
EFFECT OF DIFFERENT COMBINATION RULES
ON EXCESS PROPERTIES OF MIXTURES OF SIMPLE LIQUIDS
AS CALCULATED BY THE ONE-FLUID THEORY
OF CORRESPONDING STATES

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The one-fluid corresponding states theory was used for correlating and predicting excess thermodynamic properties of ten binary mixtures of simple liquids. The van der Waals, or, alternatively, some recently found combination rules were used for calculating the equivalent substance parameters in the theory. The latter rules correlated the excess properties better when they were combined with a special rule for the size parameter σ_{12} in the interaction potential of unlike molecules. Attempts to predict the excess properties were successful only at four systems. The reasons for the observed discrepancies are discussed.

In a recent work¹ we have established some new combination rules for the equivalence substance parameters in the one-fluid corresponding states theory which can be used successfully for predicting thermodynamic excess functions of Lennard-Jones 12 : 6 liquid mixtures at zero pressure as found by Monte-Carlo computations. We have also shown that the two-fluid version of the corresponding states treatment did not yield satisfactory results for any combination rules tested; this conclusion has been meanwhile arrived at independently by Henderson and Leonard² for the van der Waals combination rules. The comparison with the pseudoexperimental Monte-Carlo data²² enabled us to eliminate the uncertainty usual when similar comparisons are made with excess functions of real mixtures as to whether the possible discrepancies between a theory and experiments are due to the inaccuracy of the theory or to the unknown nature of intermolecular forces. If we now compare the results of the one-fluid corresponding states theory using the new combination rules with experiments on mixtures of simple liquids, the possible discrepancies between the theory and experiments may be ascribed mainly to the following reasons: 1. occasional random discrepancies between the theoretical and Monte-Carlo computations in our previous work¹, 2. inadequacy of the reference fluid properties, 3. inaccuracy of pure component force constants and 4. insufficient knowledge of intermolecular interactions between unlike molecules. The second and third obstacles have been removed partially by Bellemans and coworkers³, whose reference fluid as well as pure compo-

nent force constants we will use throughout. The remaining cases are treated in this paper.

THEORETICAL

In the one-fluid corresponding states theory, the excess functions of mixtures at zero pressure are given by the following relations^{3,4}

$$G^E(T) = f_x G_0(T/f_x) - \sum_i x_i [f_{ii} G_0(T/f_{ii}) - NkT \ln (h_{ii}/h_x)], \quad (1)$$

$$H^E(T) = f_x H_0(T/f_x) - \sum_i x_i f_{ii} H_0(T/f_{ii}), \quad (2)$$

$$V^E(T) = h_x V_0(T/f_x) - x_i h_{ii} V_0(T/f_{ii}), \quad (3)$$

where G , H and V with the subscript zero stand for the Gibbs free energy, enthalpy and volume of the reference substance at zero pressure. The remaining symbols have the following meaning: N is the Avogadro's number, k Boltzmann's constant, T absolute temperature, x_i mole fraction of the i -th component, f_x and h_x energy- and size-scaling parameters of the intermolecular potential of the equivalent substance and f_{ij} and h_{ij} the corresponding properties of the intermolecular potential $u_{ij}(r)$ of molecules i and j . The intermolecular potential $u_{ij}(r)$ must be of the type

$$u_{ij}(r) = f_{ij} \varepsilon_{00} \varphi(r^3/h_{ij} \sigma_{00}^3) \equiv \varepsilon_{ij} \varphi(r^3/\sigma_{ij}^3), \quad (4)$$

where r is the intermolecular distance and ε_{00} and σ_{00} are the energy and size parameters of the reference substance intermolecular potential. We assume this potential to be given by the following relation

$$u(r) = \varepsilon \frac{n}{n-m} \left(\frac{n}{m}\right)^{m/(n-m)} \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m \right], \quad (5)$$

where σ is the distance at which $u(r) = 0$ and ε is the depth of the potential well, *i.e.* $u(r) = -\varepsilon$ for $r = \sigma(n/m)^{1/(n-m)}$. The potential in Eq. (5) is usually called the Mie $n : m$ potential⁵. Although the original comparison with the Monte-Carlo computations¹ was made for the 12 : 6 potential, we have done some corresponding states calculations also for the 28 : 7 potential which is known to be more suitable for larger globular molecules⁴. The $n : m$ potential can be written in a simpler form

$$u(r) = C/r^n - A/r^m \quad (6)$$

which is more convenient for theoretical interpretation of constants C and A .

Several rule were proposed for calculating the unlike pair potential parameters from the pure component ones⁶⁻¹². The oldest is the Lorentz-Berthelot rule given by

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad \text{and} \quad \varepsilon_{ij} = (\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2}. \quad (7), (8)$$

Good and Hope⁶ have recently modified the arithmetic mean rule for σ_{ij} to the geometric mean rule

$$\sigma_{ij} = (\sigma_{ii} \cdot \sigma_{jj})^{1/2}. \quad (9)$$

The geometric mean rule for ε_{ij} is often replaced by the expression

$$\varepsilon_{ij} = (\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2} \cdot (1 - k), \quad (10)$$

where k is an empirical constant whose value is usually determined from experiments. If the London theory of the dispersion forces is considered for the attractive part of the potential, then^{6,13}

$$A_{ij}/(A_{ii} \cdot A_{jj})^{1/2} = 2(I_i \cdot I_j)^{1/2}/(I_i + I_j), \quad (11)$$

where I_i is the ionization potential of molecule i . From this and from Eq. (5) we have immediately¹⁴⁻¹⁶

$$\varepsilon_{ij}/(\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2} = \frac{2(I_i \cdot I_j)^{1/2}}{I_i + I_j} \cdot \frac{(\sigma_{ii} \cdot \sigma_{jj})^{m/2}}{\sigma_{ij}^m}. \quad (12)$$

From other expressions for the attractive term we can also use the formula due to Kramer and Herschbach⁷

$$A_{ij} = \frac{2A_{ii}A_{jj}}{A_{ii}\alpha_j/\alpha_i + A_{jj}\alpha_i/\alpha_j}, \quad (13)$$

where α_i is the static dipole polarisability of molecule i . Using Eq. (5) with this expression we obtain for ε_{ij}

$$\varepsilon_{ij}/(\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2} = \frac{2(\varepsilon_{ii}\varepsilon_{jj})^{1/2}}{\varepsilon_{ii}\sigma_{ii}^m\alpha_j/\alpha_i + \varepsilon_{jj}\sigma_{jj}^m\alpha_i/\alpha_j} \left(\frac{\sigma_{ii}\sigma_{jj}}{\sigma_{ij}} \right)^m. \quad (14)$$

Parameter σ_{ij} in Eqs (12) and (14) may be calculated according to Eq. (8) or (9). However, we can obtain still other formulas for σ_{ij} by taking into account the expression for the repulsive part of the potential due to Mason and Vanderslice⁹

$$C_{ij} = (C_{ii} \cdot C_{jj})^{1/2}. \quad (15)$$

When this condition is applied to Eq. (5), we can no longer choose prescriptions for both σ_{ij} and ε_{ij} arbitrarily, but only for one of them. If we retain for simplicity the prescription for ε_{ij} given by Eq. (10), we get from Eq. (15) and from the repulsive part of $u(r)$ in Eq. (5) the following relation for σ_{ij}

$$\sigma_{ij} = (\sigma_{ii} \cdot \sigma_{jj})^{1/2} / (1 - k)^{1/n}. \quad (16)$$

Parameters ε_{ij} and σ_{ij} are thus coupled by this equation. The value of constant k may be considered either as an empirical parameter or it may be easily calculated from Eq. (12) or, alternatively, from Eq. (14). It is seen that for $n \rightarrow \infty$, the value of σ_{ij} approaches that given by the geometric mean rule by Eq. (9).

For the equivalence substance parameters, f_x and h_x , we will use two different sets of rules. The first ones are the van der Waals rules

$$h_x = \sum_{i,j} x_i x_j h_{ij} \quad (17)$$

and $f_x h_x = \sum x_i x_j f_{ij} h_{ij}$ and the second ones are the rules proposed in our previous work¹

$$h_x^{4/3} = \sum x_i x_j h_{ij}^{4/3}$$

and

$$f_x^{4/3} h_x = \sum x_i x_j f_{ij}^{4/3} h_{ij}. \quad (18)$$

Parameters f and h are directly proportional to parameters ε and σ^3 according to Eq. (4) and so the rules for calculating ε_{ij} and σ_{ij} introduced in Eqs (7)–(16) can be used also here after the necessary substitutions of f for ε and $h^{1/3}$ for σ . The second set of rules for f_x and h_x should be used only for the Lorentz–Berthelot rules for parameters f_{ij} and h_{ij} and for $n : m = 12 : 6$ as the comparison with the Monte-Carlo calculations was made only for this case. However, in the absence of any other pseudoexperimental data on mixtures of Mie $n : m$ fluids we can judge on appropriateness of the different rules and different $n : m$ exponents only from a direct comparison between experiments and calculations. On the other hand we believe that the rules in Eqs (18) cannot be worse than the van der Waals rules either.

CALCULATIONS

The computations were made on ten binary mixtures of simple liquids whose excess properties at zero pressure were collected by Bellemans and coworkers^{3,17}. For the reference substance properties, we take the Bellemans' functions. The force constants ε_{ii} and σ_{ii} of the pure simple liquids were also taken from this work and they are given together with the ionization potentials and static dipole polarisabilities^{15,16} in Table I. As for the values of parameter k in Eq. (10), two sets of computations were made. In the first set they were obtained by the minimization of deviations between the calculated and experimental excess properties. In the second set, the value of k was obtained by some combination of Eqs (7)–(16) and the deviations were calculated with this value of k .

In the minimization process, we minimized the following function

$$\sum [(Q_{\text{exp}}^E - Q_{\text{calc}}^E)/(p \cdot Q_{\text{exp}}^{E(1/2)})]^2, \quad (19)$$

where the summation was performed over all excess functions denoted here by Q for $x_i = 0.3$, 0.5 and 0.7 for each excess function. The experimental accuracy p was taken from the Bellemans' work^{3,17} and $Q_{\text{exp}}^{E(1/2)}$ stands for the value of an experimental excess function at $x_i = 0.5$. The minimization was performed by the Newton method with the derivatives calculated as differences

TABLE I

Pure Component Force Constants, Ionization Potentials and Static Dipole Polarisabilities

Component	ϵ_{ii}/k , K	$N\sigma_{ii}^3$, cm ³ /mol	I , eV	$\alpha \cdot 10^{24}$, cm ³ /mol
Argon	123.2	22.91	15.8	1.63
Krypton	171.0	28.07	14.0	2.46
Nitrogen	103.0	27.44	15.6	1.73
Oxygen	123.0	23.90	12.2	1.56
Methane	156.0	30.41	13.0	2.70
Carbon monoxide	108.6	28.07	14.0	1.93

TABLE II

Differences between the Minimized and Experimental Equimolar Excess Gibbs Free Energies $\delta = G_{\text{min}}^E - G_{\text{exp}}^E$ in J/mol for the Different Combination Rules

System	t , °C	G_{exp}^E	VdW rules		4/3 rules		4/3 rules	
			δ_A	δ_G	δ_A	δ_G	δ_{M12}	δ_{M28}
Ar-CH ₄	-182.15	75	18	20	16	18	18	19
CO-CH ₄	-182.15	117	18	18	18	18	18	18
N ₂ -O ₂	-196.15	42	1	1	0	1	0	1
N ₂ -Ar	-189.15	34	12	13	11	12	14	13
O ₂ -Ar	-189.15	37	7	7	6	6	4	6
CH ₄ -Kr	-157.15	28	25	28	22	25	10	17
N ₂ -CH ₄	-182.15	141	6	6	5	5	8	7
Ar-Kr	-157.38	84	9	11	7	9	5	8
N ₂ -CO	-189.35	23	5	5	5	5	1	4
CO-Ar	-189.35	57	59	67	51	59	36	49

Subscript A in the column heading indicates that the arithmetic-mean rule for σ_{12} (Eq. (7)) was used, subscript G corresponds to the geometric-mean rule (Eq. (9)), subscripts M 12 or M 28 to the Mason's rule (Eq. (16)) with $n = 12$ or 28 , resp. For the corresponding values of constants k , see Table V.

between the values of Q for k and $k + 0.0002$. As soon as the difference between two succeeding calculated values of k decreased below 0.0006, the iteration was stopped.

The resulting deviations between the minimized and experimental excess functions $\delta = Q_{\min} - Q_{\text{exp}}$ at $x_i = 0.5$ are given in Tables II–IV; in columns denoted by VdW, the van der Waals combination rules were employed (Eq. (17)), while in those denoted by 4/3, the 4/3 combination rules were used (Eq. (18)). The corresponding values of constants k are in Table V. Table VI contains values of constant k calculated by some of the rules introduced in Eqs (7)–(16). We do not give here the values of the excess functions corresponding to the values of k from Table VI as it would lead to many additional tables. Besides, the differences between the values of the excess

TABLE III

Differences between the Minimized and Experimental Equimolar Excess Enthalpies $\delta = H_{\min} - H_{\text{exp}}$ in J/mol for the Different Combination Rules
For the description see Table II.

System	$t, ^\circ\text{C}$	H_{exp}^E	VdW rules		4/3 rules		4/3 rules	
			δ_A	δ_G	δ_A	δ_G	δ_{M12}	δ_{M28}
Ar-CH ₄	-182.15	103	1	2	-1	1	5	4
CO-CH ₄	-182.15	106	4	4	3	4	7	6
N ₂ -O ₂	-196.15	44	2	2	2	2	2	2
N ₂ -Ar	-189.15	51	1	2	0	1	4	2
O ₂ -Ar	-189.15	60	3	3	3	3	1	3

TABLE IV

Differences between the Minimized and Experimental Equimolar Excess Volumes $\delta = V_{\min} - V_{\text{exp}}$ in cm³/mol for the Different Combination Rules
For the description see Table II.

System	$t, ^\circ\text{C}$	V_{exp}^E	VdW rules		4/3 rules		4/3 rules	
			δ_A	δ_G	δ_A	δ_G	δ_{M12}	δ_{M28}
Ar-CH ₄	-182.15	0.18	-0.34	-0.39	-0.28	-0.34	-0.19	-0.27
CO-CH ₄	-182.15	-0.33	-0.39	-0.39	-0.38	-0.39	-0.27	-0.34
N ₂ -O ₂	-196.15	-0.21	-0.01	-0.02	0.00	-0.01	0.00	-0.01
N ₂ -Ar	-189.15	-0.18	-0.12	-0.14	-0.10	-0.12	-0.10	-0.12
O ₂ -Ar	-189.15	0.14	-0.06	-0.07	-0.06	-0.07	-0.02	-0.04
CH ₄ -Kr	-157.15	-0.01	0.00	0.00	0.00	0.00	0.00	0.00
N ₂ -CH ₄	-182.15	-0.21	-0.84	-0.85	-0.83	-0.84	-0.71	-0.78
Ar-Kr	-157.38	-0.50	-0.13	-0.16	-0.11	-0.13	-0.05	-0.09
N ₂ -CO	-189.35	0.13	-0.04	-0.04	-0.04	-0.04	0.00	-0.02
CO-Ar	-189.35	0.10	-0.07	-0.08	-0.06	-0.07	-0.02	-0.04

functions corresponding to the k 's from Tables V and VI are proportional to the differences between these k 's. Thus, a good orientation may be obtained by inspecting only Tables V and VI.

DISCUSSION

First, it would be interesting to compare the results of the Monte-Carlo and the corresponding states computations^{1,22} for force constants of pure components corresponding to the mixtures studied. Here, the van der Waals and the 4/3 combination rules with σ_{12} and ε_{12} given by Eqs (7)–(8) yield the values of the excess functions which are almost identical and correct within 10 J/mol for G^E and H^E or 0.02 cm³/mol for V^E for pure components force constants corresponding to the following mixtures: oxygen–argon, methane–krypton, nitrogen–carbon monoxide, nitrogen–oxygen, nitrogen–argon and carbon monoxide–argon. The Van der Waals combination rules should give somewhat better results for H^E in the systems: carbon monoxide–methane, nitrogen–methane and argon–krypton. The 4/3 rules should be better for H^E and V^E in the argon–methane system. In the remaining cases, the differences between the van der Waals and 4/3 rules are small. The cases for which the Van der Waals combination rules should yield better results correspond to mixtures of molecules of not too different sizes. This is obviously due to the fact that the 4/3 rules do not approach the random mixing approximation^{17,18} when the ratio σ_{11}/σ_{22} approaches unity. However, the error is rather small and well compensated at larger σ_{11}/σ_{22} ratios¹. Incidentally, the combination rules given by the following equations

$$h_x^{4/3} = \sum x_i x_j h_{ij}^{4/3}$$

and

$$f_x h_x = \sum x_i x_j f_{ij} h_{ij}$$
(20)

should be somewhat better in the relevant cases for all ten binary mixtures studied than both the van der Waals and the 4/3 combination rules.

If we compare the above considerations with the results of the minimization procedure in Table II–IV, we can see that there is apparently no correlation between the proposals and the actual differences. Thus, for example, the excess volumes of systems argon–methane, carbon monoxide–methane and nitrogen–methane are correlated almost equally badly by both the Van der Waals and the 4/3 combination rules. A slight improvement may be observed only with the 4/3 rules combined with the M 12 rule for σ_{12} , but even in this case the discrepancy for the system nitrogen–methane is very large. As we initially hoped¹ that especially the correlation of excess volumes would be successful with the 4/3 rules, we were rather disappointed by these results. However, an orientation calculation showed that the most probable source of the discrepancies is in the reference fluid properties. The curvature of the Belle-mans' and Singers' temperature dependences of the reference fluid volumes is quite different¹⁹. When the pure component constants ε_{11} and ε_{22} differ much from one

another, the corresponding reduced temperatures are also much apart and the reduced temperature of the equivalent substance lies usually in the middle. If we use the Belle-

TABLE V

Values of Constants $k \cdot 10^3$ for the Different Combination Rules as Calculated by the Minimization Technique

The values of the excess functions in Tables II–IV correspond to these values of k . For notation see Table II.

System	VdW rules		4/3 rules		4/3 rules	
	A	G	A	G	M 12	M 28
Ar-CH ₄	33	33	33	33	34	34
CO-CH ₄	19	20	25	25	25	25
N ₂ -O ₂	3	3	3	3	3	3
N ₂ -Ar	2	2	2	3	4	3
O ₂ -Ar	15	15	15	15	14	15
CH ₄ -Kr	10	11	9	10	6	8
N ₂ -CH ₄	18	18	25	25	26	25
Ar-Kr	17	17	20	20	20	20
N ₂ -CO	12	12	12	12	10	11
CO-Ar	34	36	30	33	25	30

TABLE VI

Values of Constants $k \cdot 10^3$ from Eq. (10) for Different Approximations according to Eqs (7)–(16)

The meaning of the first symbol in the triple in the column headings is the same as in Table II. The values of the $n : m$ exponents in the Mie potential used correspond to the second symbol equal to 6 for a 12 : 6 or to 7 for a 28 : 7 potential. The third symbol is K or L according to whether the London's (Eq. (12)) or Kramer's (Eq. (14)) rules were employed.

System	A6L	A7L	A6K	A7K	G6L	G7L	G6K	G7K	M6L	M7L	M6K	M7K
Ar-CH ₄	11	12	12	9	5	5	6	2	9	6	11	2
CO-CH ₄	1	1	3	3	1	1	3	2	1	1	6	3
N ₂ -O ₂	9	9	3	2	7	7	2	1	15	10	3	1
N ₂ -Ar	3	3	3	5	0	0	0	2	0	0	1	2
O ₂ -Ar	8	8	4	4	8	8	3	4	16	11	7	5
CH ₄ -Kr	1	1	2	2	1	1	2	1	1	1	4	1
N ₂ -CH ₄	5	5	10	8	4	4	9	7	8	6	17	9
Ar-Kr	5	6	4	4	2	2	1	0	3	2	2	0
N ₂ -CO	1	1	2	1	1	1	2	1	3	2	3	2
CO-Ar	5	6	4	4	2	2	0	0	3	2	1	0

mans' or Singers' reference fluid volumes, we may consequently obtain the excess volumes differing from one another by as much as $0.3 \text{ cm}^3/\text{mol}$ for a nitrogen-methane system. The second reason for the discrepancies may be the assumption that the pure component force constants are independent of temperature. Both reasons tend to increase the possible discrepancies for mixtures composed of molecules widely different in constants ε_{11} and ε_{22} . This is really the case of the mixtures for which the largest deviations were observed: argon-methane, carbon monoxide-methane, and nitrogen-methane. Smaller deviations in G^E and H^E in these systems are probably due to smaller differences in the curvatures of the Bellemans' and Singers' reference substance Gibbs energies and enthalpies. We believe that if we used the reference substance properties deduced from some sufficiently flexible equation of state instead of the Bellemans' reference fluid and if the pure component force constants were calculated at each temperature from orthobaric properties for each liquid present separately²⁰, the deviations would be smaller. Calculations with the Redlich-Kwong equation of state showed that this is really the case²¹.

If we look again at Tables II-IV we may observe that besides the discrepancies in V^E there is still one large disagreement in G^E for the carbon monoxide-argon system. This is caused undoubtedly by the weighting procedure in making up the sum in Eq. (19). If unity for the G^E and zero for the V^E weights are taken, the calculated values of V^E do not become remarkably worse compared to those obtained by the minimization. The disagreement in G^E for this system may be thus partially ascribed to inappropriate values of the experimental accuracy used in the minimization procedure. A further look at Tables II-IV tells us that there is probably little to choose among the different combination rules considered. The best results are observed with the 4/3 rules together with the M12 rule for σ_{12} ; this has an additional computational disadvantage as for this case both ε_{12} and σ_{12} now depend on the value of k and the calculations are necessarily more complicated. The probable reason for the small differences is that the range of the pure component force constants encompassed by the ten mixtures is too small to be able to distinguish unambiguously among the different combination rules. However, a further study²¹ has shown that once sufficiently good combination rules are used, there remains the fundamental question of appropriateness of the general functional dependence of the reference substance properties on temperature and volume. Properties of mixtures seem to be much more sensitive to this functional dependence than to different combination rules of the equivalent substance parameters provided that these have been chosen close to the van der Waals or to the 4/3 rules.

On comparing the values of k from the minimization process with those obtained by the different rules according to Eqs (7)-(16) as collected in Tables V and VI we can see that the differences are sometimes very large. The largest differences were again observed with systems for which the minimization procedure did not yield satisfactory results, *i.e.* for the systems argon-methane, carbon monoxide-methane

and nitrogen-methane. This could be ascribed to a certain extent to uncertain appropriateness of the reference substance properties and of the pure component force constants. Good agreement for all excess properties calculated with the predicted values of k was found only for the systems: nitrogen-oxygen, nitrogen-argon, methane-krypton and nitrogen-carbon monoxide. In the remaining cases, the discrepancies were usually small for one excess function and greater for the other two. Small differences were also observed among the values of δ for one system calculated with the different values of k ; the M6K approximation seemed to be better than any other, but the differences were too small to render this statement valid quite generally. Thus, much work remains to be done to find a sufficiently flexible functional dependence for the equivalent substance properties and to derive really working formulas for calculating the interaction parameters in the pair potential of unlike molecules.

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