

DENSITY-DEPENDENT MIXING RULES FOR THE CALCULATION OF FLUID PHASE EQUILIBRIA AT HIGH PRESSURES

ULRICH K. DEITERS

Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, D-4630 Bochum 1 (F.R.G.)

(Received June 3, 1986; accepted in final form November 5, 1986)

ABSTRACT

Deiters, U.K., 1987. Density-dependent mixing rules for the calculation of fluid phase equilibria at high pressures. *Fluid Phase Equilibria*, 33: 267–293.

A variable exponent is introduced into the van der Waals mixing rules in order to account for non-equiform particle distribution in mixtures of unlike molecules over a wide range of densities. The exponent is obtained by integration of radial distribution functions of rigid sphere mixtures. In connection with our own non-cubic equation of state, the modified mixing rules significantly improve the prediction of phase equilibria in cryogenic mixtures under high pressure, especially in the vicinity of critical points. The new mixing rules also lead to better predictions of thermodynamic properties of Lennard–Jones mixtures. Some details of the computational procedure are discussed.

INTRODUCTION

One of the most successful and most widely used methods for relating the thermodynamic properties of a mixture to those of a pure fluid is the so-called one-fluid theory. Its principle is to treat a mixture as a hypothetical pure substance, whose characteristic parameters (molecular diameter, potential energy, etc.) are obtained by interpolation between the parameters of the pure components. The interpolation formulae are usually referred to as mixing rules.

The mixing rules are functions of composition: they are usually assumed to be independent of density. In this case, the Helmholtz energy of a mixture, which depends on density, temperature and composition, is represented by a parametric combination of a function of density and temperature (namely the pure substance Helmholtz energy function) and a set of functions of composition (the mixing rules). The theoretical validity of such an approach is questionable: in fact, for some model fluids, such as mixtures of rigid spheres, it is positively known that their equation of state cannot be

obtained from the appropriate pure fluid equation of state and density-independent mixing rules (Lebowitz, 1964). Nevertheless, some density-independent mixing rules have been found to be very good approximations, such as the so-called van der Waals rules

$$\epsilon_0 \sigma_0^3 = \sum_i^C \sum_k^C x_i x_k \epsilon_{ik} \sigma_{ik}^3 \quad (1)$$

$$\sigma_0^3 = \sum_i^C \sum_k^C x_i x_k \sigma_{ik}^3 \quad (2)$$

Here, ϵ_{ik} and σ_{ik} denote the attractive energy parameter and collision diameter pertaining to the interaction of the molecular species i and k . The summations extend to all C components of the mixture. Throughout this paper, the subscript '0' denotes averaged properties.

The van der Waals rules are known to be reasonable for fluid mixtures at low densities. At high densities, however, different rules are to be preferred. Studies of the maximum numbers of nearest neighbours (Deiters, 1982b, 1983a; Eduljee, 1983; Sandler, 1983) indicate that, for dense fluids, the mixing rules

$$\epsilon_0 \sigma_0^\gamma = \sum_i^C \sum_k^C x_i x_k \epsilon_{ik} \sigma_{ik}^\gamma \quad (3)$$

$$\sigma_0^\gamma = \sum_i^C \sum_k^C x_i x_k \sigma_{ik}^\gamma \quad (4)$$

with $\gamma = 2$ or $\gamma = 2.4$ are more appropriate. Except for the exponent, these mixing rules agree with the van der Waals rules. It is the purpose of this work to derive the density and concentration dependence of γ from statistical thermodynamical arguments and to study its influence on thermodynamic properties, especially on phase equilibria, of fluid mixtures under high pressures.

GENERALIZED MIXING RULES

Extended one-fluid theory

The following considerations pertain to multi-component mixtures, where the molecules interact through pair potentials of approximately spherical symmetry only. Let us assume that the intermolecular pair potential can be divided into a repulsive and an attractive contribution

$$u_{ik}(r) = u_{ik}^{\text{rep}}(r) + u_{ik}^{\text{att}}(r) \quad (5)$$

and that the effects of the repulsive potential have been accounted for by an appropriate rigid body equation of state (e.g., Mansoori et al., 1971). Then, the contribution of the attractive potential to the total Helmholtz energy of the mixture is

$$A^{\text{att}} = \frac{2\pi N}{V} \sum_i^C \sum_k^C x_i x_k \int_0^\infty u_{ik}^{\text{att}}(r) g_{ik}(r) r^2 dr \quad (6)$$

We shall, furthermore, assume that the intermolecular potentials $u_{ik}^{\text{att}}(r)$ as well as the average potential $u_0^{\text{att}}(r)$ are conformal to each other and related to a reduced attractive potential $\tilde{u}(\tilde{r})$

$$u_{ik}^{\text{att}}(r) = \epsilon_{ik} \tilde{u}(r/\sigma_{ik}) \quad u_0^{\text{att}}(r) = \epsilon_0 \tilde{u}(r/\sigma_0) \quad (7)$$

Splitting off a pure fluid term and switching to reduced variables leads from eqn. (6) to

$$A^{\text{att}} = \frac{2\pi N}{V} \int_0^\infty u_0^{\text{att}}(r) g_0(r) r^2 dr \sum_i^C \sum_k^C x_i x_k \frac{\int u_{ik}^{\text{att}}(r) g_{ik}(r) r^2 dr}{\int u_0^{\text{att}}(r) g_0(r) r^2 dr} \quad (8)$$

and

$$A^{\text{att}} = \frac{2\pi N}{V} \epsilon_0 \sigma_0^3 \int_0^\infty \tilde{u}(\tilde{r}) g_0(\tilde{r}) \tilde{r}^2 d\tilde{r} \sum_i^C \sum_k^C x_i x_k \frac{\epsilon_{ik} \sigma_{ik}^3}{\epsilon_0 \sigma_0^3} \frac{\int \tilde{u}(\tilde{r}) g_{ik}(\tilde{r}) \tilde{r}^2 d\tilde{r}}{\int \tilde{u}(\tilde{r}) g_0(\tilde{r}) \tilde{r}^2 d\tilde{r}} \quad (9)$$

Usually, the radial distribution functions of real fluid mixtures are not available. Within the double sum in eqn. (9), we, therefore, replace them with the radial distribution functions of rigid sphere mixtures, which are sufficiently well known. This simplification seems to be justified for two reasons:

(1) In dense fluids the structure is determined by repulsive forces rather than by attractive forces (as can be seen from molecular dynamics studies, e.g., Hoheisel and Kohler, 1984): at low densities the repulsive forces may not prevail, but the total influence of the attractive potential is then rather small, and a minor inaccuracy of the model has little influence on the thermodynamic properties.

(2) Any influences of the attractive potentials on the fluid structure affect g_{ik} and g_0 similarly, so that they cancel to some extent.

Similar arguments have been used in several recent publications which deal with the development of more efficient mixing rules beyond one-fluid theory (Deiters, 1986; Ely, 1986). But, in these publications, only the contact

values of the radial distribution functions have been used, so that only the molecules ‘in touch’ with others contribute to the deviations from the van der Waals mixing rules. In this work, the integrals of the radial distribution functions are evaluated throughout the range of the attractive potentials, so that all neighbour particles within the attractive well of a molecule are counted.

Starting from a somewhat different consideration, namely from properties of the partition function of a square-well fluid, Sandler (1985) as well as Lee et al. (1986) arrived at improved mixing rules, which contain corrections for the true numbers of nearest neighbours and which—as far as square-well particles are concerned—are similar to eqns. (8) and (9) of this work. These equations, however, are not restricted to one kind of pair potential only. Furthermore, Lee et al. (1986) focussed their attention on molecules of different attractive well-depths, but equal sizes, and on the local compositions caused by those attractive energy differences. This work considers molecules of different sizes, and stresses the influence of the repulsive forces. The resulting thermodynamic functions and mixing rules are, therefore, different, although there is some agreement in essence.

Replacing the real fluid radial distribution functions $g_{ik}(r)$ by hard sphere functions $g_{ik}^{\text{hs}}(r)$ amounts to using a first-order perturbation theory with a hard sphere mixture as reference system. This perturbation treatment, however, is not applied to eqn. (9) as a whole, but only to the double sum.

To simplify the further evaluation of A^{att} , and in view of eqn. (3), we introduce the exponent γ_{ik} as defined by

$$\gamma_{ik} = 3 + \ln \left(\frac{\int \tilde{u}(\tilde{r}) g_{ik}^{\text{hs}}(\tilde{r}) \tilde{r}^2 d\tilde{r}}{\int \tilde{u}(\tilde{r}) g_0^{\text{hs}}(\tilde{r}) \tilde{r}^2 d\tilde{r}} \right) / \ln \left(\frac{\sigma_{ik}}{\sigma_0} \right) \quad (10)$$

In the strict sense, it is necessary to maintain a distinction between the different γ_{ik} , but it turns out that they have almost the same value (Table 1). Therefore, it seems justified to use only one exponent for all interactions in a mixture: in the following text the subscripts of γ are therefore omitted. With this definition of γ , eqn. (9) can be transformed into

$$A^{\text{att}} = \frac{2\pi N}{V} \epsilon_0 \sigma_0^3 \int_0^\infty \tilde{u}(\tilde{r}) g_0(\tilde{r}) \tilde{r}^2 d\tilde{r} \sum_i^C \sum_k^C x_i x_k \frac{\epsilon_{ik} \sigma_{ik}^\gamma}{\epsilon_0 \sigma_0^\gamma} \quad (11)$$

Until now, the average potential parameters ϵ_0 and σ_0 have been left undefined. We are, therefore, free to choose values for these parameters that let the double sum in eqn. (11) become 1. Evidently, this can be achieved by using the mixing rules (3) and (4): however, γ is now a function of density,

TABLE 1
Mixing rule exponents for the square-well 1.5 potential (binary mixture)

x_1	$\sigma_{11}/\sigma_{22} = 0.8$				$\sigma_{11}/\sigma_{22} = 0.6$			
	$\xi = 0.1$		$\xi = 0.3$		$\xi = 0.1$		$\xi = 0.3$	
	γ'_{12}	γ'_{22}	γ'_{12}	γ'_{22}	γ'_{12}	γ'_{22}	γ'_{12}	γ'_{22}
0.10	2.972	2.973	2.769	2.762	2.981	2.984	2.827	2.815
0.20	2.971	2.972	2.764	2.757	2.980	2.983	2.822	2.810
0.30	2.970	2.971	2.759	2.752	2.978	2.981	2.815	2.804
0.40	2.968	2.969	2.752	2.745	2.976	2.979	2.807	2.796
0.50	2.966	2.967	2.745	2.738	2.974	2.977	2.798	2.788
0.60	2.964	2.965	2.737	2.731	2.971	2.974	2.785	2.777
0.70	2.962	2.962	2.728	2.722	2.967	2.969	2.768	2.762
0.80	2.959	2.959	2.718	2.712	2.961	2.963	2.746	2.743
0.90	2.955	2.956	2.706	2.701	2.951	2.954	2.713	2.718
0.99	2.952	2.952	2.693	2.690	2.938	2.940	2.667	2.687

mole fraction, and diameter ratio according to its definition (10). The resulting expression for the average value of the attraction parameter is

$$\epsilon_0 = \frac{\sum \sum x_i x_k \epsilon_{ik} \sigma_{ik}^\gamma}{\sum \sum x_i x_k \sigma_{ik}^\gamma} \quad (12)$$

With the mixing rules (3) and (4), eqn. (11) finally reduces to a simple expression for a pure fluid

$$A^{\text{att}} = \frac{2\pi N}{V} \epsilon_0 \sigma_0^3 \int_0^\infty \tilde{u}(\tilde{r}) g_0(\tilde{r}) \tilde{r}^2 d\tilde{r} \quad (13)$$

This expression will later be identified with the (integrated) attractive term of an equation of state for real pure fluids. We have, therefore, arrived at an extended one-fluid formalism, namely a combination of a pure fluid equation (11) with a set of mixing rules (3) and (4). It is important to note that these mixing rules pertain to the attractive contribution to the Helmholtz energy only: the mixing rules within the repulsive contribution, where averaging of covolumes or similar parameters related to σ_{ik}^3 is preferred, are not affected by the considerations of this section.

Calculation of γ

The exponent γ has to be determined by integration of the appropriate hard sphere radial distribution functions. These can be generated in the Percus–Yevick approximation by means of Baxter’s formalism (Baxter, 1970; Fischer and Lago, 1983). For numerical convenience we have tabu-

lated γ values of binary mixtures for many densities, compositions, and diameter ratios, and then constructed interpolation functions. The shapes of these functions depend on the attractive potential function.

In the case of a shallow constant potential with an infinite range, which is the potential that leads to the van der Waals equation of state, the evaluation of eqn. (10) yields $\gamma = 3$. The same value of the exponent is obtained, if all radial distribution functions $g_{ik}(\tilde{r})$ and $g_0(\tilde{r})$ coincide. Therefore, the van der Waals mixing rules (1) and (2) are recovered as a special case.

For the practical calculation of γ values it is advantageous not to utilize eqn. (10), because this requires the averages $g_0^{\text{hs}}(r)$ and σ_0 to be known in advance, but to use one of the components, e.g. component 1, as a reference

$$\gamma'_{ik} = 3 + \ln \left(\frac{\int \tilde{u}(\tilde{r}) g_{ik}^{\text{hs}}(\tilde{r}) \tilde{r}^2 d\tilde{r}}{\int \tilde{u}(\tilde{r}) g_{11}^{\text{hs}}(\tilde{r}) \tilde{r}^2 d\tilde{r}} \right) / \ln \left(\frac{\sigma_{ik}}{\sigma_{11}} \right) \quad (14)$$

As long as the γ'_{ik} from this equation agree with each other, they agree with the γ_{ik} from eqn. (10) too. Generally, the different γ_{ik} turn out to agree quite well, except for high densities or extreme diameter ratios. But, then the Percus–Yevick treatment of the rigid-sphere problem is no longer accurate either. The results for two pair potentials, which have proven useful for the description of real fluids, namely the square well 1.5 and Lennard–Jones 12/6, are given in the following sections.

Square-well potential

The range of the potential is assumed to be 1.5 diameter units

$$\tilde{u}(\tilde{r}) = \begin{cases} -1 & \text{if } \tilde{r} \leq 1.5 \\ 0 & \text{if } \tilde{r} > 1.5 \end{cases} \quad (15)$$

The resulting interpolation formula for γ is

$$\gamma = \alpha + 0.4895655 \left(\frac{\xi}{1-\xi} \right)^{5/4} \sum_i^C q_i \sum_k^C \ln(\sigma_{ii}/\sigma_{kk}) \quad (16)$$

$$\text{with } \alpha = 3(1 - \xi^2) \text{ (main density effect)} \quad (17)$$

$$\xi = \frac{\pi}{6} \frac{N}{V} \sum_i^C x_i \sigma_{ii}^3 \text{ (reduced density)} \quad (18)$$

$$\text{and } q_i = \frac{x_i \sigma_{ii}^\alpha}{\sum_k^C x_k \sigma_{kk}^\alpha} \text{ (contact site fraction)} \quad (19)$$

This expression for γ is based on radial distribution functions of rigid sphere mixtures with densities ξ up to 0.45 and diameter ratios up to 2.5.

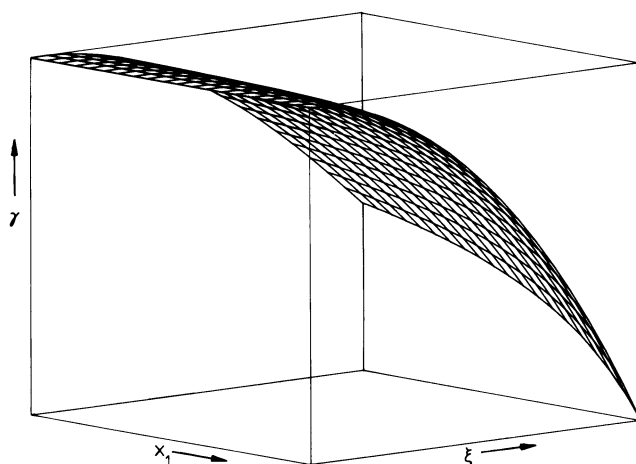


Fig. 1. Composition and density dependence of the mixing rule exponent for binary mixtures with a square-well 1.5 potential: diameter ratio, 0.6 (index '1' refers to the smaller component); mole fraction range, 0–1; reduced density range, 0–0.5; exponent range, 2.4–3.0.

As it turns out from the integration of the radial distribution functions, γ indeed approaches 3 at low densities, but decreases to values near 2.4 for high densities. It also depends slightly on the diameter ratio and the composition of the mixture. Figure 1 shows the functional behaviour of γ for a binary square-well fluid.

The good agreement of γ'_{12} and γ'_{22} for the square-well 1.5 potential is probably due to the fact that the radial distribution functions have their first

TABLE 2

Mixing rule exponents for equimolar binary mixtures at $\xi = 0.3$, calculated for square-well potentials of variable width w

w	$\sigma_{11}/\sigma_{22} = 0.8$		$\sigma_{11}/\sigma_{22} = 0.6$		$\sigma_{11}/\sigma_{22} = 0.4$	
	γ'_{12}	γ'_{22}	γ'_{12}	γ'_{22}	γ'_{12}	γ'_{22}
1.1	3.196	3.231	3.152	3.224	3.100	3.206
1.2	3.061	3.079	3.050	3.090	3.038	3.104
1.3	2.935	2.939	2.954	2.967	2.978	3.009
1.4	2.827	2.822	2.868	2.864	2.921	2.928
1.5	2.745	2.738	2.798	2.788	2.871	2.865
1.6	2.697	2.696	2.748	2.746	2.830	2.819
1.7	2.688	2.700	2.724	2.740	2.799	2.787
1.8	2.719	2.751	2.726	2.757	2.776	2.773
1.9	2.789	2.838	2.747	2.791	2.761	2.773
2.0	2.882	2.931	2.779	2.837	2.752	2.788

minimum near $1.5\sigma_{ij}$. Table 2 shows the dependence of the γ exponents on the width of the square-well potential. The values approach 3 for wide potentials, but at the same time the agreement of γ'_{12} and γ'_{22} deteriorates somewhat. For short-ranging potentials the exponents merely reflect the $g_{ij}(r)$ values at contact and may have values above 3.

Lennard–Jones 12/6 potential

In contrast to the square-well potential there is more than one convention by which the Lennard–Jones potential can be divided into a repulsive and an attractive function. We have calculated γ values for two different cases:

(1) The potential is split at its minimum according to Weeks et al. (1971)

$$\tilde{u}(\tilde{r}) = \begin{cases} -1 & \text{if } \tilde{r} \leq 2^{1/6} \\ 4(\tilde{r}^{-12} - \tilde{r}^{-6}) & \text{if } \tilde{r} > 2^{1/6} \end{cases} \quad (20)$$

The interpolation function for γ is

$$\gamma = \alpha + 0.030897\xi^{3/7} \sum_i^C q_i \sum_k^C \ln(\sigma_{ii}/\sigma_{kk}) \quad (21)$$

$$\text{with } \alpha = 3 \left(1 - \frac{\xi^{3/2}}{4} \right) \quad (22)$$

(2) The potential is split at zero energy

$$\tilde{u}(\tilde{r}) = \begin{cases} 0 & \text{if } \tilde{r} \leq 1 \\ 4(\tilde{r}^{-12} - \tilde{r}^{-6}) & \text{if } \tilde{r} > 1 \end{cases} \quad (23)$$

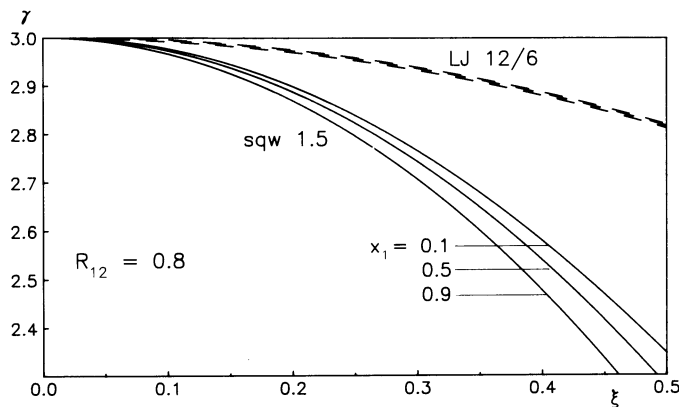


Fig. 2. Density dependence of the mixing rule exponent for binary mixtures with square-well 1.5 potentials (—) and Lennard–Jones 12/6 potentials split at their minimum (— —).

The interpolation function for γ is

$$\gamma = \alpha + 0.046889\xi^{3/5} \sum_i^C q_i \sum_k^C \ln(\sigma_{ii}/\sigma_{kk}) \quad (24)$$

$$\text{with } \alpha = 3 \left(1 - \frac{4\xi^{1.6}}{11} \right) \quad (25)$$

ξ and q_i are defined as before (eqns. (18) and (19)). Because of the wider range of the Lennard–Jones potential, its γ exponents are closer to the limiting value 3 than the exponents of the square-well 1.5 potential. For the Lennard–Jones potential the γ exponents are less dependent on composition and size ratio: the agreement between γ'_{12} and γ'_{22} is not quite as good as it is for the square-well potential. The density and concentration dependence of γ for a Lennard–Jones potential (split at its minimum) is compared to that of a square-well fluid in Fig. 2.

Quasichemical correction

The γ -exponent as defined by eqn. (10) does not account for the effect of the attractive potentials on the radial distribution functions. To compensate for this disadvantage, at least partially, we attempt a nonrandomness correction according to a quasichemical model.

The quasichemical theory of Guggenheim (1952) yields the following equation for the average attractive energy parameter of a binary mixture of molecules with equal sizes

$$\epsilon_0 = \epsilon_{11}x_1(1 - Wx_2) + 2\epsilon_{12}x_1x_2W + \epsilon_{22}x_2(1 - Wx_1) \quad (26)$$

$$\text{with } W = \frac{2}{1 + \sqrt{\left(1 + 4x_1x_2 \left[\exp\left(-\frac{\Delta\epsilon}{kT}\right) - 1 \right] \right)}}$$

$$\text{and } \Delta\epsilon = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$$

The generalization of eqn. (26) to spherical molecules of different sizes is possible approximately. Such a generalization has to account for the fact that coordination numbers for unlike molecules depend on their size ratios. In analogy to a treatment published earlier (Deiters, 1983a), we shall assume that each molecule i has zs_{ii} contact sites (z = average coordination number) and that each neighbour of species k occupies s_{ik} contact sites. Then the energy per contact site is ϵ_{ik}/s_{ik} . The maximum number of nearest neighbours of the same species to an i molecule is given by $zs_{ii}/s_{ii} = z$ = constant, whereas the maximum number of neighbours of species k is zs_{ii}/s_{ik} and depends on the ratio of s -parameters, and therefore on the

diameter ratio. If the contact sites are treated as independent from each other, the quasichemical equation of Guggenheim can be solved analytically: the result is similar to eqn. (26), but now all mole fractions must be replaced by 'contact site fractions' and all interaction energies by 'energies per contact site'

$$\left(\frac{\epsilon}{s}\right)_0 = \frac{\epsilon_{11}}{s_{11}} q_1(1 - Wq_2) + 2\frac{\epsilon_{12}}{s_{12}} q_1q_2W + \frac{\epsilon_{22}}{s_{22}} q_2(1 - Wq_1) \quad (27)$$

$$\text{with } W = \frac{2}{1 + \sqrt{\left(1 + 4q_1q_2 \left[\exp\left(-\frac{\Delta\epsilon}{kT}\right) - 1\right]\right)}}$$

$$q_i = \frac{x_i s_{ii}}{x_1 s_{11} + x_2 s_{22}} \quad (\text{contact site fraction})$$

$$\Delta\epsilon = \left(2\frac{\epsilon_{12}}{s_{12}} - \frac{\epsilon_{11}}{s_{11}} - \frac{\epsilon_{22}}{s_{22}}\right) \frac{2s_{12} + s_{11} + s_{22}}{4} \quad (\text{contact exchange energy})$$

In analogy to eqn. (27) an 'average number of molecules per contact' can be defined by

$$\left(\frac{1}{s}\right)_0 = s_{11}^{-1} q_1(1 - Wq_2) + 2s_{12}^{-1} q_1q_2W + s_{22}^{-1} q_2(1 - Wq_1) \quad (28)$$

From eqns. (27) and (28) the average interaction energy is obtained as

$$\epsilon_0 = \left(\frac{\epsilon}{s}\right)_0 / \left(\frac{1}{s}\right)_0 \quad (29)$$

This is the mixing rule for the energy parameter which is used in the following sections. The s_{ik} are related to the molecular diameters: by combining previous results (Deiters, 1983a) with the recent theory of the γ exponent, we obtain the following definitions for the s_{ik}

$$s_{ii} \sim \sigma_{ii}^\gamma \quad s_{ik} \sim \left(\frac{2}{\frac{1}{\sigma_{ii}} + \frac{1}{\sigma_{kk}}}\right)^\gamma \quad (30)$$

The proportionality constant is not important, because only ratios of s_{ik} parameters appear in the mixing rules. For numerical convenience we set the s value of the smallest molecule in a mixture equal to 1.

For high temperatures, or small values of the contact exchange energy, W becomes 1 and eqn. (27) reduces to

$$\left(\frac{\epsilon}{s}\right)_0 = \frac{\epsilon_{11}}{s_{11}} q_1^2 + 2\frac{\epsilon_{12}}{s_{12}} q_1q_2 + \frac{\epsilon_{22}}{s_{22}} q_2^2 \quad (31)$$

Equation (28) behaves similarly. Inserting eqn. (31) and the analogous high temperature limit of (28) into the mixing rule (29) and using the relations between the s_{ik} and the σ_{ik} leads to the following expression for the average interaction energy

$$\epsilon_0 = \frac{x_1^2 \epsilon_{11} \sigma_{11}^\gamma + 2x_1 x_2 \epsilon_{12} \sigma_{12}^\gamma + x_2^2 \epsilon_{22} \sigma_{22}^\gamma}{x_1^2 \sigma_{11}^\gamma + 2x_1 x_2 \sigma_{12}^\gamma + x_2^2 \sigma_{22}^\gamma} \quad (32)$$

This result agrees with the previously derived mixing rule (12). Therefore, eqn. (29) has indeed (12) as its high-temperature limit.

The identification of the quasichemical energy parameters with pair potential parameters, the treatment of 'contact sites' as independent entities, and the assumption of full interaction between nearest neighbours (and no interaction with more distant molecules) are strong simplifications of reality. However, the quasichemical model outlined above is not used as the starting point for all further thermodynamic considerations, but only as a minor correction to a mixing rule.

For most real systems the contact exchange energy is so small in comparison to kT that the quasichemical correction has little effect. However, there are cryogenic applications (see next section), where it may not be safe to neglect this correction.

APPLICATION

If the new mixing rule of the energy parameter is introduced into an equation for the Helmholtz energy of a pure fluid, and the resulting expression is applied to the calculation of phase equilibria in mixtures, a mathematical problem is encountered: because of the additional density and composition dependence, which is introduced into the Helmholtz energy equation through the new mixing rules, the formal differentiation of this equation in order to obtain the pressure or the chemical potentials is—although straightforward—rather time-consuming, at least, in connection with the complicated non-cubic equations of state which are considered below. It is therefore advantageous to utilize numerical differentiation. An algorithm for the calculation of phase equilibria which avoids the explicit calculation of chemical potentials or fugacities has been described previously (Deiters, 1985): an algorithm for the calculation of densities for given pressures and temperatures is outlined in the appendix. As a consequence, it is possible to write a computer program for the calculation of phase equilibria, or other mixture properties, in which only one subroutine, namely the Helmholtz energy calculation, depends on the thermodynamical model used.

Square-well equation of state

The mixing rule (29) is introduced into the following equation of state, which is based on the assumption of a square-well potential for the intermolecular interaction (Deiters, 1981, 1982a)

$$A_m(V_m, T, \vec{x}) = RTc_0 \frac{4\xi - 3\xi^2}{(1 - \xi)^2} - \frac{Rb\epsilon}{Vc^2k} \\ \times \left(h_0(c) \tilde{T} (\exp(\tilde{T}^{-1}) - 1) + \sum_j \sum_k \sum_l p_{jkl} \rho^j \tilde{T}^{-k} (c-1)^l \right) \\ + \sum_i^c x_i (A_{mi}(V_m^+, T) + RT \ln x_i) - RT \ln V_m \quad (33)$$

$$\text{with } \rho = \frac{b}{V_m}, \xi = \frac{\pi\sqrt{2}}{6} \rho, c_0 = 0.6887, \tilde{T} = \frac{ckT}{\epsilon}$$

$$\text{and } h_0(c) = 7.0794046(1 - 0.697816(c-1)^2)^2.$$

Here, the integrated form of the equation of state, i.e., the Helmholtz energy equation is given. The attractive term of this equation is identified with eqn. (13). Into the repulsive part of eqn. (33) quantum corrections can be introduced (Deiters, 1983b): they do not interfere with the new mixing rule. The terms $A_{mi}(V_m^+, T)$ denote Helmholtz energy contributions of the pure components of the mixture in the reference state, i.e., at the very large volume V_m^+ in the perfect gas state. The Helmholtz energy eqn. (33) contains several universal constants (c_0, p_{jkl}) and auxiliary functions, which have been explained in the original publications.

The following mixing rules are used

$$c = x_1 c_{11} + x_2 c_{22} \quad (34)$$

$$b = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad (35)$$

Equation (29) in connection with eqns. (27), (28), (30) and (16) serves as a mixing rule for the attractive energy parameter. The combining rules are

$$\epsilon_{12} = \theta(\epsilon_{11}\epsilon_{22})^{1/2} \quad (36)$$

$$b_{12} = \frac{\zeta}{2}(b_{11} + b_{22}) \quad (37)$$

$$\frac{\sigma_{22}}{\sigma_{11}} = \psi \left(\frac{c_{11}}{c_{22}} \right)^2 \left(\frac{b_{22}}{b_{11}} \right)^{1/3} \quad (38)$$

The introduction of a third binary parameter, ψ , might be regarded as a step

in the wrong direction as far as the development of a predictive calculation method is concerned. In fact, for a mixture of rigid spheres, ψ should be equal to 1. Real molecules, however, have softly repulsive potential functions, which may even be non-conformal. Therefore a ψ value different from 1 may be physically reasonable. When θ , ζ and ψ are calculated from experimental fluid equilibrium data, it is usually observed that ζ and ψ are strongly correlated. At least, for hydrogen-containing mixtures, ψ can be predicted by

$$\psi = \frac{b_{22} + (\zeta - 1)(b_{11} + b_{22})}{b_{11} + (\zeta - 1)(b_{11} + b_{22})} \left(\frac{b_{11}}{b_{22}} \right) \quad (39)$$

where the first fraction is the ratio of the partial covolumes at infinite dilution. So it is often possible to use two adjustable parameters only, even if a ψ value different from 1 is required.

To demonstrate the superiority of the new mixing rule, we calculated phase diagrams of several cryogenic mixtures, because for such mixtures the

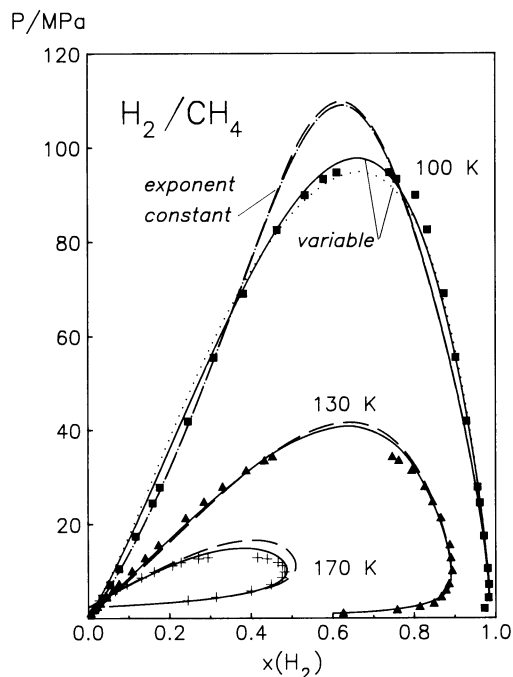


Fig. 3. Phase diagram of the hydrogen/methane system: ■, ▲, +, experimental data (Tsang et al., 1980); curves calculated from eqn. (33) (---) $\gamma = 3$, (- · -) $\gamma = 2$, (·····) γ density dependent ($\gamma = \alpha$, eqn. 17), (—) γ density and composition dependent (eqn. 16). ψ has been fitted to the experimental data.

diameter ratio can become rather large and experimental data for a large range of densities are available. Unfortunately, it is quite difficult to relate the success or failure of a phase equilibrium calculation to one element of the calculation procedure alone: usually the equation of state, the mixing rules, and the combining rules are tested simultaneously. To produce a conclusive test of the new mixing rule, we calculated isothermal phase equilibria of the hydrogen/methane system using four different formulas for the exponent γ , namely

$\gamma = 3$ (van der Waals rule)

$\gamma = 2$ (weight factors determined by contact surfaces)

$\gamma = 3(1 - \xi^2)$ (as eqn. (16), but composition and size dependence neglected)
eqn. (16)

In each case ψ has been treated as an adjustable parameter. Beyond its possible physical meaning, a second argument for the fitting of ψ is that it compensates eventual shortcomings of the combining rules and eliminates their influence on the results of the calculations. The same parameter set is used for all temperatures, of course.

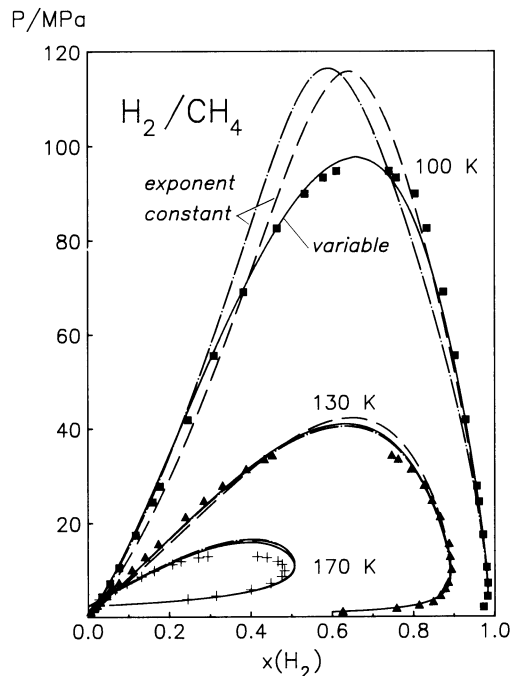


Fig. 4. Phase diagram of the hydrogen/methane system. ψ has been calculated from eqn. (39). For an explanation of symbols see Fig. 3.

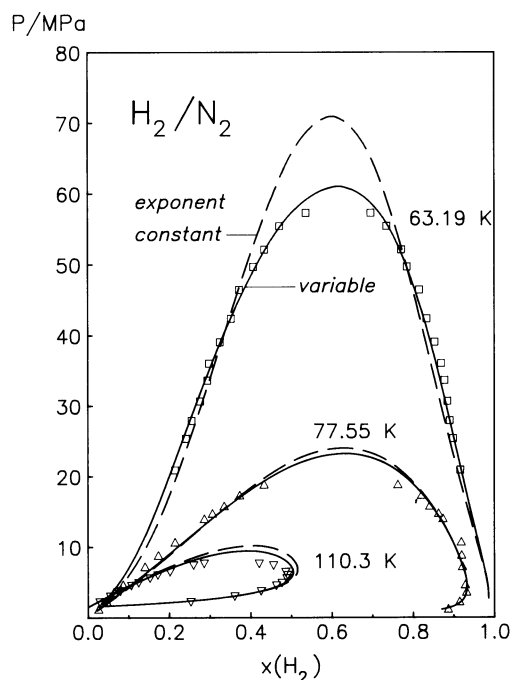


Fig. 5. Phase diagram of the hydrogen/nitrogen system: □, Δ, ▽ experimental data (Streett et al., 1978); curves calculated from eqn. (33) (---) $\gamma = 2$ or 3, (—) γ variable (eqn. 16).

From Fig. 3 it is evident that the mixing rules with constant exponents are not able to represent the experimental data (Tsang et al., 1980) at high pressures properly, whereas the density-dependent mixing rules perform quite well. If the variable exponent is also made concentration- and size-dependent, the results are slightly better than with a solely density-dependent γ . Of course, it is possible to obtain a better representation of the experimental 100 K isotherm with a constant γ , if θ , ζ and ψ are exclusively fitted to this isotherm, but then the prediction of the 170 K isotherm deteriorates significantly.

The close agreement of the $\gamma = 2$ and $\gamma = 3$ isotherms is due to the adjustable ψ parameter, which compensates the effect of the exponent to some extent. Figure 4 shows the results if ψ is not fitted but calculated from eqn. (39).

Figure 5 contains several isotherms of the H₂/N₂ system (Streett and Calado, 1978). Because of the lower densities, the $\gamma = 2$ and the $\gamma = 3$ isotherms (ψ is adjustable) almost coincide here. Again, the density-dependent mixing rule turns out to be superior.

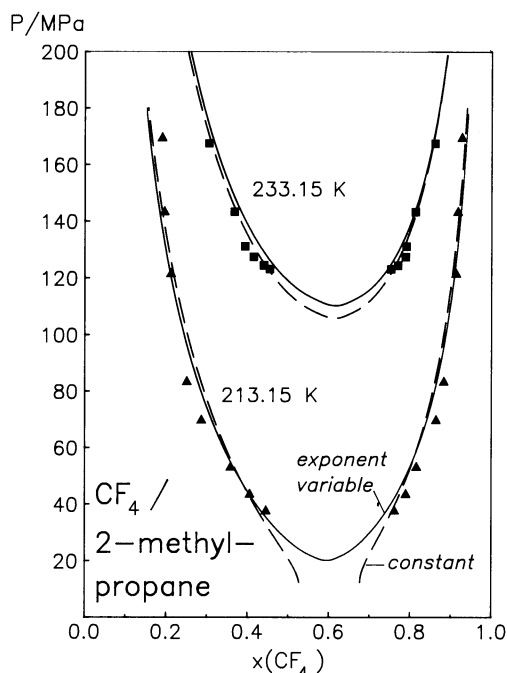


Fig. 6. Phase diagram of the tetrafluoromethane/isobutane system. ■, ▲ experimental data (Wisotzki, 1984); curves calculated from eqn. (33) (---) $\gamma = 3$, (—) γ density and composition dependent (eqn. 16).

In the system CF_4 /isobutane, the critical line of the liquid–liquid immiscibility has a positive slope, so that the isothermal phase diagrams show lower critical points (Wisotzki, 1984). Both isotherms in Fig. 6 are represented rather well by the calculations with $\gamma = 3$ and with variable γ over a wide pressure range, but only the calculation with density-dependent mixing rules describes the behaviour at low pressures at 213 K in accordance with the experiment (prediction of a critical point), whereas the calculation with constant exponent fails (prediction of overlap with vapour–liquid equilibrium).

Lennard–Jones 12/6 mixtures

It is possible to numerically calculate the radial distribution functions and the thermodynamic properties of mixtures of Lennard–Jones particles by perturbation theory (Fischer and Lago, 1983). Although such a calculation consumes so much computer time that it is not practical to use within phase equilibrium calculations, it can still be used to test the predictions of (modified) one-fluid theory. Table 3 shows the residual Helmholtz energies

TABLE 3

Dimensionless residual Helmholtz energies $a = A_m^{\text{res}}/RT$ for equimolar Lennard-Jones 12/6 mixtures.Parameters: $\epsilon_{11}/k = 119.8 \text{ K}$, $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$, $\sigma_{11} = 0.3405 \text{ nm}$, $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$

$\frac{\epsilon_{22}}{\epsilon_{11}}$	$\frac{\sigma_{22}}{\sigma_{11}}$	$T \text{ (K)}$	$\frac{N\sigma_0^3}{V}$	a Direct ^a	a $\gamma = 3$	a $\gamma = 2$	γ^b	a^b	γ^c	a^c
2.5	1.25	400	0.3	-0.3211	-0.3177	-0.2959	2.954	-0.3167	2.945	-0.3165
		400	0.6	-0.4271	-0.4236	-0.3772	2.869	-0.4175	2.831	-0.4158
		400	0.9	+0.2939	+0.2700	+0.3334	2.759	+0.2852	2.675	+0.2906
3.5	1.50	300	0.9	-0.6619	-0.6926	-0.6002	2.759	-0.6704	2.675	-0.6626
		500	0.3	-0.4057	-0.3987	-0.3477	2.956	-0.3965	2.947	-0.3961
		500	0.6	-0.5939	-0.5964	-0.4872	2.872	-0.5826	2.834	-0.5785
		500	0.9	+0.1646	+0.0320	+0.1830	2.762	+0.0676	2.679	+0.0801

^a Result of perturbation theory for the binary mixture.^b Eqn. (21).^c Eqn. (24).

of equimolar Lennard–Jones mixtures at various densities together with the one-fluid theory predictions. These have been obtained with the same computer program by setting the energy and diameter ratios to 1 and replacing all interaction parameters with average values.

The residual Helmholtz energies from pure fluid perturbation theory in connection with density-dependent mixing rules agree reasonably well with the results from the direct solution of perturbation theory for mixtures. A perfect agreement should not be expected for several reasons: the density-dependent mixing rules do not fully account for the influence of attractive potentials on fluid structure: furthermore, for the calculation of the variable exponents, the rigid sphere diameters σ_{ii} in eqn. (18) have been set equal to the Lennard–Jones size parameters, which may not be an optimal choice for some densities and temperatures. Nevertheless, it is evident from Table 3 that the mixing rules with constant exponents are useful in a narrow density range only, whereas density-dependent mixing rules can be applied over a wider range.

As an additional test for the effect of density-dependent mixing rules on the representation of fluid properties, we have applied the mixing rule (29) in connection with (21) to an equation of state for the Lennard–Jones fluid, namely the Nicolas equation (Nicolas et al., 1979). This equation of state is of the Benedict–Webb–Rubin type and contains 32 coefficients. Since the original paper does not explicitly give the Helmholtz energy expression, we present it here for convenience

$$A_m(V_m, T, \vec{x}) = R \frac{\epsilon}{k} \left(\sum_{j=1}^8 j^{-1} p_j \rho^j + \sum_{n=0}^5 n! \frac{p'_n}{2D} \left(D^{-n} - e^{-D\rho^2} \sum_{j=0}^n \frac{D^{-j} \rho^{2(n-j)}}{(n-j)!} \right) \right) + \sum_i^C x_i (A_{mi}(V_m^+, T) + RT \ln x_i) - RT \ln V_m \quad (40)$$

with $\rho = N\sigma^3/V$ and $D = 3$.

The coefficients p_j and p'_j are simple functions of the reduced temperature, which can easily be identified with expressions in the original publication.

Again, we have chosen the H_2/CH_4 system as the test mixture and calculated its phase equilibria at high pressures (Fig. 7). The mixing and combining rules are the same as before. It is not surprising that the Nicolas equation does not lead to such a good agreement of calculated and experimental equilibrium states as the square-well equation of state (33): the Nicolas equation has been designed to fit the PVT properties of the hypothetical Lennard–Jones fluid, whereas (33) is a semiempirical equation of state which describes the behaviour of real fluids. However, the Nicolas equation has been used as an isotropic reference equation of state within the

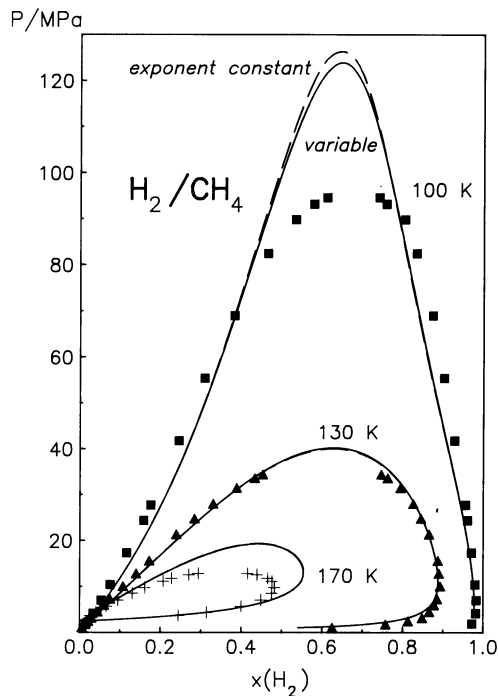


Fig. 7. Phase diagram of the hydrogen/methane system. Curves calculated from the Nicolas equation of state (40): for an explanation of symbols see Fig. 3.

perturbation theory of fluids (Clancy and Gubbins, 1981), and, therefore, its behaviour with respect to density-dependent mixing rules has some practical importance.

In Fig. 7 the differences between the equilibrium compositions calculated with density-dependent mixing rules and the van der Waals rules, respectively, show at very high pressures only. But, as in Fig. 3, three binary parameters have been fitted to the experimental data, and so Fig. 7 shows only those differences that cannot be compensated by the adjustable binary parameters. The differences between the phase diagrams calculated from the same set of parameters would be very much larger. In this context, it is interesting to note that the calculation with density-dependent mixing rules requires smaller deviations of the binary parameters from the Lorentz–Berthelot rule (e.g. density-dependent, $\theta = 1.18$; van der Waals, $\theta = 1.22$).

DISCUSSION

A detailed study of the structure of mixtures of rigid spheres shows that their radial distribution functions differ by more than only a distance scaling

factor, so that the van der Waals mixing rules do not strictly hold. But by assuming a variable exponent in the mixing rules it is possible to take the dissimilarities of the radial distribution functions into account to some extent, while the mathematical structure of the one-fluid theory is retained. So it is relatively easy to introduce the new density-dependent mixing rule into well-established equations of state for pure fluids. (The application of density-dependent mixing rules to cubic equations of state is discussed in the Appendix).

The functional dependence of the variable exponent on density, composition and size ratios is determined by the shape of the attractive intermolecular potential. If the new density-dependent mixing rules are to be used in connection with an equation of state, it is necessary to know the potential function on which this equation of state is based.

Although the evaluation of the variable exponents from the hard sphere radial distribution functions is a theoretically rigid procedure, the interpolation functions for γ , which have been used in this work, are purely empirical expressions. The limitations of the Percus–Yevick method, the uncertainties of numerical integrations, and the resulting differences between the γ'_{ik} made the development of better interpolation functions impossible: in view of their influence on phase equilibria, the present set of interpolation functions seems to be sufficient.

The density-dependent mixing rules lead to a significantly better representation of phase equilibria and thermodynamic functions in connection with a square-well equation of state as well as for Lennard–Jones mixtures. Usually the density-dependent mixing rules improve the calculation of the vicinity of critical points at high densities: one might say that the density-dependent mixing rules have a positive influence on the critical lines of liquid–liquid immiscibilities, gas–gas equilibria, and high-pressure vapour–liquid equilibria. The application of the new mixing rules to a number of hydrocarbon mixtures, for which it is superfluous to present phase diagrams, shows that the influence on low-pressure vapour–liquid equilibria is only marginal. So there are ranges of pressure and temperature where the density-dependence of the mixing rules may be safely neglected (and the validity of the van der Waals rules assumed), whereas, with equilibria between dense phases, the density-dependent mixing rules may have a decisive effect.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. J. Fischer and U. Heinbuch from the Institut für Thermo- und Fluidodynamik, Ruhr-Universität Bochum, for making available computer programs for the calcula-

tion of structural and thermodynamical properties of mixtures of rigid spheres or Lennard–Jones particles. He also thanks Professor G.M. Schneider for friendly support of this work. Financial support by the Deutsche Forschungsgemeinschaft and by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen is gratefully acknowledged.

APPENDIX

Calculation of densities

The calculation of densities or molar volumes for a given pressure and temperature is one of the most frequently taken steps in a phase equilibrium calculation. Because of the density-dependent mixing rules it is not only impossible to reduce the equation of state (33) to a polynomial in density, but even the differentiation of (33) in order to obtain the pressure is rather cumbersome. Therefore, an algorithm is proposed that makes use of the residual Helmholtz energy only and obtains all other variables by numerical differentiation.

It is advantageous to perform the calculation in terms of reduced densities

$$\rho = \frac{V_{\min}}{V_m} \quad (\text{A1})$$

where V_{\min} is the smallest physically reasonable molar volume of the fluid mixture under consideration, so that $0 \leq \rho \leq 1$. Usually V_{\min} is a multiple of the covolume.

Let a dimensionless residual Helmholtz energy be defined by

$$a(V_m, T, \vec{x}) = \frac{1}{RT} A_m(V_m, T, \vec{x}) + \ln V_m - \sum_i^c x_i \left(\frac{1}{RT} A_{mi}(V_m^+, T) + \ln x_i \right) \quad (\text{A2})$$

where $A_{mi}(V_m^+, T)$ denotes the molar Helmholtz energy of the pure component i in the perfect gas state (very large molar volume V_m^+) and $A_m(V_m, T, \vec{x})$ the molar Helmholtz energy of the mixture with the concentration vector \vec{x} . Since, in this section, only the density dependence of the Helmholtz energy is of interest, we shall denote the dimensionless residual Helmholtz energy by $a(\rho)$. The pressure and its density derivative can then be written as

$$P(\rho) = - \left(\frac{\partial A}{\partial V} \right)_{T, \vec{x}} = \frac{RT}{V_{\min}} \left(\rho^2 \frac{\partial a(\rho)}{\partial \rho} + \rho \right) \quad (\text{A3})$$

$$\frac{\partial P(\rho)}{\partial \rho} = \frac{RT}{V_{\min}} \left(1 + 2\rho \frac{\partial a(\rho)}{\partial \rho} + \rho^2 \frac{\partial^2 a(\rho)}{\partial \rho^2} \right) \quad (\text{A4})$$

The derivatives of $a(\rho)$ can be replaced by difference quotients:

$$\frac{\partial a(\rho)}{\partial \rho} = \frac{1}{2\delta\rho} (a(\rho + \delta\rho) - a(\rho - \delta\rho)) \quad (\text{A5})$$

$$\frac{\partial^2 a(\rho)}{\partial \rho^2} = \frac{1}{\delta\rho^2} (a(\rho + \delta\rho) - 2a(\rho) + a(\rho - \delta\rho)) \quad (\text{A6})$$

Calculating the density ρ at the given pressure P^0 , i.e., solving the equation $P(\rho) = P^0$, can be accomplished by Newton's algorithm

$$\rho := \rho - \frac{P(\rho) - P^0}{\frac{\partial P(\rho)}{\partial \rho}} \quad (\text{A7})$$

By combining the eqns. (A3)–(A7) the iteration prescription is obtained as

$$\begin{aligned} \rho := \rho & \left(\left(\frac{P^0}{RT} V_m + \frac{\rho}{2\delta\rho} (a(\rho + \delta\rho) - a(\rho - \delta\rho)) + \left(\frac{\rho}{\delta\rho} \right)^2 (a(\rho + \delta\rho) \right. \right. \\ & \left. \left. - 2a(\rho) + a(\rho - \delta\rho)) \right) \left(1 + \frac{\rho}{\delta\rho} (a(\rho + \delta\rho) - a(\rho - \delta\rho)) \right) \right. \\ & \left. + \left(\frac{\rho}{\delta\rho} \right)^2 (a(\rho + \delta\rho) - 2a(\rho) + a(\rho - \delta\rho)) \right)^{-1} \end{aligned} \quad (\text{A8})$$

For the evaluation of eqn. (A8) it is necessary to calculate three Helmholtz energies, whereas eqn. (A7) requires only two references to thermodynamic functions ($P(\rho)$ and its derivative). If $a(\rho)$, $P(\rho)$, and $\partial P(\rho)/\partial\rho$ are equations of similar complexity, the iteration using eqn. (A8) should execute slower than the iteration using eqn. (A7) and formal differentiation by a factor 1.5. But, if, as is often the case, the thermodynamic functions grow more complicated by differentiation, the iteration by means of eqn. (A8) may even become faster.

As long as the slope $\partial P(\rho)/\partial\rho$ is positive, the iteration converges rapidly towards the nearest solution. If a liquid-type solution is expected, the initial value of ρ should be on the liquid branch of the $P(\rho)$ diagram, namely close to 1: if a gas-type solution is expected, the initial value should be on the gas branch and can be calculated from the perfect gas law. If a negative slope is encountered, the iteration becomes unstable: it must be re-started with an initial value on another branch than before.

If, during the iteration, the object function $P(\rho) - P^0$ changes its sign, an even faster convergence can be achieved by using the regula falsi instead of Newton's algorithm. The slightly lower convergence order of the Regula falsi is usually more than compensated by the fact that it requires fewer evalua-

tions of the object function. The regula falsi does not use the local slope, so that it is not necessary to calculate $a(\rho)$ at each iteration step. But, before switching to the regula falsi, it is important to make sure that there is only one solution within its searching interval, because otherwise it is difficult to predict to which solution it will converge.

The best size of the density increment $\delta\rho$ depends on the computer. We have used increment sizes between 10^{-4} and 10^{-5} on a machine with a real precision of approximately 12 decimal digits.

Application to a cubic equation of state

To demonstrate the effect of density-dependent mixing rules on phase equilibrium calculations with simple cubic equations of state, we have applied our mixing rule (29) to the equation of Redlich and Kwong (1949) and again computed the high pressure vapour-liquid equilibria of the hydrogen/methane system. We have used the original version of the Redlich-Kwong equation with the $T^{-1/2}$ temperature dependence. To make the relationship between the Redlich-Kwong equation and the statistical thermodynamics approach more transparent, we have replaced the usual attraction parameter of the Redlich-Kwong equation by a combination of pair potential parameters

$$a_{\text{RK}} = 8R\epsilon^{1.5}\sigma^3 \quad (\text{A9})$$

The resulting expression for the Helmholtz energy of a mixture is then

$$A_{\text{m}}(V_{\text{m}}, T, \vec{x}) = -RT(\ln(1 - \rho) + 8\tilde{T}^{-1.5} \ln(1 + \rho)) \\ + \sum_i^C x_i (A_{\text{mi}}(V_{\text{m}}^+, T) + RT \ln x_i) - RT \ln V_{\text{m}} \quad (\text{A10})$$

$$\text{with } \rho = \frac{b}{V_{\text{m}}} \text{ and } \tilde{T} = \frac{kT}{\epsilon}$$

We have fitted the parameters of H_2 to PVT data in the range 100–200 K; furthermore, we have calculated isothermal phase equilibria only. Therefore, the problem of choosing the best Redlich-Kwong version (i.e., choosing the best temperature dependence of the attractive term) has little importance for these calculations.

For the application of the density-dependent mixing rules we have assumed that the Redlich-Kwong covolume parameter b is equal to four times the hard sphere volume (excluded volume model): therefore, the relation between the reduced density variables in eqns. (16)–(18) and (A10) is

$$\xi = \frac{\rho}{4} \quad (\text{A11})$$

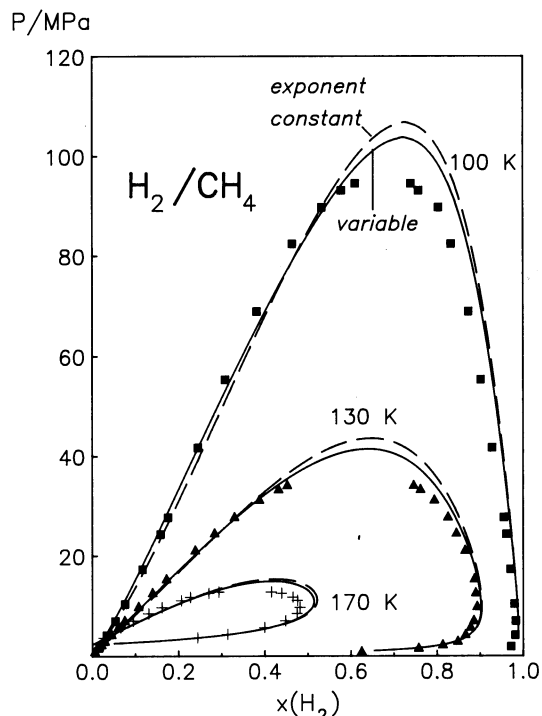


Fig. 8. Phase diagram of the hydrogen/methane system. Curves calculated from the Redlich–Kwong equation of state (A10): for an explanation of symbols see Fig. 3.

Furthermore, we have assumed that the pair potential underlying the Redlich–Kwong equation can be approximated by a square-well potential, so that the mixing rule exponent is given by eqn. (16).

Figure 8 shows the results of the phase equilibrium calculations. Again, three binary parameters have been adjusted to facilitate comparison with Figs. 3 and 7. The overall agreement of the calculated equilibrium curves with the experimental data is quite good, although the calculation yields too high critical pressures. This behaviour is often observed with cubic equations of state. Again, the calculation with density-dependent mixing rules turns out to yield better results in the critical region than the calculation with fixed mixing rule exponents. It must be pointed out, however, that the introduction of density-dependent mixing rules into a cubic equation of state turns it into a non-cubic one, and that the advantage of cubic equations of state, namely the higher computational speed, is, therefore, lost.

LIST OF SYMBOLS

- A Helmholtz energy
 a residual dimensionless Helmholtz energy

b	covolume parameter
C	number of components
c	anisotropy parameter
g	radial distribution function
k	Boltzmann's constant
N	number of particles
P	pressure
p	equation of state coefficient
q	contact site fraction
R	universal gas constant
r	distance
s	contact site ratio
T	temperature
u	intermolecular potential
V	volume
W	quasichemical correction
x	mole fraction
z	coordination number

Greek letters

α	main density influence on γ
γ	mixing rule exponent
δ	increment for numerical differentiation
ϵ	interaction energy parameter
ζ	binary covolume correction
θ	binary energy correction
ξ	reduced density (with respect to occupied volume)
ρ	reduced density (with respect to minimum volume)
σ	interaction diameter parameter
ψ	binary diameter ratio correction

Superscripts

att	attractive
hs	hard sphere
rep	repulsive
~	reduced property
+	perfect gas state

Subscripts

- i* referred to component *i*
m molar property
0 average value

REFERENCES

- Baxter, R.J., 1970. Ornstein–Zernike relation and Percus–Yevick approximation for fluid mixtures. *J. Chem. Phys.*, 52: 4559–4562.
- Clancy, P. and Gubbins, K.E., 1981. The thermodynamics of hydrogen and hydrogen–methane mixtures. *Molec. Phys.*, 44: 581–595.
- Deiters, U.K., 1981. A new semiempirical equation of state for fluids, Part I: Derivation. *Chem. Eng. Sci.*, 36: 1139–1146; Part II: Application to pure substances. *Chem. Eng. Sci.*, 36: 1147–1151.
- Deiters, U.K., 1982a. A new semi-empirical equation of state for fluids, Part III: Application to phase equilibria in binary mixtures. *Chem. Eng. Sci.*, 37: 855–861.
- Deiters, U.K., 1982b. Coordination numbers for rigid spheres of different size—estimating the number of nearest-neighbour interactions in a mixture. *Fluid Phase Equilibria*, 8: 123–129.
- Deiters, U.K., 1983a. Reply to a letter by G.H. Eduljee. *Fluid Phase Equilibria*, 12: 193–197.
- Deiters, U.K., 1983b. Special aspects of the calculation of phase equilibria in cryogenic mixtures at very high pressures. *Fluid Phase Equilibria*, 13: 109–120.
- Deiters, U.K., 1985. A modification of Newton–Raphson algorithm for phase equilibria calculations using numerical differentiation of the Gibbs energy. *Fluid Phase Equilibria*, 19: 287–293.
- Deiters, U.K., 1986. Calculation of fluid–fluid and solid–fluid equilibria in cryogenic mixtures at high pressures. In: K.C. Chao and R.L. Robinson, Jr. (Editors), *Equations of State: Theories and Applications*. ACS Symposium Series No. 300, Am. Chem. Soc., Washington DC, pp. 371–388.
- Eduljee, G.H., 1983. Coordination numbers for rigid spheres of different sizes—estimating the number of next-neighbour interactions in a mixture. *Fluid Phase Equilibria*, 12: 190–192.
- Ely, J.F., 1986. Improved mixing rules for one-fluid conformal solution calculations. In: K.C. Chao and R.L. Robinson, Jr. (Editors), *Equations of State: Theories and Applications*. ACS Symposium Series No. 300, Am. Chem. Soc., Washington DC, pp. 331–351.
- Fischer, J. and Lago, S., 1983. Thermodynamic perturbation theory for molecular liquid mixtures. *J. Chem. Phys.*, 78: 5750–5758.
- Guggenheim, E.A., 1952. *Mixtures*. Clarendon Press, Oxford, pp. 29–48.
- Hoheisel, C. and Kohler, F., 1984. Local compositions in liquid mixtures. *Fluid Phase Equilibria*, 16: 13–24.
- Lebowitz, J.L., 1964. Exact solution of the generalized Percus–Yevick equation for a mixture of hard spheres. *Phys. Rev. A*, 133: 895–899.
- Lee, K.-H., Sandler, S.I. and Patel, N.C., 1986. The generalized van der Waals partition function—III. Local composition models for a mixture of equal size square-well molecules. *Fluid Phase Equilibria*, 25: 31–49.
- Mansoori, G.A., Carnahan, N.F., Starling, K.E. and Leland, T.W., 1971. Equilibrium thermodynamic properties of the mixture of hard spheres. *J. Chem. Phys.*, 54: 1523–1525.

- Nicolas, J.J., Gubbins, K.E., Streett, W.B. and Tildesley, D.J., 1979. Equation of state for the Lennard-Jones fluid. *Molec. Phys.*, 37: 1429–1454.
- Redlich, O. and Kwong, J.N.S., 1949. On the thermodynamics of solutions: V. An equation of state—fugacities of gaseous solutions. *Chem. Reviews*, 44: 233–244.
- Sandler, S.I., 1983. On the coordination numbers for rigid spheres. *Fluid Phase Equilibria*, 12: 189–190.
- Sandler, S.I., 1985. The generalized van der Waals partition function—I. Basic theory. *Fluid Phase Equilibria*, 19: 233–257.
- Streett, W.B. and Calado, J.C.G., 1978. Liquid–vapour equilibrium for hydrogen + nitrogen at temperatures from 63 to 110 K and pressures to 57 MPa. *J. Chem. Thermodyn.*, 10: 1089–1100.
- Tsang, C.Y., Clancy, P., Calado, J.C.G. and Streett, W.B., 1980. Phase equilibria in the H_2/CH_4 system at temperatures from 92.3 to 180.0 K and pressures to 140 MPa. *Chem. Eng. Commun.*, 6: 365–383.
- Weeks, J.D., Chandler, D. and Andersen, H.D., 1971. Role of repulsive forces in determining the equilibrium structure of simple liquids. *J. Chem. Phys.*, 54: 5237–5247.
- Wisotzki, K.-D., 1984. Doctoral dissertation: Fluid-Phasengleichgewichte und kritische Erscheinungen in den binären Systemen N_2 + Ethan, N_2 + Pentan und CF_4 + 2-Methylpropan zwischen 88 K und 313 K und bei Drücken bis 200 MPa. Ruhr-Universität Bochum.