COMBINATION RULES FOR CONSTANTS IN DIFFERENT EQUATIONS OF STATE FOR CALCULATING THERMODYNAMIC PROPERTIES OF LIQUID MIXTURES

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A new method based on the two- and three-parameter principles of corresponding states was developed for determining combination rules of constants in different pressure- or volume-explicit equations of state for use in calculating thermodynamic properties of liquid mixtures. The method employs in a consistent way the binary interaction parameters k_{ij}, which characterize the strength of the i–j interaction.

Equation-of-state approach to the calculation of thermodynamic properties of mixtures of gases or liquids is still widely used in chemical engineering. As soon as combination rules are known for evaluating constants in the equations of state of mixtures from those of the pure components, the properties of mixtures are readily calculated. However, the methods for determining these combination rules are often empirical without any theoretical justification.

This is especially true when the properties of liquids are concerned, as for gaseous mixtures some theory is offered by the virial expansion of the Helmholtz free energy or pressure in powers of density[1,2]. It is well known that this expansion can be applied neither for liquids nor for their mixtures and followingly the combination rules based on the virial expansion may be inappropriate when the properties of liquid mixtures are to be calculated. On the other hand the properties of liquid mixtures may be obtained successfully by using the principle of corresponding states, namely its one-fluid version[3–6]. A two-parameter principle of corresponding states for pure fluids may be derived by assuming a pairwise-additive intermolecular potential of the form

$$u(r) = f\varepsilon_0 \, \Phi(r^3/h\sigma_0^3) \,, \qquad (1)$$

where r is the intermolecular distance, Φ is a function common for all fluids concerned, ε_0 and σ_0^3 are force constants of the reference fluid and f and h are energy well depth- and size-scaling parameters of the particular substance. Then it is possible to show[7] that for example the compressibility factor $z = pV/RT$ of the fluid is a function only of the reduced temperature $T_r = T/f$ and the reduced volume $V_r = V/h$ as follows

$$z = F(T/f, V/h) \,. \qquad (2)$$

If we assume the same principle to hold for mixtures, which is of course only a rough approxima-

tion even when Eq. (1) is valid for all components present, then we may write for z the corresponding equation

$$z = F(T/f_x, V/h_x),\qquad(3)$$

where f_x and h_x are the scaling parameters of the so-called equivalent substance. For the case of mixtures of Lennard–Jones 6 : 12 fluids, the following rules were found to be suitable[6]

$$f_x^\eta h_x = \sum x_i x_j f_{ij}^\eta h_{ij},\quad \text{for}\quad \eta \in (1,3/2); \quad h_x^\mu = \sum x_i x_j h_{ij}^\mu, \quad \text{for}\quad \mu \in (1,4/3),\qquad(4),(5)$$

together with

$$h_{ij}^{1/3} = (h_{ii}^{1/3} + h_{jj}^{1/3})/2, \quad f_{ij} = (1 - k_{ij})\,(f_{ii} \cdot f_{jj})^{1/2},\qquad(6),(7)$$

where the constants with identical indexes refer to pure components, x_i is the mole fraction of the i-th component and the constant k_{ij} measures the strength of the $i - j$ interaction. Although the best values of η and μ were determined to be $\eta = 4/3$ and $\mu = 4/3$, for practical purposes it should be sufficient to use any values of η and μ from the ranges indicated in Eqs (4) and (5). For $\eta = \mu = 1$, the rules reduce to the van der Waals ones[5].

Most of equations of state are pressure-explicit and so they can be written both for pure components and for mixtures in the form

$$z = G(T, V, K_1, \ldots K_n),\qquad(8)$$

where n is the number of empirical constants in the equation of state. If we assume that the two-parameter principle holds both for pure components and mixtures as expressed by Eqs (2) or (3), then by comparing a particular form of Eq. (8) with Eqs (2) or (3) we find that for each of the constants $K \in (K_1, \ldots K_n)$ it must hold

$$K = f^k h^l \quad \text{for pure components}\qquad(9)$$

and

$$K = f_x^k h_x^l \quad \text{for mixtures}.\qquad(10)$$

The values of exponents k and l can be of course different for different constants K. With more complicated equations of state, the values of k and l do not coincide with the allowed range of η and μ and, moreover, we need to separate the f from the h constants for evaluating the interaction constant k_{ij} in Eq. (7). As all equations of state contain at least one constant directly related to the excluded fluid volume (such are for example the b-constants in the van der Waals or Redlich–Kwong equations or the B_0-constants in the Beattie–Bridgeman or Benedict–Webb–Rubin equations), we may determine first the combination rule for this constant denoted here as K_v by use of Eqs (5) and (6) with a convenient but fixed value of μ and by finding the value of l in Eq. (9) with the result

$$K_v^{\mu/l} = \sum x_i x_j K_{vij}^{\mu/l}, \quad K_{vij}^{1/3l} = (K_{vii}^{1/3l} + K_{vjj}^{1/3l})/2.\qquad(11)(12)$$

This procedure may be adopted for all constants which do not contain the f-constant. For the remaining K constants we may proceed similarly with a convenient but fixed value of η in Eq. (4) by employing the value of h_x determined from the constant K_v and by finding corresponding values of k and l in Eq. (9) from the equation of state. Thus, for the van der Waals equation of state and for $\mu = \eta = 1$ we obtain $b = h$ and

$$K_v \equiv b = \sum x_i x_j b_{ij} \qquad (13)$$

and from $a = fh \equiv fb$

$$a = \sum x_i x_j a_{ij}. \qquad (14)$$

These rules coincide with the original van der Waals ones only for

$$b_{ij} = (b_{ii} + b_{jj})/2, \quad a_{jj} = (a_{ii}a_{jj})^{0.5} \qquad (15)$$

but not for the relations suggested by Eqs (6) and (7)

$$b_{ij}^{1/3} = (b_{ii}^{1/3} + b_{jj}^{1/3})/2, \quad a_{ij} = (1 - k_{ij})(a_{ii}a_{jj}/b_{ii}b_{jj})^{0.5} b_{ij}. \qquad (16)$$

If we introduce the empirical factor $(1 - k_{ij})$ to a_{ij} in Eq. (15), the difference between Eqs (15) and (16) is quite negligible when correlating one property of a binary system, but the deviations may rise[8] when the same interaction constant k_{ij} is then used to calculate another property of this binary or when it is used for computing some property of a multicomponent mixture containing i and j among other components. The proposed method could be especially useful for equations of state containing more constants; the interaction constant k_{ij} could be thus introduced in a straightforward and consistent manner into the Benedict–Webb–Rubin equation of state.

For polar or asymmetric molecules Eqs (2) and (3) do not hold and we must add at least one further, dimensionless parameter Θ to obtain a three-parameter principle of corresponding states:

$$z = F(T/f, V/h, \Theta). \qquad (17)$$

For such fluids, a rule was proposed[9] for finding the value of this parameter in the mixture

$$\Theta_x = \sum x_i \Theta_i. \qquad (18)$$

This three-parameter principle of corresponding states could be also obtained from Eqs (8) and (9) if we found a constant K in an equation of state for which $k = l = 0$. However, all existing equations of state do not contain such constant explicitly

so we must expand[10] the constants K in powers of Θ as

$$K = K^0(1 + \alpha\Theta + \beta\Theta^2 + \ldots) \qquad (19)$$

to obtain the three-parameter principle of corresponding states.

For volume-explicit equations of state, Eq. (9) is replaced by

$$K = z_c^m f^{k+m} h^{-m} , \qquad (20)$$

where z_c is the critical compressibility factor. This follows from the relation between the pressure- and volume-scaling factors for fluids obeying the three-parameter principle of corresponding states. The z_c of the mixture is then calculated by Eq. (18) and the resulting combination rules for constants K are obtained by separating all three z_c, f, and h factors in Eq. (20).

Thus, we have developed a new method based on the two- and three-parameter principles of corresponding states for determining combination rules of constants in different pressure- or volume-explicit equations of state for use in calculating thermodynamic properties of liquid mixtures. This method employs in a consistent way the binary interaction parameters k_{ij}, which characterize the strength of the $i - j$ interaction. Calculations of properties of liquid mixtures using the Redlich–Kwong equation of state with the new rules are promising[8].

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