

# COMBINING RULES IN MOLECULAR THEORIES OF SOLUTIONS

In the last few years a great deal of attention has been drawn to the development and testing of theories of mixtures of non-electrolytes. For this purpose binary mixtures of small and very similar molecules (the rare gases, nitrogen, oxygen, carbon monoxide and methane) have been chosen, in the hope that the theories under inspection would then stand the best chance of success. Whatever the theory, it is necessary to adopt combining rules for the unlike interaction parameters, and these have been most commonly estimated by the so-called arithmetic mean rule, first introduced by LORENTZ (1), and geometric mean rule due to BERTHELOT (2).

$$\sigma_{12} = \frac{1}{2} [\sigma_{11} + \sigma_{22}] \quad (1)$$

$$\varepsilon_{12} = (\varepsilon_{11} \cdot \varepsilon_{22})^{1/2} \quad (2)$$

It soon became obvious that the results obtained with these rules were, at the most, only qualitative (3), and this led ECKERT *et al.* to introduce an empirical factor  $k_{12}$  to correct for deviations from the geometric mean (4)

$$\varepsilon_{12} = (1 - k_{12}) (\varepsilon_{11} \cdot \varepsilon_{22})^{1/2} \quad (3)$$

while retaining the arithmetic mean rule which holds exactly for the hard-sphere model. This is not surprising since the geometric mean rule should apply only to mixtures of molecules of the same size and identical ionization potentials (5); on the basis of LONDON's theory of dispersion forces one should then expect positive values for  $k_{12}$  and this has been confirmed by experiment (4). On the other hand, LELAND *et al.* were able to show an unmistakable correlation between independent determinations of  $k_{12}$  from two methods, viz. the one based on second virial coefficients and that based on the excess Gibbs function  $G^E$ , for nine binary mixtures, thus proving that  $k_{12} > 0$  is something more than a mere empirical, correcting factor (6). In fact, HIZA and DUNCAN managed to relate  $k_{12}$  to the difference between the ionization potentials of the component species, although their correlation fails when the two molecules have very similar properties.

In theories of liquid mixtures values of  $k_{12}$  can be determined from the adjustment of calculated and experimental values of one of the excess functions, or some other independent source, and then be used for the calculation of the remaining excess properties. Because of the availability of experimental data, the excess Gibbs function  $G^E$ , rather than the more suitable excess enthalpy  $H^E$ , has been used to calculate the parameter  $k_{12}$ . The results have shown, however, that the adjustment of one thermodynamic function does not usually lead to an internal agreement for all the other functions or indeed the same one at a different temperature, even in the case of a successful approach like the van der Waals approximation as developed by ROWLINSON and his collaborators (8). We have thus been led to think that perhaps the combination rule for molecular diameters should also be reformulated so as to allow for small departures from the arithmetic mean, as follows

$$\sigma_{12} = (1 + y_{12}) \left( \frac{\sigma_{11} + \sigma_{22}}{2} \right) \quad (4)$$

It seems that such an assumption was first introduced by BUFF and SCHINDLER as part of a perturbation theory for the solution properties of systems with

comparable intermolecular interactions (9), but it was never extensively developed to fit available experimental data. Later BELLEMANS *et al.* used departures from the Lorentz rule as a last step towards bringing the experimental results into agreement with their own calculations based on the Average Potential Model (10), but the random values obtained for such deviations evinced the lack of theoretical support; it is now known that any approach based on random mixing is bound to fail because a certain degree of ordering always prevails in liquid mixtures.

More recently GOOD and HOPE discussed the relative merits of several combination rules, and proposed a new one for the molecular diameters, based on the geometric mean rule (11)

$$\sigma_{12} = (\sigma_{11} \cdot \sigma_{22})^{1/2} \quad (5)$$

They were able, in this way, to describe more accurately the second virial coefficient of binary mixtures (12). But, since the geometric mean is smaller than the arithmetic mean, their conclusion that deviations  $y'_{12}$  from the former, written as

$$\sigma_{12} = (\sigma_{11} \cdot \sigma_{22})^{1/2} (1 + y'_{12}) \quad (6)$$

are smaller than those from the latter,  $y_{12}$ , is simply not true. Following this, we decided to retain the form of the arithmetic mean rule and extensively study the effect that small deviations might have on the calculation of the excess thermodynamic functions. We have selected, for the purpose, eleven simple systems and calculations were done with the van der Waals approximation, in the one-fluid version (8), one of the most successful of the current theories of mixtures of non-electrolytes, as confirmed by Monte-Carlo computations (13). Values of the intermolecular parameters, chosen according to criteria formulated by BELLEMANS *et al.* (10), are shown in Table I.

The best available experimental data for  $G^E$  and  $V^E$  were used to compute  $k_{12}$  and  $y_{12}$  in the following way: first it was assumed that  $y_{12} = 0$  and a first approximation of  $k_{12}$  was calculated so as to bring the theoretical and experimental values of  $G^E$  into agreement; this value of  $k_{12}$  was then used in

Table I  
Intermolecular Parameters

Molecule	$\sigma/\text{\AA}$	$(\epsilon/k)/\text{K}$
Ar	3.402	122.1
Kr	3.603	167.8
Xe	3.997	229.4
N <sub>2</sub>	3.664	99.3
O <sub>2</sub>	3.448	121.9
CO	3.671	104.4
CH <sub>4</sub>	3.783	152.1
C <sub>6</sub> H <sub>6</sub>	4.702	428.3
c-C <sub>6</sub> H <sub>12</sub>	5.330	342.7

the calculation of  $V^E$  and the adjustment made by estimating a first value for  $y_{12}$ . The whole process was recycled until complete agreement was reached between the calculated and theoretical values of both  $G^E$  and  $V^E$ , within the sensibility of  $k_{12}$  and  $y_{12}$ . It was expected that  $V^E$  would be more sensitive to differences in the combination rule for the diameters, and  $G^E$  more sensitive to changes in the molecular energies, but the two parameters  $k_{12}$  and  $y_{12}$  are probably coupled together for, as MASON *et al.* pointed out, it is hard to disentangle  $\sigma_{12}$  and  $\epsilon_{12}$  (14).

The calculated values of  $k_{12}$  and  $y_{12}$  were then used to estimate  $H^E$ , thus providing a first test for these parameters in the cases for which enthalpy of mixing has been measured. According to LEONARD *et al.*  $H^E$  is roughly twice as sensitive to changes in  $k_{12}$  as is  $G^E$  (15). The results are summarized in Table II — for each system the values of the excess functions in the first line are the experimental ones, whereas those in the second line were calculated according to the present approach. With the exception of the Ar-CH<sub>4</sub> and Kr-CH<sub>4</sub> systems, the calculated and experimental values of  $H^E$  agree within 2 cal mol<sup>-1</sup> (values of  $H^E$  with an asterisk \* were obtained indirectly, from a plot of  $G^E$  against temperature). The benzene-cyclohexane system, though far from simple, was included because it is the most studied hydrocarbon mixture, and it provides an example of a system with large excess functions, but the agreement for the  $H^E$  values is poor, as expected.

Table II

Experimental and calculated values for the excess functions of simple liquid mixtures, and corrections for the combination rules

System	$G^E/\text{J mol}^{-1}$	$V^E/\text{cm}^3 \text{mol}^{-1}$	$H^E/\text{J mol}^{-1}$	$k_{12} \quad y_{12}$
Ar-CH <sub>4</sub> 116 K	+ 76 <sup>a</sup> + 77	+ 0.06 <sup>b</sup> + 0.09	+ 103 <sup>c</sup> + 84	$k_{12} = 0.028$ $y_{12} = 0.0024$
Kr-CH <sub>4</sub> 116 K	+ 29 <sup>d</sup> + 28	- 0.025 <sup>d</sup> - 0.025	+ 55* + 39	$k_{12} = 0.0025$ $y_{12} = 0.0014$
Ar-Kr 116 K	+ 84 <sup>e</sup> + 84	- 0.52 <sup>e</sup> - 0.51	+ 69* + 66	$k_{12} = 0.015$ $y_{12} = 0.0030$
Kr-Xe 161 K	+ 118 <sup>f</sup> + 116	- 0.69 <sup>f</sup> - 0.67	— + 43	$k_{12} = 0.021$ $y_{12} = 0.0006$
Ar-CO 84 K	+ 57 <sup>g</sup> + 56	+ 0.10 <sup>h</sup> + 0.13	— + 74	$k_{12} = 0.0080$ $y_{12} = 0.0080$
Ar-N <sub>2</sub> 84 K	+ 34 <sup>h</sup> + 37	- 0.19 <sup>h</sup> - 0.19	+ 51 <sup>h</sup> + 45	$k_{12} = - 0.0040$ $y_{12} = 0.0064$
N <sub>2</sub> -CO 84 K	+ 23 <sup>h</sup> + 23	+ 0.13 <sup>h</sup> + 0.11	+ 43* + 36	$k_{12} = 0.010$ $y_{12} = 0.0004$
N <sub>2</sub> -O <sub>2</sub> 78 K	+ 41 <sup>i</sup> + 42	- 0.21 <sup>j</sup> - 0.18	+ 67* + 60	$k_{12} = - 0.0020$ $y_{12} = 0.0042$
Ar-O <sub>2</sub> 84 K	+ 37 <sup>h</sup> + 36	+ 0.14 <sup>h</sup> + 0.14	+ 60 <sup>h</sup> + 53	$k_{12} = 0.013$ $y_{12} = 0.0016$
CO-CH <sub>4</sub> 91 K	+ 115 <sup>k</sup> + 113	- 0.32 <sup>k</sup> - 0.35	+ 106 <sup>c</sup> + 102	$k_{12} = 0.015$ $y_{12} = 0.0100$
C <sub>6</sub> H <sub>6</sub> -c-C <sub>6</sub> H <sub>12</sub> 298 K	+ 320 <sup>l</sup> + 327	+ 0.64 <sup>m</sup> + 0.62	+ 810 <sup>n</sup> + 521	$k_{12} = 0.0260$ $y_{12} = 0.0184$

a Calado, J. C. G. and Staveley, L. A. K., *J. Chem. Phys.*, **56**, 4718 (1972).

b Liu, Y.-P. and Miller, R. C., *J. Chem. Thermodyn.*, **4**, 85 (1972).

c Lambert, M. and Simon, M., *Physica*, **28**, 1191 (1962).

d Calado, J. C. G. and Staveley, L. A. K., *Trans. Faraday Soc.*, **67**, 1261 (1971).

e Davies, R. H., Duncan, A. G., Saville, G. and Staveley, L. A. K., *Trans. Faraday Soc.*, **63**, 855 (1967).

f Calado, J. C. G. and Staveley, L. A. K., *Trans. Faraday Soc.*, **67**, 289 (1971).

g Duncan, A. G. and Staveley, L. A. K., *Trans. Faraday Soc.*, **62**, 548 (1966).

h Pool, R. A. H., Saville, G., Herrington, T. M., Shields, B. D. C. and Staveley, L. A. K., *Trans. Faraday Soc.*, **58**, 1692 (1962).

i Knobler, C. M., van Heijningen, R. J. J. and Beenakker, J. J. M., *Physica*, **27**, 296 (1961).

j Knapp, H. F. P., Knoester, M. and Beenakker, J. J. M., *Physica*, **27**, 309 (1961).

k Mathot, V., Staveley, L. A. K., Young, J. A. and Parsonage, N. G., *Trans. Faraday Soc.*, **52**, 1488 (1956).

l Scatchard, G., Wood, S. E. and Mochel, J. M., *J. Phys. Chem.*, **43**, 119 (1939).

m Reddy, K. C., Subrahmanyam, S. V. and Bhimasenachar, J., *J. Phys. Soc. Japan*, **19**, 559 (1964).

n Rowlinson, J. S., *«Liquids and Liquid Mixtures»*, 2nd ed., Butterworths, London, 1969 (rev. 1971), p. 136.

An interesting conclusion is that  $y_{12}$  is always *positive*, with the implication that the cross-interaction parameter  $\sigma_{12}$  is always *larger* than the value predicted from the arithmetic mean rule, the deviation being of the order of 0.4 %. This should be compared with the deviations from the geometric mean rule which are usually in the opposite direction (*negative*) and of the order of 2 %; the exceptions are the  $N_2$ - $O_2$  (already an exception in the treatment of ECKERT *et al.* (4)) and the  $Ar$ - $N_2$  systems which show a negative value for  $k_{12}$  and thus a positive deviation from the geometric mean rule.

A first inspection of the relative values of  $y_{12}$  for the several systems tested seems to show that the larger the difference in the size of the molecules (as measured by  $\sigma_{11}/\sigma_{22}$ ) the larger  $y_{12}$ ; for the  $N_2$ - $CO$  system, where the molecules are practically of the same size ( $\sigma_{11}/\sigma_{22} = 0.998$ ),  $y_{12}$  is almost zero,  $y_{12} = 0.0004$ , whereas for the  $Ar$ - $N_2$  system, whose molecules differ considerably in size ( $\sigma_{11}/\sigma_{22} = 0.928$ ),  $y_{12}$  is appreciably larger,  $y_{12} = 0.0064$ .

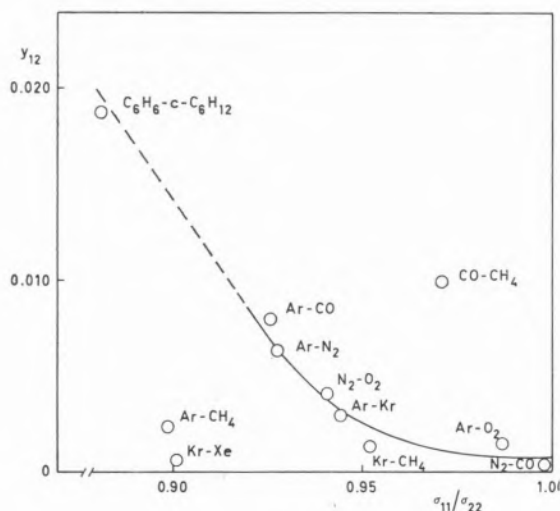


Fig. 1

Correlation between  $y_{12}$  and  $\sigma_{11}/\sigma_{22}$  for eleven mixtures

This is better seen in fig. 1 which shows a reasonable correlation between  $y_{12}$  and  $\sigma_{11}/\sigma_{22}$  for eight out of the eleven systems chosen. It is not surprising that the  $CO$ - $CH_4$  system should show such a marked deviation, due to the orientation forces involved, but there is no reason why such simple systems as  $Kr$ - $Xe$  and  $Ar$ - $CH_4$  should fall off the general trend. However, there is some uncertainty

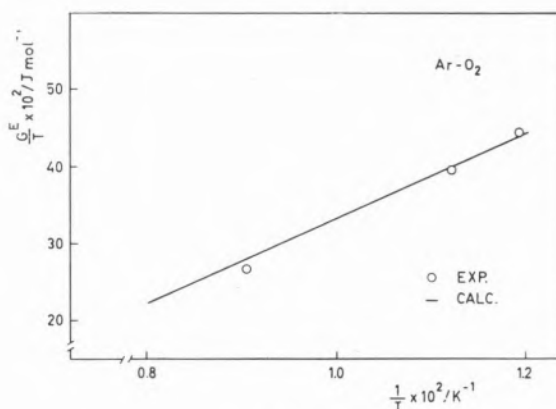


Fig. 2

Experimental and calculated values of  $G^E/T$  for the  $Ar$ - $O_2$  system as a function of temperature

about the intermolecular parameters of xenon, which may well account for the deviation, and some discrepancies in the experimental results for the  $Ar$ - $CH_4$  system have not yet been completely solved (16).

In principle  $y_{12}$  and  $k_{12}$  should be independent of temperature; calculated values of  $k_{12}$  and  $y_{12}$  at one temperature should then be able to reproduce the experimental values of the excess functions at other temperatures. Experimental data for  $G^E$  and  $V^E$  as a function of temperature are, however, very scarce, but recently LIU and MILLER measured  $V^E$  for the  $Ar$ - $CH_4$  and  $N_2$ - $CH_4$  systems at temperatures ranging from 91 to 115 K (17).  $G^E$  data for the  $Ar$ - $O_2$  and  $Ar$ - $CH_4$  mixtures over a range of temperatures are also available (18, 16).

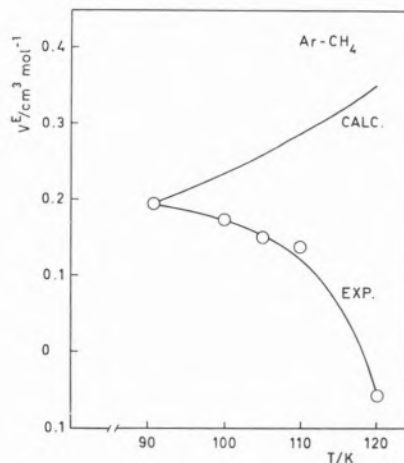


Fig. 3

Experimental and calculated values of  $V^E$  for the  $Ar$ - $CH_4$  system as a function of temperature

Table III

Calculated values of  $y_{12}$  at different temperatures  
for the Ar-CH<sub>4</sub> system

T	$y_{12}$
90.7	0.0066
100.03	0.0054
105.09	0.0045
110.05	0.0038
119.98	—0.0004

The calculations for these systems show that while it is possible to predict, with an acceptable accuracy, the behaviour of  $G^E$ , the theory fails with  $V^E$ , giving a temperature coefficient of the wrong sign. This is better seen with two typical examples — figs. 2 and 3. In both cases  $k_{12}$  and  $y_{12}$  were calculated so that the experimental and theoretical values of the excess functions coincide at the lowest temperature. For the Ar-O<sub>2</sub> system the plot shows that there is good agreement for the both  $H^E$  and  $S^E$ ; for the Ar-CH<sub>4</sub> system the theory predicts an increase of  $V^E$  with temperature, whereas the experimental results show the opposite behaviour. Assuming that  $k_{12}$  does not vary with temperature (19), then  $y_{12}$  is shown to decrease with temperature, eventually becoming negative — Table III. This is equivalent to a decrease of the intermolecular diameter with temperature, as the molecular collisions become more and more violent.  $V^E$  is mostly sensitive to  $y_{12}$  whereas  $G^E$  is mostly sensitive to  $k_{12}$  and it can be shown that

$$\frac{\partial G^E}{\partial k_{12}} > 0 \quad \frac{\partial G^E}{\partial y_{12}} < 0 \quad (7)$$

$$\frac{\partial V^E}{\partial k_{12}} > 0 \quad \frac{\partial V^E}{\partial y_{12}} > 0 \quad (8)$$

Work already in progress based on a «hard-sphere» equation of state of the type used by SNIDER and HERRINGTON (20), instead of the van der Waals one-fluid approach, has met with considerable success in predicting the excess thermodynamic functions and their temperature coefficients with constant values of  $k_{12}$  and  $y_{12}$ . The results will be published elsewhere.

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