

## **On Combination Rules for Molecular Van der Waals Potential-Well Parameters**

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Combination rules are proposed for the depth and position parameters of the effective potential well for interactions between molecules. They are an extension, by the introduction of a rigid-core parameter that can be determined independently from known dispersion coefficients, of the Tang-Toennies rules for interactions between noble-gas atoms. Such rules permit the calculation of many mixture properties of molecular gases via known correlation equations, without involving any attempt to predict the entire anisotropic intermolecular potential. The rules are tested with the few known potentials, and with more extensive experimental data on mixture properties, and appear to work satisfactorily.

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**KEY WORDS:** combination rules; mixtures; potential-well parameters.

### **1. INTRODUCTION**

The problem of calculating the properties of mixtures from those of its components is one of long-standing and increasing urgency, since the number of possible mixtures of interest is so large. In terms of an underlying statistical-mechanical theory, the problem becomes that of determining the interaction between two unlike molecules in terms of the interactions between pairs of like molecules. This latter problem has now been essentially solved for the noble gases by Tang and Toennies [1]. The purpose of this paper is to suggest an extension of the Tang-Toennies combination rules that can be used to predict the potential-well parameters for the effective spherical potentials of molecular systems.

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Our goal here for molecular gases is, however, more limited than that achieved for noble gases. We do not seek to determine the entire potential energy curve, including its complicated dependence on orientation, or even its effective spherical average; these are important but difficult problems whose resolution still lies in the future. Instead, we seek to determine just the depth of the potential energy well,  $\varepsilon$ , and the separation,  $\sigma$ , at which the potential energy is zero. The reason is that these parameters should be sufficient to determine many properties of gaseous mixtures, because of the existence of a successful limited principle of corresponding states for low-density molecular gases [2], in which the parameters  $\varepsilon$  and  $\sigma$  are used as scale factors of energy and molecular size for the correlation and prediction of both equilibrium and transport properties. Earlier work [3] on the viscosities of binary gas mixtures strongly indicated that a similar correlation can be developed for mixtures in terms of the mixed-interaction parameters  $\varepsilon_{12}$  and  $\sigma_{12}$ . Accurate combination rules for  $\varepsilon_{12}$  and  $\sigma_{12}$  would thus enable such a correlation scheme to predict the properties of mixtures without the need for any measurements on the mixtures themselves. In short, the prediction of just the parameters  $\varepsilon_{12}$  and  $\sigma_{12}$  for molecular systems would enable many thermophysical properties of mixtures to be calculated without the need for any further information on the entire anisotropic intermolecular potential or for any measurements on mixtures. In what follows, we present combination rules for molecular parameters  $\varepsilon_{12}$  and  $\sigma_{12}$  that are extensions of the Tang–Toennies rules for noble-gas atoms, by introducing a rigid-core parameter into the potential to account for molecular size. The introduction of this parameter does not require any new experimental data beyond what is already required for the noble gases.

## 2. COMBINATION RULES

Any extension of the noble-gas combination rules must in some way incorporate information on molecular structure, that is, on the molecular size and shape. Since we are concerned here only with effective spherical potentials, molecular shape itself does not enter the problem and we can consider only some sort of average molecular size to be the leading candidate as a parameter for the extension. A straightforward procedure is to introduce a rigid core into the potential to mimic average molecular size. This sort of core model for intermolecular potentials was suggested long ago by Kihara [4] and has been used since then by a number of workers in different problems. That is, the spherical potential-energy function  $V(r)$  of the noble-gas type is imagined to be replaced by an effective spherical potential displaced from the origin,

$$V(r) \rightarrow \langle V(\bar{r} - a) \rangle \quad (1)$$

where  $\bar{r}$  is the distance between molecular centers of mass, and  $a$  is the core

diameter. The combination rule for the new parameter  $a$  is then the same as for rigid spheres,

$$a_{12} = \frac{1}{2}(a_1 + a_2) \quad (2)$$

Values of  $a_1$  and  $a_2$  for the single components can be calculated from information on the long-range  $C^{(6)}$  dispersion coefficients, as discussed in what follows. Since this information is already needed for the noble-gas combination rule for  $\varepsilon_{12}$ , the introduction of the core parameter does not require any new experimental data.

We first recall briefly the assumptions and approximations that underlie the noble-gas combination rules, in order to see how the introduction of a core changes them. We also wish to make some minor generalizations. There are four main assumptions or approximations, two for  $\sigma_{12}$  and two for  $\varepsilon_{12}$ .

The assumptions leading to the rule for  $\sigma_{12}$  are applied only in the immediate vicinity of the potential minimum or zero crossing point, where it is safe to use a simple mathematical expression for  $V(r)$ . The first and most important assumption is the adoption of an atomic-distortion model [5-7] for the repulsive component of the forces, and the second is a semiempirical geometric-mean combination rule for the attractive component of the forces. The selection of a mathematical form for  $V(r)$  then yields an explicit expression for  $\sigma_{12}$  in terms of  $\varepsilon_1$ ,  $\sigma_1$  and  $\varepsilon_2$ ,  $\sigma_2$  [plus any dimensionless parameters included in  $V(r)$ ]. The introduction of a core simply moves the origin from 0 to  $-a$ , which has the effect of replacing  $r$  by  $(\bar{r}-a)$ , as indicated by Eq. (1), and the combination rule keeps the same form but with each  $\sigma$  replaced by  $(\sigma-a)$ . If a Lennard-Jones (12, 6) potential is used for  $\langle V(\bar{r}-a) \rangle$ , the result is

$$(\sigma_{12} - a_{12})^{n-6} = \frac{[\frac{1}{2}\varepsilon_1^{1/(n+1)}(\sigma_1 - a_1)^{n/(n+1)} + \frac{1}{2}\varepsilon_2^{1/(n+1)}(\sigma_2 - a_2)^{n/(n+1)}]^{n+1}}{(\varepsilon_1\varepsilon_2)^{1/2}(\sigma_1 - a_1)^3(\sigma_2 - a_2)^3} \quad (3)$$

With  $n=12$  and the  $a$ 's equal to zero, this is the rule proposed by Tang and Toennies [1]. If an (exp, 6) potential is used instead of a (12, 6), the result is

$$\sigma_{12} - a_{12} = \frac{1}{2} [(\sigma_1 - a_1) + (\sigma_2 - a_2)] \left\{ 1 + \frac{7}{\alpha} \left[ \ln(\sigma_{12} - a_{12}) - \frac{1}{7} \ln E \right] \right\} \quad (4)$$

where

$$\begin{aligned} \ln E = & \frac{1}{2} \ln(\varepsilon_1\varepsilon_2) + 3 \ln(\sigma_1 - a_1)(\sigma_2 - a_2) \\ & - \frac{\sigma_1 - a_1}{(\sigma_1 - a_1) + (\sigma_2 - a_2)} \ln \left( \frac{\varepsilon_1}{\sigma_1 - a_1} \right) \\ & - \frac{\sigma_2 - a_2}{(\sigma_1 - a_1) + (\sigma_2 - a_2)} \ln \left( \frac{\varepsilon_2}{\sigma_2 - a_2} \right) \end{aligned} \quad (5)$$

Here  $\alpha$  is the dimensionless parameter of the (exp, 6) potential that characterizes the steepness of the repulsion; a value of  $\alpha = 14$  represents a real potential reasonably well in the vicinity of the minimum. Although Eq. (4) is an implicit equation for  $\sigma_{12}$ , the factor in braces is very close to unity and a solution by iteration converges rapidly. Despite their different appearances, Eqs. (3) and (4) give numerical results that differ by very little, the difference being of the order of 1%.

The combination rule of Eq. (4) shows explicitly how the old arithmetic-mean rule for  $\sigma_{12}$  [8] emerges as a first approximation. Both Eq. (3) and Eq. (4) merely furnish rather modest corrections (<10%) to the arithmetic-mean rule, although this fact is not so obvious in the case of Eq. (3). The numerical results are not very sensitive to the values chosen for  $n$  and  $\alpha$ .

We can see explicitly from Eq. (4) that the introduction of the rigid core can have only a modest effect on  $\sigma_{12}$ , as follows. To the first approximation of taking the expression in braces equal to unity, the  $a$ 's cancel out because  $a_{12} = \frac{1}{2}(a_1 + a_2)$  according to Eq. (2). A different way to demonstrate the modest effect of the core on  $\sigma_{12}$  is to rewrite Eqs. (3)–(5) in terms of a reduced core parameter,

$$a^* \equiv a/\sigma \quad (6)$$

If the different  $a^*$ 's happen to be equal, then all the factors of  $(1 - a^*)$  in Eqs. (3)–(5) cancel out. Thus the cores do not modify the value of  $\sigma_{12}$  unless the values of  $a_1^*$  and  $a_2^*$  are quite different.

The above arguments serve as justification for the applicability of the Tang-Toennies rule for  $\sigma_{12}$ —or its modification with an (exp, 6) in place of a (12, 6) potential—to molecules as well as noble-gas atoms. Numerical calculations that we have carried out for a wide variety of systems show that the introduction of the rigid cores affects the calculated values of  $\sigma_{12}$  by less than 1%.

The effect of the core is somewhat more pronounced for  $\epsilon_{12}$ . The fundamental assumption for  $\epsilon_{12}$  is that the dominant attractive contribution to  $\epsilon$  comes from  $C^{(6)}$ . In the case of noble-gas atoms this implies that the effects of  $C^{(8)}$ ,  $C^{(10)}$ , etc., are small, or can at least be included empirically in  $C^{(6)}$ . In the case of molecules, there is the additional implication that the effects of the molecular permanent multipole moments (dipoles, quadrupoles, etc.) on the effective spherical potential are small. This is not unreasonable, inasmuch as the electrostatic interactions between permanent multipoles vanish on averaging over all orientations. Nevertheless, this is probably the most severe of the assumptions involved in finding  $\epsilon_{12}$ . The two specific approximations used in calculating  $\epsilon_{12}$  are an accurate

theoretical combining law for  $C_{12}^{(6)}$  and a near-universality of the dimensionless group  $C^{(6)}/\varepsilon(\sigma - a)^6$ . The latter condition directly gives the rule for  $\varepsilon_{12}$  once  $\sigma_{12}$  and  $C_{12}^{(6)}$  are known.

A very accurate combination rule for  $C_{12}^{(6)}$  is known to be

$$\frac{\alpha_1 \alpha_2}{C_{12}^{(6)}} = \frac{1}{2} \left[ \frac{\alpha_1^2}{C_1^{(6)}} + \frac{\alpha_2^2}{C_2^{(6)}} \right] \quad (7)$$

where  $\alpha_1$  and  $\alpha_2$  are the dipole polarizabilities. This rule is not affected by the introduction of a core, since it is based on an asymptotic theory valid for large  $r$ , where  $a$  is negligible. The accuracy of this formula has been tested for a large number of atoms and molecules and found to be correct within about 1% [9–11].

It has been noted a number of times for the noble gases that the numerical value of  $C^* = C^{(6)}/\varepsilon\sigma^6$  varies only weakly from system to system and is, thus, nearly universal. It follows that almost any reasonable combination rule for  $C_{12}^*$  will be satisfactory. Tang and Toennies used  $C_{12}^* = (C_1^* C_2^*)^{1/2}$ . The near-universality of  $C^*$  can be justified via simple models of  $V(r)$  if the dominant attractive contribution to  $\varepsilon$  comes from the  $C^{(6)}$  energy [12]. The introduction of a core leads us to expect the near-universality to apply not to  $C^*$  but to the quantity

$$\frac{C^{(6)}}{\varepsilon(\sigma - a)^6} = \frac{C^*}{(1 - a^*)^6} \quad (8)$$

Then the combination rule for  $\varepsilon_{12}$  is immediately found from the geometric-mean rule for this quantity to be

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2} \left( \frac{(\sigma_1 - a_1)^3 (\sigma_2 - a_2)^3}{(\sigma_{12} - a_{12})^6} \right) \left( \frac{C_{12}^{(6)}}{[C_1^{(6)} C_2^{(6)}]^{1/2}} \right) \quad (9)$$

This formula shows explicitly how the old geometric-mean rule for  $\varepsilon_{12}$  [8] emerges as a first approximation. It also shows that  $\varepsilon_{12}$  will not be affected by the introduction of the cores if all the  $a^*$ 's are equal, just as was the case for  $\sigma_{12}$ . In other cases, however, the effect of the core is more substantial than for  $\sigma_{12}$ ; numerical calculations on a large number of systems show effects on  $\varepsilon_{12}$  of up to 10%.

It remains only to specify the procedure for determining the core diameters. If we can assign a numerical value to  $C_1^{(6)}/\varepsilon_1(\sigma_1 - a_1)^6$  for a particular system, say by analogy with the value of  $C_1^*$  for a similar noble-gas interaction, then we can calculate  $a_1^*$  directly from Eq. (8), since  $C_1^*$  for the molecular system is known. Such an assignment is simplified by the observation that the values of  $C^*$  for the interactions among the heavy noble-gas

atoms Ar, Kr, and Xe are, within about 5%, all equal to 2.2 [13]. Choosing this as a universal value for the molecules of interest, we obtain the value of  $a_1$  for each homonuclear system as

$$a_1 = \sigma_1 [1 - (C_1^*/2.2)^{1/6}] \quad (10)$$

where  $C_1^*$  is the known value of  $C_1^{(6)}/\epsilon_1 \sigma_1^6$  for the molecular system.

We can now summarize the combination rules for molecules. We still require only the same information on the single components as for noble gases, namely, the parameters  $\epsilon$  and  $\sigma$ , the dipole polarizabilities  $\alpha$ , and the  $C^{(6)}$  dispersion coefficients. The first step is to calculate  $a_1$  and  $a_2$  from Eq. (10); if  $C^*$  happens to be greater than 2.2, then  $a^*$  is taken to be zero. In the next steps  $a_{12}$  is calculated from Eq. (2),  $\sigma_{12}$  from Eq. (3) or (4),  $C_{12}^{(6)}$  from Eq. (7), and finally,  $\epsilon_{12}$  from Eq. (9).

One final observation is relevant. Since the ratio  $r_m/\sigma$  is nearly constant for the models used for  $V(r)$ , where  $r_m$  is the position of the potential minimum, it follows that the ratio  $(r_m - a)/(\sigma - a)$  is also constant for the core models. Hence the quantities denoted by  $\sigma$  in the combination rules of Eqs. (3), (4), and (9) can be interpreted as the position either of the potential minimum or of the zero crossing point.

### 3. COMPARISON WITH EXPERIMENT

There are only few actual potential parameters  $\epsilon$  and  $\sigma$  (or  $r_m$ ) known for molecular gases, with which to test the proposed combination rules. All of these are based on low-energy molecular-beam measurements of scattering cross sections, combined with analysis of transport and virial coefficient data [14–19]. Results are summarized in Table I, and the necessary input data are recorded in Table II. The entries for He–Ar and Ne–Ar serve merely as an indication of the level of agreement attained for the noble gases and as a standard of comparison. The agreement between the calculations and the direct experiments for He–O<sub>2</sub>, Ne–CH<sub>4</sub>, and Ar–CH<sub>4</sub> is nearly as good as for the noble-gas systems. In these cases the core sizes are small or zero, so that the Tang–Toennies combination rules are in effect being used unchanged. The comparison for the systems involving SF<sub>6</sub> is indirect, since no direct measurements of the SF<sub>6</sub>–SF<sub>6</sub> interaction exist. This interaction was calculated from the measured mixed interactions via the combination rules, and the average then used to back-calculate the original mixed interactions. This is a consistency check only, and the results are seen to be less good than for the others.

The level of agreement for  $\epsilon$  is generally poorer than for  $r_m$ , a phenomenon that has been noted many times previously. However,

**Table I.** Test of Combination Rules for Directly Measured Interactions

System	$r_m$ (Å)		$\epsilon/k$ (K)		$a$ (Å)	Ref. No.
	Calc.	Expt.	Calc.	Expt.		
He-Ar	3.45	3.48	31.9	29.8	0	1
Ne-Ar	3.464	3.417	67.6	69.2	0	1
He-O <sub>2</sub>	3.45	3.45	35.2	29.3	0	16
Ne-CH <sub>4</sub>	3.630	3.676	71.7	65.9	0.01 <sub>5</sub>	18
Ar-CH <sub>4</sub>	3.899	3.850	166.6	169.6	0.01 <sub>5</sub>	18
He-SF <sub>6</sub>	4.33	4.22	41	62	0.16	17
Ne-SF <sub>6</sub>	4.29	4.30	95	111	0.16	17
Ar-SF <sub>6</sub>	4.48	4.44	255	237	0.16	15
Kr-SF <sub>6</sub>	4.57	4.61	322	272	0.16	15
SF <sub>6</sub> -SF <sub>6</sub>	5.06	—	600	—	0.32	Indirect

calculated properties are less sensitive to  $\epsilon$  than to  $r_m$ , so the differences tend to compensate. It also frequently happens that the deviations are in opposite directions for  $\epsilon$  and  $r_m$  and tend to compensate each other in the calculation of gas properties.

Despite the scarcity of directly measured potential parameters, other kinds of data exist for testing the combination rules. The first kind consists of a large number of the correlation parameters  $\sigma$  and  $\epsilon$  obtained from analysis of accurate viscosity data [20]. The second kind consists of

**Table II.** Input Data for Table I<sup>a</sup>

System	$r_m$ (Å)	$\epsilon/k$ (K)	$C^{(6)}$ ( $e^2 a_0^5$ )	$\alpha$ ( $a_0^3$ )	$a$ (Å)	Ref. No. for $r_m$ and $\epsilon$
He-He	2.967	10.8	1.4608	1.3831	0	1
Ne-Ne	3.087	42.25	6.875	2.663	0	1
Ar-Ar	3.759	143.2	67.2	11.08	0	1
Kr-Kr	4.012	199.9	133	16.74	0	1
O <sub>2</sub> -O <sub>2</sub>	3.94	133	62.01	10.59	0	14
CH <sub>4</sub> -CH <sub>4</sub>	4.03	201	129.6	17.47	0.03	19
SF <sub>6</sub> -SF <sub>6</sub>	5.06 ± 0.05	600 ± 180	951	44.14	0.32	Indirect: 15, 17

<sup>a</sup> Data on  $C^{(6)}$  and  $\alpha$  taken from the compilation in Appendix B of Ref. 33.

**Table III.** Ratios of Calculated to Experimental Values of Potential-Energy Scaling Parameters for Unlike Interactions;  $\sigma$  Above the Diagonal and  $\varepsilon$  Below<sup>a</sup>

$\varepsilon_{12}$	$\sigma_{12}$										
	Ar	Kr	Xe	N <sub>2</sub>	CO	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub> O	CH <sub>4</sub>	CF <sub>6</sub>	SF <sub>6</sub>
Ar		1.002	0.995	1.003	0.997	1.001	0.990	1.009	1.029	1.004	1.030
Kr	0.98		0.990	0.991	0.991	1.005	1.012	—	0.991	0.998	1.016
Xe	1.02	1.05		—	—	—	—	—	—	—	—
N <sub>2</sub>	1.01	1.11	—		1.000	0.998	0.999	1.006	1.007	1.005	1.039
CO	1.05	1.11	—	1.00		—	0.999	1.000	1.000	1.006	—
O <sub>2</sub>	1.00	0.99	—	1.04	—		0.996	—	—	1.003	1.033
CO <sub>2</sub>	1.16	1.08	—	1.05	1.00	1.11		1.002	1.005	1.001	1.025
N <sub>2</sub> O	1.00	—	—	0.97	0.96	—	0.99		—	—	—
CH <sub>4</sub>	0.85	0.72	—	0.99	1.01	—	1.04	—		0.990	0.993
CF <sub>4</sub>	0.95	1.04	—	0.96	0.97	0.95	1.06	—	1.07		1.019
SF <sub>6</sub>	0.79	0.90	—	0.77	—	0.76	0.93	—	1.03	0.89	

<sup>a</sup> Data on  $C^{(6)}$  and  $\alpha$  taken from the compilation in Appendix B of Ref. 33.

measurements of mixture properties, which can be compared with values calculated from the combination rules via correlation equations [2, 3].

Although the correlation parameters summarized in Ref. 20 are probably not true potential-well parameters, they are the very quantities needed to predict mixture properties, and are thus worth examining. The results are shown in Table III. We have omitted any interactions involving He and Ne because the well depths for He-He and Ne-Ne are so shallow that their values of  $\varepsilon$  cannot be determined satisfactorily from viscosity data at and above room temperature. On the whole, the agreement shown in Table III is good, although there are a few notable discrepancies. Most of the  $\sigma$  values agree within 1%, although a few of the interactions disagree by up to 4%; the average absolute deviation for all the entries is 0.9%. Similarly, most of the  $\varepsilon$  values agree within 5%, although a few deviations are larger and range up to 28%; the average absolute deviation for all the entries is still only 7%. In almost all cases the deviations for  $\sigma$  and  $\varepsilon$  are in opposite directions. Thus, the combination rules predict the unlike scaling parameters for viscosity fairly well. The few systems for which agreement seems poor in Table III nevertheless give good predictions for mixture properties, owing to compensation between  $\sigma$  and  $\varepsilon$ , as illustrated below. The prediction of mixture properties is, of course, the primary aim of the present combination rules.



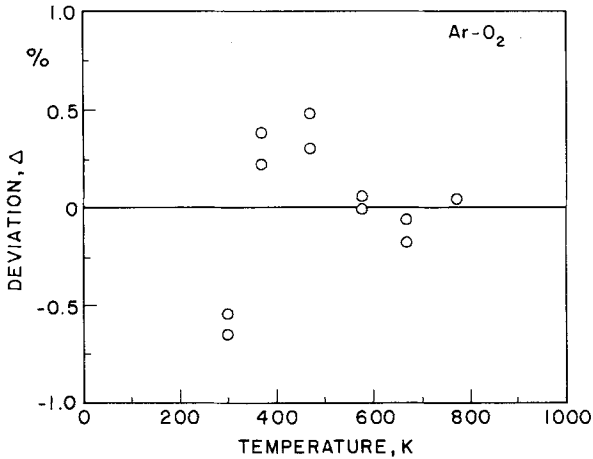


Fig. 1. Deviation plot for the viscosity of Ar-O<sub>2</sub> mixtures as a function of temperature. Several points at a given temperature refer to different mixture compositions. Data from Ref. 21.  $\Delta = \{ [\eta(\text{expt}) - \eta(\text{calc})] / \eta(\text{expt}) \} \times 100\%$ .

For comparison with measurements of mixture properties, we select three systems from Table III, as follows: one which shows excellent agreement for  $\sigma$  and  $\epsilon$  (Ar-O<sub>2</sub>), one which shows more typical agreement (N<sub>2</sub>-CO<sub>2</sub>), and one which shows rather poor agreement (N<sub>2</sub>-SF<sub>6</sub>).

Figures 1-3 show the deviations of the calculated mixture viscosities from the measured values [21-24]. Experimental viscosities for the single

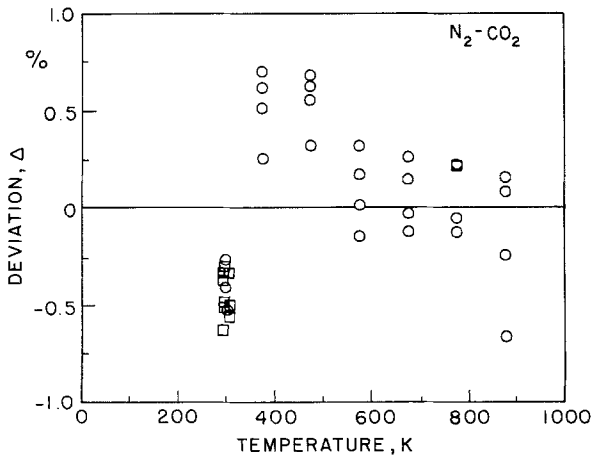


Fig. 2. Same as Fig. 1, for N<sub>2</sub>-CO<sub>2</sub> mixtures. (□) Ref. 23; (○) Ref. 24.

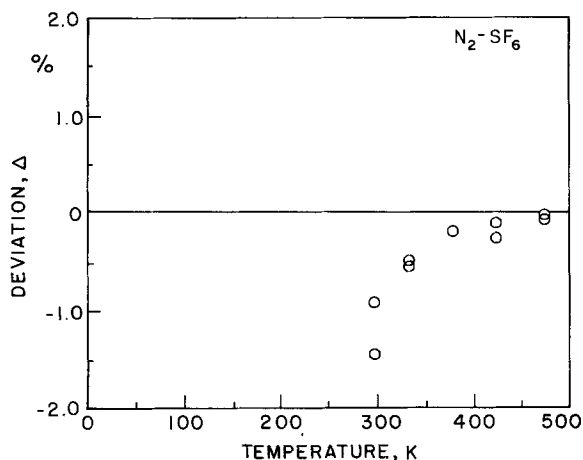


Fig. 3. Same as Fig. 1, for  $N_2$ - $SF_6$  mixtures. Data from Ref. 22.

components have been used in the calculations, so that the deviations shown reflect more directly the effects of the unlike interactions in the mixtures. The agreement for  $Ar-O_2$  and  $N_2-CO_2$  is about as good as that obtained for single gases [2], namely, deviations of the order of 0.5%. Even for  $N_2-SF_6$  the deviations are only of the order of 1%; this is a rather dramatic example of the compensating effect of opposite deviations in  $\sigma$  and  $\epsilon$ .

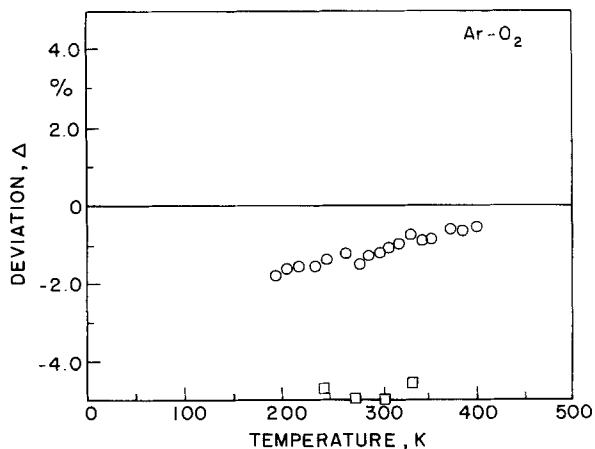


Fig. 4. Deviation plot for the diffusion coefficient of  $Ar-O_2$  as a function of temperature. ( $\square$ ) Ref. 28; ( $\circ$ ) Ref. 30.  
 $\Delta = \{ [D(\text{expt}) - D(\text{calc})] / D(\text{expt}) \} \times 100\%$ .

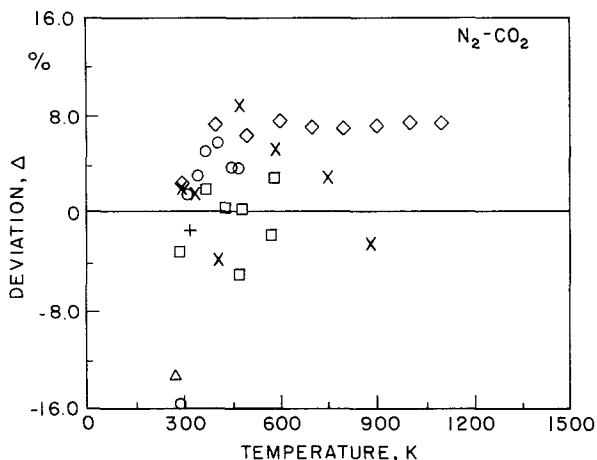


Fig. 5. Same as Fig. 4, for N<sub>2</sub>-CO<sub>2</sub>. (+) Ref. 25; (x) Ref. 26; (o) Ref. 27; (Δ) Ref. 29; (□) Ref. 31; (◇) Ref. 32.

Mixture viscosities, useful in their own right, are not a very sensitive test of unlike interactions, because the like interactions contribute on an equal footing. A more sensitive mixture property, which depends almost exclusively on the unlike interactions, is the binary diffusion coefficient. However, the experimental accuracy of the measurements [25–32] for the same three systems is distinctly lower than in the case of viscosity. The results are shown in Figs. 4–6 as deviation plots. Scatter in the data can be seen to run as high as about ± 10%; the only really accurate measurements

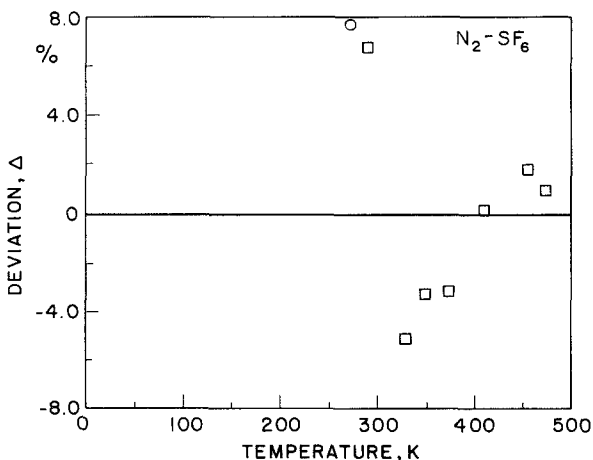


Fig. 6. Same as Fig. 4, for N<sub>2</sub>-SF<sub>6</sub>. (□) Ref. 27; (o) Ref. 29.

are those by Trengove et al. [30] on Ar-O<sub>2</sub>, which have better than 1% accuracy. The combination rules appear to predict diffusion coefficients within the experimental scatter.

Insofar as they can be tested, then, the modified combination rules seem to work satisfactorily. Certainly none of the experimental tests indicates any noticeable flaw in them.

#### 4. CONCLUSIONS

The present study shows that the Tang-Toennies combination rules for noble-gas atoms can be extended, with only minor modifications, to molecular gases, at least for the restricted problem of determining the two scale parameters of the effective potential-energy well. These modified rules make possible the prediction of the properties of many mixtures for which experimental data are scanty or lacking. Further testing of the rules, without additional experimental work, involves their application to the prediction of the properties of a large number of mixtures; the results of such work will be reported elsewhere.

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