equation (9.28), and any excess Gibbs-energy model may be used in Equation (9.32).

This EOS/activity-coefficient-model mixing rule combination satisfies the low-density boundary condition that the second virial coefficient is quadratic in composition, and the high-density condition of producing an excess Gibbs energy like that produced by currently used

activity-coefficient models, while the mixing rule itself is independent of density. This model provides a more correct alternative to earlier *ad-hoc* density-dependent mixing rules (19,20,21) that violate the one-fluid model in that the equations of state for pure fluids and mixtures have different density dependencies. This mixing rule has been successful in a number of ways. First, when combined with any cubic EOS that gives the correct saturation pressures for organic chemicals and an appropriate activity-coefficient model for the G^{ex} term, it has been shown to lead to excellent correlations of vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibria. Indeed, these correlations are generally comparable to those obtained when the same activity-coefficient models are used directly (5). Consequently, this new mixing rule extends the range of application of equations of state to mixtures that previously could be correlated only with activity-coefficient models.

Second, since low-pressure G^{ex} information has been used in developing this mixing rule, Wong *et al.* (22) found that activity-coefficient parameters reported in databanks, such as the DECHEMA Data Series (5), could be used directly and with good accuracy in the new mixing rule without the need of refitting experimental data. Further, they found that, as a result of the inherent temperature dependence in equations of state, the parameters in the excess-Gibbs-energy model used in the EOS mixing rule were much less temperature dependent than when the same excess-energy model was used directly. In fact, for many mixtures the Gibbs-energy-model parameters in the EOS could be taken to be independent of temperature, thereby allowing extrapolation of phase behavior over wide ranges of temperature and pressure. This is shown in Figure 9.6 for the system ethanol + water (23), where activity-coefficient-model
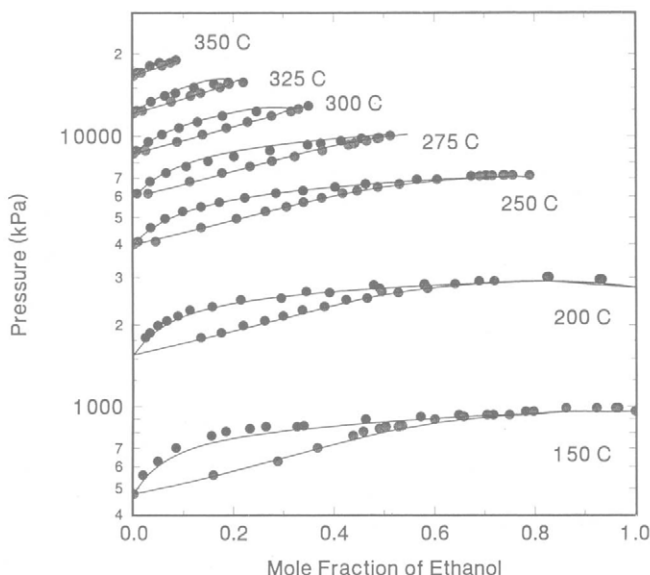

Figure 9.6 Predictions of the vapor-liquid equilibrium for the ethanol + water system with the modified Peng-Robinson equation of state and the Wong-Sandler mixing rule with temperature-independent parameters (22). The experimental data shown as points are from reference 23.

parameters reported in the DECHEMA Chemistry Data Series (5) at 4 bar are seen to lead to excellent predictions up to 200 bars. A third observation is that, since this mixing rule uses information at low pressure, it can also be used to make predictions at high pressure based on low-pressure prediction techniques, such as UNIFAC and other group contribution methods (24). This is demonstrated in Figure 9.7 for the n-pentane + ethanol (25) binary system, where the UNIFAC predictions at 20°C are shown as dashed lines, and the solid line shows the predictions using the Wong-Sandler mixing rule fitted to UNIFAC predictions. The remaining solid lines are the extrapolations of this model to higher temperatures and pressures with temperature-independent UNIQUAC parameters. The predictions at temperatures of 373 K and 423 K are seen to be in excellent agreement with the experimental data.
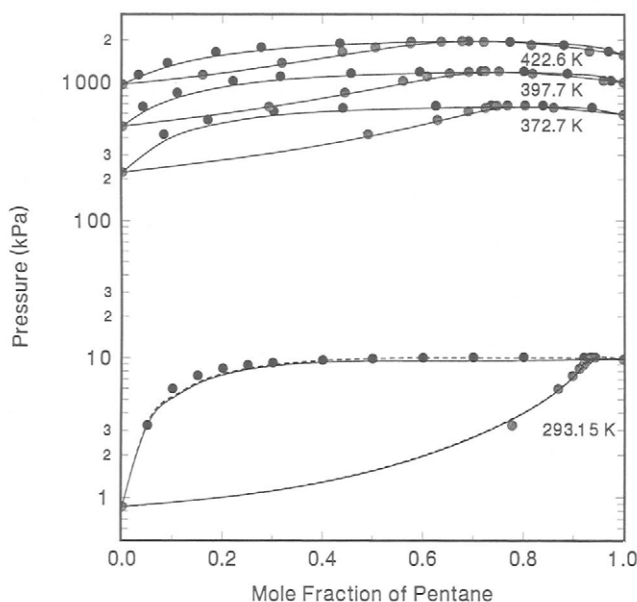

Figure 9.7 Prediction of the vapor-liquid equilibrium for the n-pentane + ethanol system with the modified Peng-Robinson equation of state and the Wong-Sandler mixing rule with parameters obtained from low-pressure predictions of the UNIFAC model (24). The dashed lines are predictions based on the UNIFAC activity-coefficient model at 293 K, and the points are experimental data (25).

A desirable characteristic of an excess-energy-based mixing rule is that it converges smoothly to the conventional van der Waals one-fluid mixing rules for some values of its parameters. This is useful because in multicomponent mixtures it may occur that only some of the binary pairs form highly nonideal mixtures requiring mixing rules such as those described in this section, while other binary pairs in the same mixture can be adequately described by use of Equations (9.10) and (9.11). Orbey and Sandler (26) have recently shown that, by a slight reformulation of the Wong-Sandler mixing rule, convergence to the van der Waals one-fluid mixing rules can be accomplished. They did this by retaining the mixing rule of Equations (9.31) and (9.32), but replacing the combining rule of Equation (9.28) by

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}(b_i + b_j) - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \tag{9.33}$$

This introduces the binary interaction parameter in a manner similar to that in Equation (9.12) of the van der Waals one-fluid mixing rule. Next the following modified form of the NRTL equation was used for the excess-Gibbs-energy term:

$$\frac{G^{ex}}{RT} = \sum_i x_i \left[\frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \right] \tag{9.34}$$

with

$$G_{ji} = b_j \exp(-\alpha \tau_{ji}) \tag{9.35}$$

where b_j is the volume parameter in the equation of state for species j. This modified NRTL form was suggested earlier by Huron and Vidal (17) for use in their model.

For binary mixtures there are four dimensionless parameters in the above equations, α, τ_{12}, τ_{21} and k_{12}. This mixing rule can be used as a four-parameter model to correlate the behavior of complex mixtures, or in a number of other ways that have fewer adjustable parameters. For example, for selected values of α and k_{12}, one can solve Equation (9.34) in the infinite-dilution limit for τ_{21} as

$$\tau_{21} = \ln \gamma_{12}^\infty - \tau_{12} \frac{b_1}{b_2} \exp(-\alpha \tau_{12}) \tag{9.36}$$

where γ_{12}^∞ is the infinite-dilution activity coefficient of species 1 in 2. A similar relation for τ_{12} is obtained by index rotation. In fact, Orbey and Sandler (26) found that setting α=0.1 and k_{12}=0 worked quite well for several nonideal mixtures of organic chemicals, so that one could use the model to predict the complete phase behavior over large ranges of temperature and pressure from infinite-dilution activity coefficients at a single temperature. This model could also be used in a completely predictive fashion, in the absence of any experimental data, with infinite-dilution activity coefficients obtained from the UNIFAC model. Various forms of this reformulated Wong-Sandler mixing rule have been shown to be successful for highly nonideal binary mixtures. An example is shown in Figure 9.8 for the 2-propanol + water binary mixture. Also, by setting α=0 and solving for τ_{21} from

$$\tau_{21} = \frac{C}{RT} \left[\frac{2\sqrt{a_1 a_2}}{b_1 + b_2}(1 - k_{12}) - \frac{a_1}{b_1} \right] \tag{9.37}$$

(τ_{12} is obtained by index rotation) one recovers the van der Waals one-fluid mixing rule with a single binary-interaction parameter k_{12} that can be used for the slightly nonideal binary pairs in a multicomponent mixture. It should be noted that Equation (9.37) is not unique, and other expressions that lead to the van der Waals mixing rules are possible (26).
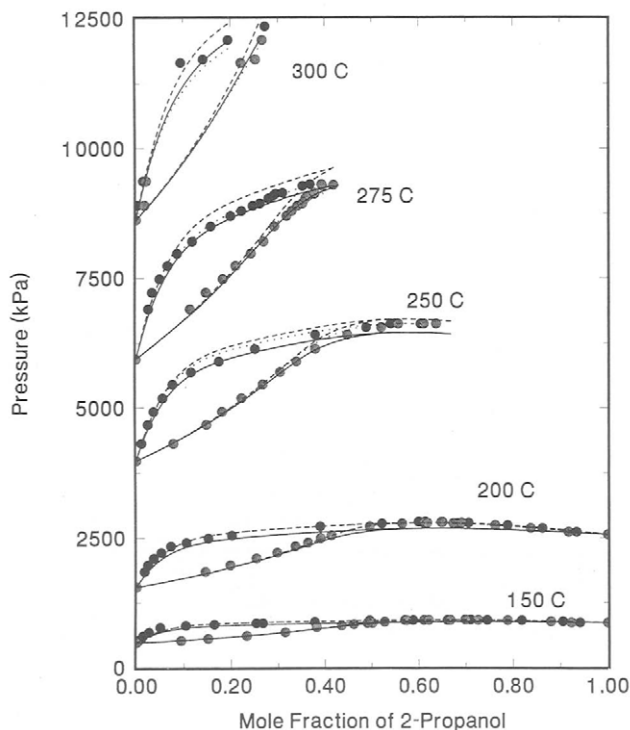
Figure 9.8 Predictions of the vapor-liquid equilibrium for the 2-propanol + water system with the reformulated Wong-Sandler mixing rule and the modified Peng-Robinson equation of state. The solid lines are predictions made with parameters determined from infinite-dilution activity coefficients predicted with the UNIFAC model, the dashed lines are predictions with parameters from the correlation of the lowest temperature isotherm, and the dotted lines are correlations with parameters obtained by correlating each isotherm separately (26). The experimental data (points) are from reference 23.

The correlative capabilities of the Wong-Sandler mixing rule have also been investigated for systems for which no equation-of-state model worked very well. One example is correlation of the vapor-liquid equilibrium of polymer-solvent systems which is important for the design of solvent devolatilization processes. Mixtures of ethylene and long-chain alkanes can be considered as prototypes for low-molecular-weight polymers in supercritical solvents. Such systems were recently studied by Orbey and Sandler (27) by coupling the Wong-Sandler mixing rule with the Flory-Huggins model for the excess Gibbs energy. A three-parameter correlation of data for the ethylene + n-tetracontane system (28) to the critical point of that mixture by this approach is shown in Figure 9.9.
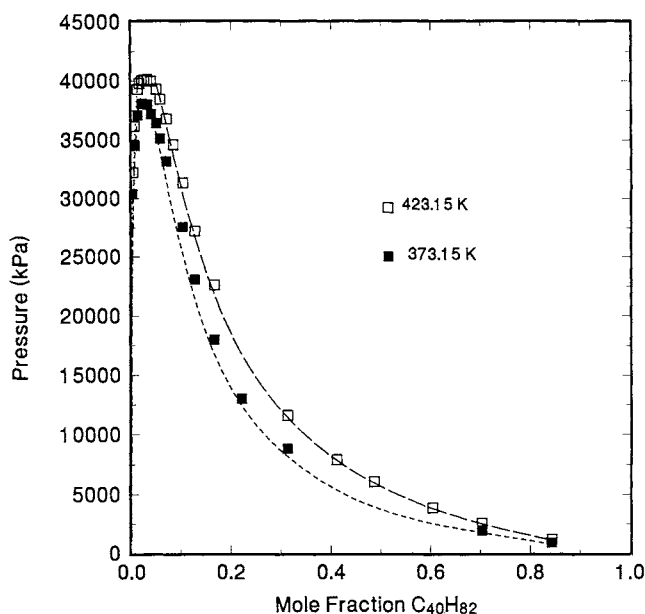
Figure 9.9 Partial pressure of ethylene in n-tetracontane. The lines are the result of a three-parameter correlation obtained with the Peng-Robinson equation of state and the Wong-Sandler mixing rule (27), and the experimental data (points) are from reference 28.

This mixing rule has also been applied to hydrogen + hydrocarbon mixtures (29). However, in this case there can be a problem, depending on the temperature, if the conventional temperature dependence is used for the parameter a of the equation of state. This arises from the fact that the temperature-dependent a term in cubic equations of state is usually obtained by fitting vapor pressure and other subcritical data, and consequently is poorly defined at high reduced temperatures. As discussed in Chapter 4, several different temperature functions have been proposed. Some of these temperature functions, including the ones originally proposed for the Peng-Robinson and Soave-Redlich-Kwong equations, lead to the following problem in the Wong-Sandler mixing rule with hydrogen due to its low critical temperature and with other asymmetric mixtures containing very light components. The b parameter in this mixing model is, from Equations (9.31) and (9.32)

$$b = \frac{\sum\sum x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right)}{1 - \left[\sum x_i \frac{a_i}{b_i RT} + \frac{G_{\gamma}^{ex}}{CRT} \right]} \tag{9.38}$$

The denominator of this equation contains three terms. The excess Gibbs-energy term can be negative or positive, and should vanish at high temperatures. For simplicity this term is neglected in the discussion here. In this case, unless the (a_i/b_iRT) term is larger than unity for all the components of the mixture, there will be a composition of the (liquid or gas) mixture at which the denominator becomes zero or even changes sign from negative to positive. The first of these is theoretically not allowed because of the discontinuity that results in the value of b of the mixture, the second case is not allowed because it leads to meaningless negative values for the b parameter. To avoid this, it is necessary at all temperatures to have

$$b_i - \frac{a_i}{RT} < 0 \tag{9.39}$$

for all the components of the mixture, which ensures that the (a_i/b_iRT) term is always larger than unity. For cubic equations of state this term can be written in a generalized form; for example, for the Peng-Robinson equation of state

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T)$$

$$b = 0.0778 \frac{RT_c}{P_c} \tag{9.40}$$

$$\frac{a}{bRT} = \left(\frac{0.45724}{0.0778}\right) \frac{\alpha(T)}{T_r} = 5.87712 \left(\frac{\alpha(T)}{T_r}\right)$$

where subscript c denotes the critical property, $T_r = T/T_c$, and $\alpha(T)$ is the temperature-dependent generalized function specific to each EOS. Thus the requirement of Equation (9.39) becomes $\alpha(T) \geq T_r/5.87712$ for the Peng-Robinson equation of state. For most cubic equations of state at reduced temperatures below 2 this requirement is met but, depending upon the temperature dependence of $\alpha(T)$, may not be satisfied at higher reduced temperatures. A simple solution for mixtures with one or more highly supercritical components is to use the equation $\alpha(T) = T_r/M$ for the highly supercritical component, with M being an EOS-dependent constant, for example 5.87712 for the Peng-Robinson EOS. This removes the singularity, and does not cause any problems or inaccuracies in the calculation of phase behavior or thermodynamic properties.

One final observation, setting G^{ex} equal to zero in the Wong-Sandler mixing rule does lead to the prediction of almost ideal solution behavior, as shown in Figure 9.2 for the acetone + water system. The predictions in this figure are to be compared with the unrealistic results of setting $k_{12} = 0$ in the van der Waals one-fluid model, also shown in that figure. A conclusion that can be drawn from this figure is that, while using a default value of G^{ex} equal to zero in the Wong-Sandler mixing rule may not lead to accurate predictions, it will not result in unphysical predictions that could cause difficulties in process simulations.

9.1.3.3 Combination of Excess-Energy Models and Equations of State at Low or Zero Pressure

The problem with the Huron-Vidal model, which results from the pressure dependence of the excess Gibbs energy of mixing, has led a number of modifications based on the idea of equating the excess Gibbs energies of mixing from an equation of state and from an activity-coefficient model at low (or zero) pressures, as originally suggested by Mollerup (30). For example, in developing the UNIWAALS equation, Gupte *et al.* (31) used the combination of Equations (9.4) and (9.14) at the experimental pressure. However, this approach has the disadvantages of not satisfying the second-virial-coefficient boundary condition, and having to solve the volumetric equation of state for the liquid density three times for each step in the iterative solution of a phase-behavior calculation for a binary mixture, first for each of the two pure components, and then for the mixture.

Another complication that arises with this method and, in fact, with most finite-pressure combinations of equations of state and activity-coefficient models, is that there may not be a liquid-density solution for one or more of the pure components at the temperature and pressure of the mixture. This either restricts the method to mixtures in which all the pure components are liquids at the temperature and pressure of interest, or requires some sort of extrapolation technique. Further, there is an essential inconsistency in this method in that it produces mixture-equation of state parameters that are functions of pressure (or density). Consequently, when applying the same equation of state to both the pure fluids and their mixture, the volumetric dependence of the equation of state for the mixture is different from that for the pure fluids due to the implicit pressure dependence of the mixture parameters. Gani *et al.* (32) eliminated some of these problems, however, the computational aspects of the resulting model remain too complex for routine use.

To eliminate, or at least simplify, the problem of requiring multiple solutions of the equation of state, most other modifications of the Huron-Vidal mixing rule have made the connection between G_γ^{ex} and G_{EOS}^{ex} at a fixed pressure, usually at zero pressure. Before analyzing these models, several general comments need to be made. The starting point for combining excess-energy and equation of state models is, for the case of the excess Gibbs energy of mixing,

$$\frac{G_{EOS}^{ex}(T,P,x)}{RT} = \ln\phi_{mix}(T,P,x) - \sum_i x_i \ln\phi_i(T,P)$$

$$= \left(Z_{mix}(T,P,x) - \sum_i x_i Z_i(T,P) \right) - \left(\ln Z_{mix}(T,P,x) - \sum_i x_i \ln Z_i(T,P) \right) \qquad (9.41)$$

$$- \left[\int_\infty^{v_{mix}(T,P,x)} \frac{Z_{mix}-1}{v_{mix}} dv_{mix} - \sum_i x_i \int_\infty^{v_i(T,P)} \frac{Z_i-1}{v_i} dv_i \right]$$

and equivalently, for the excess Helmholtz energy of mixing,

$$\frac{A_{EOS}^{ex}(T,P,x)}{RT} = -\left(\sum_i x_i \ln \frac{Z_{mix}(T,P,x)}{Z_i(T,P)} \right) - \left[\int_\infty^{v_{mix}(T,P,x)} \frac{Z_{mix}-1}{v_{mix}} dv_{mix} - \sum_i x_i \int_\infty^{v(T,P_i)} \frac{Z_i-1}{v_i} dv_i \right] \qquad (9.42)$$

From the conventional definition of an excess-property change on mixing, it is necessary that the pure components and the mixture be in the same state of aggregation. It is obvious from these equations that the excess Gibbs or Helmholtz free energies of mixing computed from an equation of state is a function of pressure, whereas activity-coefficient models are independent of pressure or density. Therefore, the equality between G^{ex} (or A^{ex}) from an equation of state and from an activity-coefficient model can be made at only a single pressure. Models that combine equations of state and activity-coefficient models can be categorized into two groups: those that make this link at infinite pressure, such as the models discussed in the previous section, and those that make this connection at low or zero pressure. Here we are concerned with the latter group.

For van der Waals-type cubic equations, Equations (9.41) and (9.42) take the form

$$\frac{G^{ex}_{EOS}}{RT} = Z_{mix} - \sum_i x_i Z_i - \sum_i x_i \ln\left(\frac{Z_{mix}}{Z_i}\right) - \sum_i x_i \ln\left[\frac{1-\dfrac{b_{mix}}{v_{mix}}}{1-\dfrac{b_i}{v_i}}\right] +$$

$$\left(\frac{a_{mix}}{b_{mix}RT}\right)C(v_{mix}) - \sum_i x_i\left(\frac{a_i}{b_iRT}\right)C(v_i) \tag{9.43}$$

and

$$\frac{A^{ex}_{EOS}}{RT} = -\sum_i x_i \ln\left(\frac{Z_{mix}}{Z_i}\right) - \sum_i x_i \ln\left[\frac{1-\dfrac{b_{mix}}{v_{mix}}}{1-\dfrac{b_i}{v_i}}\right] + \left(\frac{a_{mix}}{b_{mix}RT}\right)C(v_{mix}) - \sum_i x_i\left(\frac{a_i}{b_iRT}\right)C(v_i) \tag{9.44}$$

Here $C(v)$ is a molar volume-dependent function specific to the EOS chosen; for the Peng-Robinson equation $C(v) = 1/(2\sqrt{2})\ln\{(v+(1-\sqrt{2})b)/(v+(1+\sqrt{2})b)\}$. For later reference we note that, in the limit of infinite pressure, $v_i \to b_i$ and $v_{mix} \to b_{mix}$ [so that $(v_{mix}=b_{mix})=C(v_i=b_i)=C^*$, and for the Peng-Robinson equation $C^* = [\ln(\sqrt{2}-1)]/\sqrt{2} = -0.62323$].

The modified Huron-Vidal mixing rule of Michelsen (33,34) is the most used of the category of mixing rules discussed in this section. Its basis is to use Equation (9.43) at $P=0$ to obtain

$$\frac{G^{ex}_{EOS}(P=0)}{RT} = -\sum_i x_i \ln\left(\frac{v^o_{mix}-b_{mix}}{v^o_i-b_i}\right) - \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right) + \left(\frac{a_{mix}}{b_{mix}RT}\right)C(v^o_{mix}) - \sum_i x_i\left(\frac{a_i}{b_iRT}\right)C(v^o_i) \tag{9.45}$$

which, to look more like the Michelsen expression, can be rewritten as

$$q\{\alpha_{mix}\} = \sum_i x_i q\{\alpha_i\} + \frac{G^{ex}_\gamma(T,P=0,x)}{RT} + \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right) \tag{9.46}$$

with

$$q\{\alpha\} = -\ln\left(\frac{v(T,P=0)}{b} - 1\right) + \frac{a}{bRT}C(v^\circ)$$ (9.47)

In Equations (9.46) and (9.47), the notation $q\{\alpha\}$ is being used to indicate that q is a function of $\alpha = a/bRT$. These equations use one of the degrees of freedom in choosing the mixture-equation of state parameters. The second equation that is used to define the mixing rule completely is Equation (9.14). However, it should be noted that since it is no longer necessary to be concerned with the divergence of the excess Gibbs energy at infinite pressure, it is not necessary to impose Equation (9.14); other choices, such as the last equality of Equation (9.27), could be used as well.

A problem that arises with this and other versions of the zero-pressure mixing rules is what to do at temperatures when there is no liquid root to the equation of state for some of the pure components or the mixture. Michelsen (33) eliminated this problem by choosing a cut-off value of α, α_{cutoff}, for which a liquid root exists, and for smaller values of α using the linear extrapolation

$$q(\alpha) = q_0 + q_1\alpha$$ (9.48a)

It was then suggested that Equation (9.48a) be used for all values of α, resulting in Equation (9.46) being replaced by

$$\alpha_{mix} = \sum_i x_i\alpha_i + \frac{1}{q_1}\left[\frac{G_\gamma^{ex}(T,P=0,\boldsymbol{x})}{RT} + \sum_i x_i\ln\left(\frac{b_{mix}}{b_i}\right)\right]$$ (9.49a)

The combination of Equations (9.14), (9.46) and (9.49a) is referred to as the MHV1 model. Later, for better accuracy, a quadratic extrapolation for $q(\alpha)$ was proposed

$$q(\alpha) = q_0 + q_1\alpha + q_2\alpha^2 \quad \text{for} \quad \alpha < \alpha_{cutoff}$$ (9.48b)

with the constants q_0, q_1 and q_2 chosen to insure continuity of the function $q(\alpha)$ and its derivatives. This gives the following quadratic equation to be solved for $\alpha_{mix} = a_{mix}/(b_{mix}RT)$:

$$q_1\left(\alpha_{mix} - \sum_i x_i\alpha_i\right) + q_2\left(\alpha_{mix}^2 - \sum_i x_i\alpha_i^2\right) = \frac{G_\gamma^{ex}(T,P=0,\boldsymbol{x})}{RT} + \sum_i x_i\ln\left(\frac{b_{mix}}{b_i}\right)$$ (9.49b)

which, together with Equations (9.14) and (9.48b), is the MHV2 model (35).

An alternate derivation of the MHV1 model is to start with Equation (9.45) and assume that $v_{mix}^\circ/b_{mix} = v_i^\circ/b_i = $ constant, so that $C(v_{mix}^\circ) = C(v_i^\circ) = q_1$, which immediately gives Equation (9.49a). From this derivation we see that an assumption inherent in the MHV1 model is that the ratio of the zero-pressure liquid molar volume to the close packing parameter b is the same for the mixture and for each of the pure components.

In spite of the fact that the MHV1 and MHV2 models do not satisfy the second-virial-coefficient boundary condition, and include an extrapolation procedure, they have been found to give quite reasonable correlations and predictions of experimental data for highly nonideal systems. However, the MHV2 model is less accurate than the Wong-Sandler mixing rule for extrapolations over large temperature ranges, and when using binary data to make ternary and multicomponent predictions (36).

Recently Tochigi et al. (37), using the observation we have discussed, proposed a modified Huron-Vidal mixing rule consistent with the second-virial-coefficient boundary condition by combining Equations (9.27), (9.45) or (9.46), and (9.48b). In their implementation they have eliminated the binary interaction parameter in Equation (9.27) leading to

$$\frac{a_{mix}}{RT} = b_{mix}\left[\sum_i x_i \frac{a_i}{b_i RT} + \frac{1}{q_1}\left\{\frac{G_\gamma^{ex}(T,x)}{RT} + \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right)\right\}\right] \tag{9.50a}$$

and

$$b_{mix} = \frac{\sum_i x_i\left(b_i - \frac{a_i}{RT}\right)}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{1}{q_1}\left\{\frac{G_\gamma^{ex}(T,x)}{RT} + \sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right)\right\}} \tag{9.50b}$$

This mixing rule model has been tested for several binary and three ternary systems and shown to be approximately equivalent in accuracy to the MHV1 model.

Boukouvalas et al. (38) proposed a new mixing rule by forming the following linear combination of the Huron-Vidal and Michelsen models

$$\frac{a_{mix}}{b_{mix} RT} = \left(\frac{\lambda}{C^*} + \frac{1-\lambda}{q_1}\right)\frac{G_\gamma^{ex}}{RT} + \frac{1-\lambda}{q_1}\sum_i x_i \ln\left(\frac{b_{mix}}{b_i}\right) + \sum_i x_i \frac{a_i}{b_i RT} \tag{9.51}$$

In deriving this mixing rule the authors have ignored the pressure dependence of the excess Gibbs energy of mixing (which is why activity-coefficient parameters had to be recorrelated when using the Huron-Vidal model) and have assumed that G_γ^{ex} of the Huron-Vidal model which is evaluated at infinite pressure, and G_γ^{ex} of the Michelsen model, which is evaluated at zero pressure, are identical. They have then shown that using the UNIFAC model in their mixing rule, with an appropriate choice of the additional parameter λ (0.36 for the original UNIFAC model, and in the range from 0.65 to 0.75 for the modified UNIFAC model), led to reasonable predictions for many systems.

An earlier activity-coefficient-based equation of state mixing rule is that of Heidemann and Kokal (39). Their zero-pressure based mixing rule is, like Michelsen's, based on Equation (9.45) and the two are identical at temperatures below which there is a zero-pessure solution for the liquid volume. At higher temperatures for which there is no zero pressure solution for the liquid volume, they obtain an apparent zero-pressure liquid volume by solving (following their notation)

$$\xi_i = \left(\frac{b_i}{v_i}\right)_{P=0} = 1 + \beta\left(\frac{a_i}{b_i RT}\right)^2 + \delta\left(\frac{a_i}{b_i RT}\right)^3 \tag{9.52}$$

where β and δ are equation of state-dependent parameters chosen to insure continuity of ξ and its temperature derivative at temperatures at which a zero-pressure-volume solution can no longer be obtained. Heidemann and Kokal also set the standard-state pressure by demanding that

$$Z_{\text{mix}} = \left(\frac{Pv}{RT}\right)_{\text{mix}} = \sum_i x_i Z_i \tag{9.53}$$

They then have ξ_{mix}, $\alpha_{\text{mix}} = (a_{\text{mix}}/b_{\text{mix}}RT)$, and b_{mix} as unknowns; these are obtained by an iterative process using the set of nonlinear equations that includes Equations (9.45), (9.52) and (9.53), and the equation of state.

A simple model similar to the zero-pressure models discussed above has recently been proposed by Orbey and Sandler (40). This has an easy-to-understand basis, results in equations that are almost identical to other models of this class in use, and leads to predictions of vapor-liquid equilibria over a broad range of temperatures with temperature-independent parameters, and is comparable in quality to other models in this class. The basis is to assume that for all fluids there is a universal parameter, u, that relates the liquid molar volumes to their close-packed hard-core volumes by $v = ub$, where u is positive in value and larger than unity at any given temperature. This simple relation is used for both the mixtures and for the pure liquids. In this case Equation (9.44) can be rewritten as

$$
\begin{aligned}
\frac{A_{\text{EOS}}^{\text{ex}}}{RT} &= -\sum_i x_i \ln\left(\frac{ub_{\text{mix}}}{ub_i}\right) - \sum_i x_i \ln\left[\frac{1-u}{1-u}\right] + \left(\frac{a_{\text{mix}}}{b_{\text{mix}}RT}\right)C(ub_{\text{mix}}) - \sum_i x_i\left(\frac{a_i}{b_i RT}\right)C(ub_i) \\
&= -\sum_i x_i \ln\left(\frac{b_{\text{mix}}}{b_i}\right) + \left(\frac{a_{\text{mix}}}{b_{\text{mix}}RT}\right)C(ub_{\text{mix}}) - \sum_i x_i\left(\frac{a_i}{b_i RT}\right)C(ub_i)
\end{aligned}
\tag{9.54}
$$

Further, u is unity at both infinite pressure and at very low temperatures; for simplicity, as an approximation, setting $u=1$ at all conditions (so $C(b)=C^*$) the following equation results:

$$\frac{A_{\text{EOS}}^{\text{ex}}}{RT} = -\sum_i x_i \ln\left(\frac{b_{\text{mix}}}{b_i}\right) + C^*\left(\frac{a_{\text{mix}}}{b_{\text{mix}}RT} - \sum_i x_i\frac{a_i}{b_i}\right) \tag{9.55}$$

The relation given by Equation (9.55) uses only one degree of freedom in determining the a and b parameters for the mixture equation of state, so that this equation can be coupled with either Equations (9.11), (9.14) or (9.27) to obtain a new mixing rule. The first alternative, Equations (9.11) and (9.55), leads to an algebraically simple mixing rule that is very similar to the MHV1 model, but with the q_1 replaced with C^*, and, like that model, does not satisfy the second-virial-coefficient composition dependence. For the Peng-Robinson equation of state, $q_1 = -0.53$ (34), while $C^* = -0.62323$ as discussed earlier. However, this small difference is
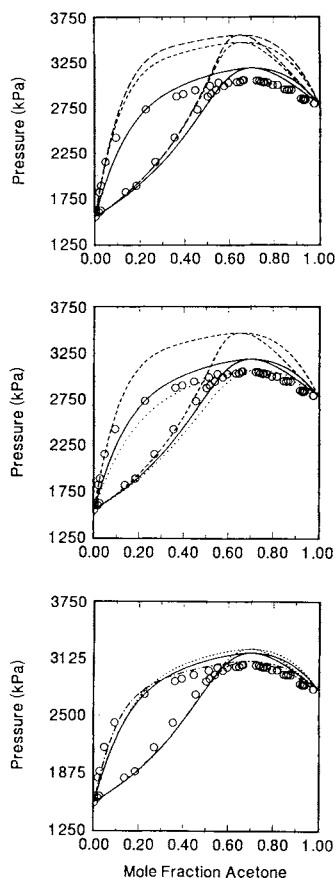
Figure 9.10 Comparison of various predictive models for the vapor-liquid equilibria of the acetone + water binary system at 200°C with the modified Peng-Robinson equation of state with the experimental data (points) of reference 6. (a) The solid lines are the results of Equations (9.14) and (9.55), and the short and long dashed lines are from MHV1 and MHV2 models, respectively. (b) The results of the Equations (9.14) and (9.55) with $C^*= -0.623$ (solid lines), -0.52 (dashed lines) and -0.68 (dotted lines). (c) The results of Equations (9.14) and (9.55) (solid lines) and the models of Wong and Sandler (dash-dot lines) and Boukouvalas *et al.* (dotted lines).

significant when extrapolating or predicting vapor-liquid equilibria. An example is shown in Figure 9.10 in which the VLE of the acetone + water binary mixture is predicted at 200°C based on a van Laar-excess-Gibbs-energy model with parameters obtained at 20°C which were reported in the tables of the DECHEMA Chemistry Data Series (5). This figure includes predictions based on the MHV1, MHV2, Wong-Sandler, Boukouvalas *et al.* models, and the zero-pressure model discussed above with various values of the parameter C^*. The most

accurate predictions are obtained with the Wong-Sandler model. The results of the model discussed immediately above and the Boukouvalas *et al.* model are comparable, though the former is better in the midconcentration range. Of the zero-pressure models, the simple one proposed above is clearly superior in extending-low pressure information to higher temperatures and pressures. Another mixing rule can be developed by combining Equations (9.27) and (9.55); this model satisfies the second-virial-coefficient boundary condition, and results in a mixing rule that is slightly more complex than the one above, and very similar to the model of Tochigi *et al.* (37), again with q_l replaced with C^*. This model has not yet been tested.

9.1.4 Commentary on Mixing Rules for Cubic Equations of State

For almost a century, the van der Waals one-fluid mixing rules were the only ones used to apply cubic equations of state, developed for pure fluids, to mixtures. Initially, the only innovation was the use of one or more binary interaction parameters. Even with that change, cubic equations of state led to reasonable correlations and predictions only for mixtures with small excess Gibbs energies of mixing, such as hydrocarbons, and hydrocarbons with inorganic gases. After a number of unsuccessful attempts at extending the range of equations of state by introducing ideas such as density-dependent mixing rules and other *ad hoc* procedures, theoretically-based mixing rules have now emerged that allow equations of state to describe mixtures with large excess Gibbs energies of mixing. These mixing rules also allow extrapolations and predictions over large ranges of temperature and pressure. However, each of these mixing and combining rules for cubic equations of state has some limitations, as has been discussed in this section, so that this area is one that continues to deserve further research.

9.2 MIXING RULES FOR THE VIRIAL FAMILY OF EQUATIONS OF STATE

9.2.1 The Van der Waals One-Fluid Model

The virial equation of state of Equation (9.1) represents the volumetric behavior of real gases as an infinite power series in inverse molar volume about the ideal gas state. This equation is a MacLaurin series in that each term is a correction to the sum of the preceding terms. Following the suggestion by Kamerlingh Onnes (41) B is called the second virial coefficient, C is the third virial coefficient, and so on. From statistical mechanics, these coefficients are related to the forces between molecules, and for a pure fluid these virial coefficients are functions of temperature only. Also, the composition dependence of each of the virial coefficients in a mixture is known from statistical mechanics, and is given by Equations (9.2) and (9.3). Since the virial equation is only applicable to gases, it is of limited use; however, the known composition dependence of the virial coefficients provides the basis for the mixing rule for this family of equations of state.

Augmented forms of the virial EOS that include terms to represent the infinite number of terms in the series have been proposed for use in accurate PvT and phase behavior calculations. Among these is the equation of Benedict, Webb, and Rubin, (BWR) (42)

$$Z = 1 + \frac{\left(B_0 - \dfrac{A_0}{RT} - \dfrac{C_0}{RT^3} \right)}{v} + \frac{\left(b - \dfrac{a}{RT} \right)}{v^2} + \frac{\alpha a}{RTv^5} + \frac{c}{RT^3 v^2}(1 + \frac{\gamma}{v^2})\exp(-\frac{\gamma}{v^2}) \tag{9.56}$$

developed to fit the PvT data of methane, ethane, propane, and n-butane, and later extended to include eight addditional hydrocarbons up to n-heptane (43). In Equation (9.56), a, b, c, A, B, C, α and γ are the equation-of-state parameters. This equation is useful for the high-accuracy calculation of density and derived properties, such as enthalpy, fugacity, vapor pressure, and latent heat of vaporization. The BWR equation is a closed form of the virial EOS as it contains an exponential term that can be expanded into an infinite series in reciprocal molar volume representing all the remaining terms in the series. This exponential term makes a large contribution to the equation of state at high density and in the critical region. Expanding the BWR equation in virial form, we obtain the following

$$Z = 1 + \frac{\left(B_0 - \dfrac{A_0}{RT} - \dfrac{C_0}{RT^3} \right)}{v} + \frac{\left(b - \dfrac{a}{RT} + \dfrac{c}{RT^3} \right)}{v^2} - \frac{\gamma c}{RT^3 v^4} + ... \tag{9.57}$$

The most common method of extending the BWR equation to mixtures is based on the van der Waals one-fluid idea that the mixture and the pure fluids should satisfy the same equation of state, and on insuring the correct composition dependence of as many virial coefficients as possible by using the equations

$$B_0 = \sum_{i=1}^{n} x_i B_{0i}$$

$$A_0 = \left[\sum_{i=1}^{n} x_i \left(A_{0i} \right)^{\frac{1}{2}} \right]^2, \qquad C_0 = \left[\sum_{i=1}^{n} x_i \left(C_{0i} \right)^{\frac{1}{2}} \right]^2$$

$$b = \left[\sum_{i=1}^{n} x_i \left(b_i \right)^{\frac{1}{3}} \right]^3, \qquad a = \left[\sum_{i=1}^{n} x_i \left(a_i \right)^{\frac{1}{3}} \right]^3 \tag{9.58}$$

$$c = \left[\sum_{i=1}^{n} x_i \left(c_i \right)^{\frac{1}{3}} \right]^3, \qquad \alpha = \left[\sum_{i=1}^{n} x_i \left(\alpha_i \right)^{\frac{1}{3}} \right]^3$$

as originally proposed by Benedict, Webb, and Rubin (42). These combining rules, that do not contain any adjustable parameters, are satisfactory for light hydrocarbon mixtures, but not for mixtures containing nonhydrocarbons or even heavy hydrocarbons. Stotler and Benedict (44) first proposed the use of a single interaction parameter m_{ij} (which is similar to the interaction parameter used with cubic equations of state) in the mixing rule for A_0 in the BWR equation

$$A_0 = \sum \sum x_i x_j \left(A_{0i} A_{0j} \right)^{\frac{1}{2}} m_{ij} \tag{9.59}$$

This mixing rule was later used by Orye (45) for hydrocarbon mixtures, and by Nohka *et al.* (46) for refrigerant mixtures with nitrogen, argon, methane, *etc.*

A shortcoming of extended virial equations of state in their application to mixtures in the manner described above arises from the fact that, given the uncertainty in experimental data, the many pure-component equation of state parameters cannot be uniquely determined. Consequently, many sets of constants are possible depending on the source of the experimental data and the weighting factors used in the regression. In fact, significantly different sets of constants have been reported by different investigators for the same pure fluids as discussed below. Although all these sets of the constants are, in general, satisfactory for the representation of a pure fluid, they can lead to quite different results for mixtures. This is especially true when mixing rules such as those above are used for a mixture containing components whose equation of state constants differ considerably in magnitude. This problem can be alleviated by using generalized forms for the equation of state parameters, as will be discussed in the next section.

Many modifications have been proposed for improving the overall accuracy of the BWR equation by increasing the number of terms, and thus increasing the number of constants. One of the first such modifications was by Strobridge (47):

$$P = RT\rho + \left(C_1 RT + C_2 + \frac{C_3}{T} + \frac{C_4}{T^2} + \frac{C_5}{T^4} \right)\rho^2 + \left(C_6 RT + C_7 \right)\rho^3 + C_8 T \rho^4 + C_{15}\rho^6$$
$$+ \left[\left(\frac{C_9}{T^2} + \frac{C_{10}}{T^3} + \frac{C_{11}}{T^4} \right) + \left(\frac{C_{12}}{T^2} + \frac{C_{13}}{T^3} + \frac{C_{14}}{T^4} \right)\rho^2 \right]\rho^3 \exp(-\gamma \rho^2) \tag{9.60}$$

where ρ is molar density and the C_i are equation of state constants. This 16-constant equation set the pattern for many of the later modifications, including those by Bender (48), (20 constants), Morsy (49), (10 constants), Starling (50), (11 constants), Jacobsen and Stewart (51), (32 constants), Lee and Kesler (52), (12 constants), Nishiumi and Saito (53), (15 constants), Schmidt and Wagner (54), (32 constants), and the AGA Natural Gas Equation by Starling (55), (53 terms). Each of these equations uses mixing rules much like those of Equations (9.58). The increased number of terms and constants generally improves the accuracy of the equation for pure fluids, but for the reasons discussed above, may not result in increased accuracy when applied to mixtures. A more detailed description of equations of state of this class can be found elsewhere in this book, Chapters 10 and 12 and elsewhere (56).

9.2.2 Generalized Extended Virial Equations of State and Their Mixing Rules

One method of avoiding the problem of nonuniqueness of the parameters of the extended virial equation, based on the principle of corresponding states, is to change from temperature and density as the variables with fluid-specific parameters to reduced properties and parameters that are either universal constants or that are generalized in terms of some fluid property, such as the acentric factor ω. Joffe (57) was the first to generalize the parameters in the BWR equation of state by following the suggestion of Kamerlingh Onnes (41) and expressing the reduced pressure ($P_r = P/P_c$) as a function of reduced temperature ($T_r = T/T_c$) and ideal reduced volume ($P_c v/RT_c$) with eight universal constants. In this way the equation becomes a two-parameter (P_c and T_c) corresponding-states method that is not very accurate. Later Opfell *et al.* (58) put the BWR equation in corresponding-states form using the reduced

pressure, reduced temperature and acentric factor by making its constants, except for γ, linear functions of the acentric factor. Similarly, Edmister *et al.* (59) made seven of the eight constants quadratic functions of the acentric factor to improve accuracy, keeping the product of α and a constant. A more extensive generalization by Starling and Han (60) used the 11-constant form of Starling's modified BWR equation

$$
P = \rho RT + \left(B_\circ RT - A_\circ - \frac{C_\circ}{T^2} + \frac{D_\circ}{T^3} - \frac{E_\circ}{T^4} \right)\rho^2 + \left(bRT - a - \frac{d}{T} \right)\rho^3
$$
$$
+ \alpha\left(a + \frac{d}{T} \right)\rho^6 + \frac{c\,\rho^3}{T^2}(1 + \gamma\,\rho^2)\exp(-\gamma\,\rho^2) \tag{9.61}
$$

but made the ten constants linear functions of the acentric factor, and $E_\circ$ an exponential function of the acentric factor, and used the critical volume in the generalization. The dimensionless constants in reduced form are

$$
\rho_{ci} B_{oi} = A_1 + B_1 \omega_i \qquad \frac{\rho_{ci} A_{oi}}{RT_{ci}} = A_2 + B_2 \omega_i
$$

$$
\frac{\rho_{ci} C_{oi}}{RT_{ci}^3} = A_3 + B_3 \omega_i \qquad \rho_{ci}^2 \gamma_i = A_4 + B_4 \omega_i
$$

$$
\rho_{ci}^2 b_i = A_5 + B_5 \omega_i, \qquad \frac{\rho_{ci}^2 a_i}{RT_{ci}} = A_6 + B_6 \omega_i
$$

$$
\rho_{ci}^3 \alpha_i = A_7 + B_7 \omega_i, \qquad \frac{\rho_{ci}^2 c_i}{RT_{ci}^3} = A_8 + B_8 \omega_i
$$

$$
\rho_{ci}^3 \alpha_i = A_7 + B_7 \omega_i, \qquad \frac{\rho_{ci}^2 c_i}{RT_{ci}^3} = A_8 + B_8 \omega_i
$$

$$
\frac{\rho_{ci}^2 D_{oi}}{RT_{ci}^4} = A_9 + B_9 \omega_i, \qquad \frac{\rho_{ci}^2 d_i}{RT_{ci}^2} = A_{10} + B_{10} \omega_i
$$

$$
\frac{\rho_{ci} E_{oi}}{RT_{ci}^5} = A_{11} + B_{11} \omega_i \exp(-3.8\,\omega_i) \tag{9.62}
$$

Starling and Han (60) used the original BWR mixing rules, Equations (9.58), except for introducing a binary interaction parameter, as follows

$$
A_\circ = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \left(A_{oi} A_{oj} \right)^{1/2} (1 - k_{ij}),
$$

$$
C_\circ = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \left(C_{oi} C_{oj} \right)^{1/2} (1 - k_{ij})^3
$$

$$D_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(D_{oi} D_{oj}\right)^{1/2} \left(1 - k_{ij}\right)^4$$

$$d = \left(\sum_{i=1}^{n} x_i d_i^{1/3}\right)^3$$

$$E_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(E_{oi} E_{oj}\right)^{1/2} \left(1 - k_{ij}\right)^5 \tag{9.63}$$

The approach discussed above for the generalization of extended virial equations is to write the equation in reduced form and then make the constants functions of the acentric factor. In this approach, even though the EOS constants are linear functions of the acentric factor, the calculated thermodynamic properties are not. It is not possible, with this type of generalization, to produce an equation of state in which the molar volume (or the compressibility factor) and other derived properties are linear functions of the acentric factor, even though such behavior is experimentally observed.

Pitzer and co-workers (61-63) and Curl and Pitzer (64) developed correlations for the compressibility factor (and thus other thermodynamic properties) as a linear function of the acentric factor at given reduced pressure and reduced temperature in the following form

$$Z(T_r, P_r, \omega) = Z^{(0)}(T_r, P_r) + \omega \, Z^{(1)}(T_r, P_r) \tag{9.64}$$

Here $Z^{(0)}$ is the compressibility factor of a simple fluid ($\omega = 0$) and $Z^{(1)}$ is a departure function, both of which are only functions of reduced pressure and reduced temperature. Lee and Kesler (52) expanded on this idea and made it useable with computers by proposing

$$Z(T_r, P_r, \omega) = Z^{(0)}(T_r, P_r) + \omega \, \frac{Z^{(r)}(T_r, P_r) - Z^{(0)}(T_r, P_r)}{\omega^{(r)}} \tag{9.65}$$

where $Z^{(0)}$ and $Z^{(r)}$ are the compressibility factors for a simple reference fluid (noble gas, $\omega = 0$) and a second reference fluid (essentially n-octane for which $\omega^{(r)}$ is 0.3978) at the same reduced conditions. Lee and Kesler used the following reduced form of the modified BWR equation of state to represent both $Z^{(0)}$ and $Z^{(r)}$:

$$Z = \left(\frac{P_r v_r}{T_r}\right) = 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^5} + \frac{c_4}{T_r^3 v_r^2}\left(\beta + \frac{\gamma}{v_r^2}\right)\exp\left(-\frac{\gamma}{v_r^2}\right) \tag{9.66}$$

where

$$v_r = \frac{v P_c}{R T_c}$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}$$

and

$$D = d_1 + \frac{d_2}{T_r} \tag{9.67}$$

They also suggested the following mixing rules for the effective critical parameters

$$T_c = \frac{1}{v_c} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j v_{cij} T_{cij}$$

$$v_c = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j v_{cij}$$

and

$$\omega = \sum_{i=1}^{n} x_i \omega_i \tag{9.68}$$

with the following combining rules

$$v_{cij} = \left(\frac{v_{ci}^{1/3} + v_{cj}^{1/3}}{2} \right)^3$$

$$v_{ci} = \frac{Z_{ci} R T_{ci}}{P_{ci}}$$

$$T_{cij} = \sqrt{T_{ci} T_{cj}}$$

$$Z_{ci} = 0.2905 - 0.085 \omega_i \tag{9.69}$$

$$P_c = \frac{(0.2905 - 0.085\omega) R T_c}{v_c}$$

Note that the mixing rules here for the generalized, extended virial equations are of a different nature than the ones considered previously in this section. While the previous mixing rules combined the values of the equation of state parameters of the pure fluids to obtain the mixture parameters, the mixing rules here use values of the critical temperature, critical pressure, and acentric factor of the pure components to obtain effective values for these physical properties of the mixture. To apply the Lee-Kesler equation to vapor-liquid equilibria, Joffe (65) proposed adding an interaction parameter to Equation (9.68), which Ploecker et al. (66) and Oellrich et al. (67) also did, as well as modifying the mixing rule for T_c as follows

$$T_c = \frac{1}{v_c^{1/4}} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j v_{cij}^{1/4} T_{cij}$$

$$T_{cij} = \sqrt{T_{ci}T_{cj}}\, k_{ij} \tag{9.70}$$

Other, similar mixing and combining rules have been proposed, and it is difficult to establish that one set is clearly superior to the others.

The two classes of mixing rules discussed here (one for the equation of state parameters and the other for the effective critical properties) are the only ones used for the family of extended virial equations of state. Unfortunately, these mixing and combining rules are only suitable for mixtures of hydrocarbons, and for hydrocarbons with inorganic gases. Perhaps future work based on using a different mixing rule for each term of the extended virial equations will allow this family of equations of state to be used for more nonideal mixtures than is currently the case.

9.3 MIXING RULES BASED UPON THEORY AND COMPUTER SIMULATION

One important contribution to the theory of mixing rules comes from the exact results for the composition dependence of the virial coefficients that we have already used in the formulation of boundary conditions. However, from theory and computer simulation, we also have other information that can be used in developing mixing and combining rules. For the case of a fluid of hard spheres (without attractive forces), we now know that an accurate equation of state is the Carnahan-Starling expression (68):

$$P = \frac{RT}{v}\left[\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right] \tag{9.71}$$

where $\eta = \pi\rho\sigma^3/6$ with σ being the hard-sphere diameter and ρ the density. The comparable expression for a mixture of hard spheres, due to Mansoori $et\ al.$ (69), is

$$P = \frac{RT}{v}\frac{6}{\pi}\left[\frac{\eta_o}{1-\eta_3} + \frac{3\eta_1\eta_2}{\left(1-\eta_3\right)^2} + \frac{3\eta_2^3}{\left(1-\eta_3\right)^3} + \frac{\eta_3\eta_2^3}{\left(1-\eta_3\right)^3}\right] \tag{9.72}$$

where $\eta_j = \left(\pi/6\right)\sum_i \rho_i\sigma_i^j$. Note that, while the combining rules for each of the η_i are different (due to the different exponent on σ), the mixture equation has the same overall density dependence as the pure fluid equation, and reduces to it in the limit of all components becoming identical. Also, no binary-interaction parameters are used, as is typical in the repulsive or hard-sphere part of an equation of state.

To match the results of molecular dynamics computer simulations for square-well molecules, Alder $et\ al.$ (70) used a double-power-series expansion in reduced inverse temperature and volume for the attractive part of an equation of state. Modifications of their attractive term have been used in a number of equations of state, such as the augmented and perturbed-hard-sphere equations, the perturbed-hard-chain equation, and the BACK equations of state (71). The general form of this attractive term is

$$P^{attr} = - \sum_{n} \sum_{m} A_{nm} \left(\frac{u}{kT} \right)^{n} \left(\frac{v_{o}}{v} \right)^{m} \tag{9.73}$$

where the A_{mn} are universal constants, v_{o} is the close-packed volume and u is an effective well depth, both of which are taken to be depend upon temperature in using these equations to describe real fluids. In this case the mixing rules commonly used are

$$v_{o} = \sum_{i} \sum_{j} x_{i} x_{j} v_{o,ij} \quad \text{and} \quad u = \sum_{i} \sum_{j} x_{i} x_{j} u_{ij} \tag{9.74}$$

with the combining rules

$$v_{o,ij} = \left(1 - l_{ij} \right) \left(\frac{\left(v_{o,ii} \right)^{1/3} + \left(v_{o,jj} \right)^{1/3}}{2} \right)^{3} \quad \text{and} \quad u = \sqrt{u_{ii} u_{jj}} \left(1 - k_{ij} \right) \tag{9.75}$$

Consequently, in all the equations that include the double power-series expansion above (or its variations), such as the family of perturbed-hard-chain equations, the equation of state parameters are related to molecular rather than critical properties, and the mixing and combining rules are quadratic in composition for the attractive term, and based on hard-sphere theory for the repulsive term. Of course, the Carnahan-Starling expression is only correct for hard spheres, and most molecules are not spherical. Therefore, other equations of the same general form have been proposed for molecules of various geometrical shapes. For example, there is the equation of Boublik (72) for hard convex bodies

$$\frac{Pv}{RT} = Z = \frac{1 + (3\alpha - 2)\xi + (3\alpha^{2} - 3\alpha + 1)\xi^{2} - \alpha^{2}\xi^{3}}{(1 - \xi)^{3}} \tag{9.76}$$

where a is the surface integral of the radius of curvature divided by three times the molecular volume, and

$$\xi = \frac{\pi\sqrt{2}}{6} \frac{v_{o}}{v} \tag{9.77}$$

where v_{o} is the hard-core volume. However, there is no obvious or theoretically based mixing rule to extend this equation (and related equations by others) to mixtures of nonspherical molecules.

The last type of equation of state that we will consider is the Statistical Associating-Fluid Theory (SAFT) of Chapman *et al.* (73) and Huang and Radosz (74). In the SAFT model, a molecule is considered to consist of a collection of segments, and the Helmholtz energy is written as:

$$A = A^{ig} + A^{seg} + A^{chain} + A^{assoc} \tag{9.78}$$

which is a sum of contributions from the ideal gas, the intermolecular interactions between segments, the formation of chains from segments, and association due to hydrogen bonding and donor-acceptor interactions. The sum of the Carnahan-Starling and Alder *et al.* expressions for interactions among spheres is used for the segment term (A^{seg}), the first-order perturbation expression of Wertheim (75-79) is used to account for association (A^{assoc}) and, based on the work of Chapman (80), also for chain formation (A^{chain}). The segment Helmholtz energy per mole of molecules, A^{seg}, is

$$A^{seg} = r\, A_o^{seg} = r\left(A_o^{hs} + A_o^{disp}\right) \tag{9.79}$$

where r is the number of segments per chain, and the subscript o refers to a property of a single segment. The segment properties are further assumed to be a combination of a hard sphere term represented by the Helmholtz energy form of the Carnahan-Starling expression and a dispersion term given by the expression of Alder *et al.* with constants as modified by Chen and Kreglewski (80). The contribution to the Helmholtz energy for chain formation comes from an expression due to Chapman (80) and Chapman *et al.* (73) based on Wertheim's first order perturbation theory (75-79)

$$\frac{A^{chain}}{RT} = (1-r)\ln\left[\frac{2-r\eta}{2(1-r\eta)^3}\right] \tag{9.80}$$

The association term from Wertheim's theory, is given by

$$\frac{A^{assoc}}{RT} = \sum_A\left[\ln X^A - \frac{X^A}{2}\right] + \frac{M}{2} \tag{9.81}$$

where the sum is over all association sites, M is the number of association sites on each molecule and X^A is the mole fraction of molecules which are *not* bonded at site A. The application of this equation of state requires the replacement of the Carnahan-Starling term with the expression above due to Mansoori *et al.*, and more complicated chain and association terms given by the authors. We will not reproduce these mixture-model expressions here. However, the important point to note in the SAFT equation, and other equations of this type, is that each of the terms has its own theoretically-based mixing rule that is different from the mixing rules for other terms in the same equation.

9.4 CONCLUSIONS

Equations of state have been used for the accurate description of the *P-v-T* behavior and thermodynamic properties of fluids for decades. It is mixing and combining rules that allow an equation of state developed for pure fluids to be used for mixtures. Historically, there have been many examples in which an equation of state could be used to accurately describe the properties of two or more pure fluids, but not of their mixtures. This is clearly a failure of the mixing and/or combining rules used. For almost a century, only the simplest mixing rules were widely used; the classical van der Waals one-fluid rules for cubic equations of state, and mixing rules based on the virial equation for more complicated equations of state

In recent years there has been a great deal of research on mixing rules and some real advances. Perhaps the most important has been the combination of equation of state and free energy models. These mixing rules, discussed in this chapter, have resulted in simple cubic equations of state providing accurate descriptions of the phase behavior of highly nonideal mixtures over large ranges of temperature and pressure with temperature-independent parameters. Further, these new mixing rules can incorporate mixture group contribution methods, such as UNIFAC, allowing for a simple extension of these models to high temperatures and high pressures with the existing parameter tables. New mixing rules have also been developed for other classes of equations of state. In this area the progress has been slow and less noteworthy. One interesting feature that has emerged, largely from molecular theory, is the use of different mixing rules for the attractive and repulsive contributions to the equation of state.

Much remains to be done in the area of mixing rules. In fact, the formulation of each new equation of state brings with it the question of the mixing rules to be used.

REFERENCES

1. D.Y. Peng and D.B. Robinson, *Ind. Eng. Chem. Fund.* **15**, 59 (1976).
2. G. Soave, *Chem. Eng. Sci.* **27**, 1197 (1972).
3. J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, *Molecular Theory of Gases and Liquids,* Sec. 1.3 and Ch. 13, Wiley, New York (1954).
4. R. Stryjek and J.H. Vera, *Can. J. Chem. Eng.* **64**, 820 (1986).
5. J. Gmehling and U. Onken, *Vapor-Liquid Equilibrium Data Compilation, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt am Main (1977).
6. J. Griswold and S.Y. Wong, *Chem. Eng. Symp. Ser.* **48**, 18 (1952).
7. J.H. Hildebrand, J.M. Prausnitz, and R.L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York (1970)
8. A.Z. Panagiotopoulos and R.C. Reid, *ACS Symp. Ser.* **300**, 571 (1986).
9. Y. Adachi and H. Sugie, *Fluid Phase Equilib.* **23**, 103 (1986).
10. R. Sandoval, G. Wilczek-Vera, and J.H. Vera, *Fluid Phase Equilib.* **52**, 119 (1989).
11. J. Schwartzentruber and H. Renon, *Fluid Phase Equilib.* **52**, 127 (1989).
12. J. Schwartzentruber and H. Renon, *Ind. Eng. Chem. Res.* **28**, 1049 (1989).
13. C. Torres-Marchal, A.L. Cantalino, and R.M. DeBrito, *Fluid Phase Equilib.* **52**, 111 (1989).
14. K.A. Pividal, C. Sterner, S.I. Sandler, and H. Orbey, *Fluid Phase Equilib.* **72**, 227 (1992).
15. M.L. Michelsen and H. Kistenmacher, *Fluid Phase Equilib.* **58**, 229 (1990).
16 J. Vidal, *Chem. Eng. Sci.* **33**, 787 (1978).
17. M.-J. Huron and J. Vidal, *Fluid Phase Equilib.* **3**, 255 (1979).
18. D.S.H. Wong and S.I. Sandler, *AIChE J.* **38**, 671 (1992).
19. S. Michel, H.H. Hooper, and J.M. Prausnitz, *Fluid Phase Equilib.* **45**, 173 (1989).
20. T.W. Copeman and P.M. Mathias, *ACS Symp. Ser.* **300**, 352 (1986).
21. S.I. Sandler, K.-H. Lee, and H. Kim, *ACS Symp. Ser.* **300**, 180 (1986).
22. D.S.H. Wong, H. Orbey, and S.I. Sandler, *Ind. Eng. Chem. Res.* **31**, 2033 (1992).
23. F. Barr-David and B.F. Dodge, *J. Chem. Eng. Data* **4**,107 (1959).
24. H. Orbey, S.I. Sandler, and D.S.H. Wong, *Fluid Phase Equilib.* **85**, 41 (1993).
25. S.W. Campbell, R.A. Wilsak, and G. Thodos, *J. Chem. Thermodyn.* **19**, 449 (1987).
26. H. Orbey and S.I. Sandler, *AIChE J.* **41**, 683 (1995).
27. H. Orbey and S.I. Sandler, *AIChE J.* **40**, 1203 (1994).
28. T.W. de Loos, W. Poot, and R.N. Lichtenthaler, *Ber. Bunsenges. Phys. Chem.* **88**, 855 (1984).

29. H. Huang, S.I. Sandler, and H. Orbey, *Fluid Phase Equilib.* **96**, 143 (1994).
30. J. Mollerup, *Fluid Phase Equilib.* **25**, 323 (1986).
31. P.A. Gupte, P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem. Fund.* **25**, 636 (1986).
32. R. Gani, N. Tzouvaras, P. Rasmussen, and A. Fredenslund, *Fluid Phase Equilib.* **47**, 133 (1989).
33. M.L. Michelsen, *Fluid Phase Equilib.* **60**, 47 (1990).
34. M.L. Michelsen, *Fluid Phase Equilib.* **60**, 213 (1990).
35. S. Dahl and M.L. Michelsen, *AIChE J.* **36**, 1829 (1990).
36. H. Huang and S.I. Sandler, *Ind. Eng. Chem. Res.* **32**, 1498 (1993).
37. K. Tochigi, P. Kolar, T. Izumi, and K. Kojima, *Fluid Phase Equilib.* **96**, 215 (1994).
38. C. Boukouvalas, N. Spiliotis, P. Coutsikos, and N. Tzouvaras, *Fluid Phase Equilib.* **92**, 75 (1994).
39. R.A. Heidemann and S.L. Kokal, *Fluid Phase Equilib.* **56**, 17 (1990).
40. H. Orbey and S.I. Sandler, *Fluid Phase Equilib.* **111**, 53 (1995).
41. H.K. Kamerlingh Onnes, *Archives Neerlandaises* **6**, 874 (1901).
42. M. Benedict, G.B. Webb, and L.C. Rubin, *J. Chem. Phys.* **8**, 334 (1940).
43. M. Benedict, G.B. Webb, and L.C. Rubin, *Chem. Eng. Prog.* **47**, 449 (1951).
44. H.H. Stotler and M. Benedict, *Chem. Eng. Prog. Symp. Ser.* **49**, 25 (1953).
45. R.V. Orye, *Ind.Eng.Chem. Process Design Dev.* **8**, 579 (1969).
46. J. Nohka, S. Eiji, Y. Arai, and S. Saito, *J. Chem. Eng. Japan* **6**, 10 (1973).
47. T.R. Strobridge, NBS Technical Note No. **129** (1962).
48. E. Bender, *Proceedings on the 5th Symposium on Thermophysical Properties*, ASME, New York (1970), p. 227.
49. T.E. Morsy, *J. Chem. Eng. Data* **15**, 256 (1970).
50. K.E. Starling, *Hydrocarbon Process.* **50**, 101 (March 1971).
51. R.T. Jacobsen and R.B. Stewart, *J. Phys. Chem. Ref. Data*, **2**, 275 (1973).
52. B.I. Lee and M.G. Kesler, *AIChE J.* **21**, 510 (1975).
53. H. Nishiumi, *J. Chem. Eng. Japan* **13**, 178 (1980).
54. R. Schmidt and W. Wagner, *Fluid Phase Equilib.* **19**, 175 (1985).
55. K.E. Starling, *Revision of AGA No.8 Equation*, Gas Research Institute, Chicago (1991).
56. S.I. Sandler, H. Orbey, and B.I. Lee, *Models for Thermodynamic and Phase Equilibria Calculations*, Ch. 2, S.I. Sandler, ed., Marcel Dekker, New York (1994).
57. J. Joffe, *Chem. Eng. Prog.* **45**, 160 (1949).
58. J.B. Opfell, B.H. Sage, and K.S. Pitzer, *Ind. Eng. Chem.* **48**, 2069 (1956).
59. W.C. Edmister, J. Vairogs, and A.J. Klekers, *AIChE J.* **14**, 479 (1968).
60. K.E. Starling and M.S. Han, *Hydrocarbon Process.* **51**, 129 (March 1972).
61. K.S. Pitzer, *J. Am. Chem. Soc.* **77**, 3427 (1955).
62. K.S. Pitzer and R.F. Curl, Jr, *Ind. Eng. Chem.* **49**, 2369 (1957).
63. K.S. Pitzer, D.Z. Lippmann, R.F. Curl, Jr., and C.M. Huggins, *J. Am. Chem. Soc.* **77**, 3433 (1955).
64. R.F. Curl, Jr. and K.S. Pitzer, *Ind. Eng. Chem.* **50**, 265 (1958).
65. J. Joffe, *Ind. Eng. Chem. Fund.* **15**, 298 (1976).
66. U. Ploecker, H. Knapp, and J.M. Prausnitz, *Ind. Eng. Chem. Process Design Dev.* **20**, 127 (1978).
67. L. Oellrich, U. Ploecker, J.M. Prausnitz, and H. Knapp, *Int. Chem. Eng.* **21**, 1 (1981).
68. N.F. Carnahan and K.E. Starling, *AIChE J.* **18**, 1184 (1972).
69. G.A. Mansoori, *ACS Symp. Ser.* **300**, 314 (1986).
70. B.J. Alder, D.A. Young, and M.A. Mark, *J. Chem. Phys.* **56**, 3013 (1972).
71. S.S. Chen and A. Kreglewski, *Ber. Bunsenges. Phys. Chem.* **81**, 1049 (1977).
72. T. Boublik, *J. Chem. Phys.* **63**, 4084 (1975).
73. W.G. Chapman, K.E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.* **29**, 1709 (1990).
74. S.H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **29**, 2284 (1990).

75. M.S. Wertheim, *J. Stat. Phys*. **35**, 19 (1984).
76. M.S. Wertheim, *J. Stat. Phys*. **35**, 35 (1984).
77. M.S. Wertheim, *J. Stat. Phys*. **42**, 459 (1986).
78. M.S. Wertheim, *J. Stat. Phys*. **42**, 477 (1986).
79. M.S. Wertheim, *J. Chem. Phys*. **85**, 2929 (1986).
80. W.G. Chapman, *J. Phys. Chem*. **93**, 4299 (1990).