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Citation: *J. Chem. Phys.* **59**, 2464 (1973); doi: 10.1063/1.1680358

View online: <http://dx.doi.org/10.1063/1.1680358>

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Combining rules for intermolecular potential parameters. II. Rules for the Lennard-Jones (12-6) potential and the Morse potential

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(Received 18 April 1973)

A new set of combining rules for intermolecular pair potentials of simple molecules has been formulated based on an atomic distortion model for the repulsive interactions and a geometric mean relationship for the attractive interactions. The rules are shown to be satisfactory in correlating the pair interactions of noble gas atoms when the effective pair interactions are represented by simple analytical potential functions such as the Lennard-Jones (12-6) potential and the Morse potential.

INTRODUCTION

In Part I of this series,¹ it has been shown that the consideration of the combining rules for the long-range dispersion energy constants alone would not lead to a successful correlation of effective intermolecular potentials unless other contributions to the pair interactions are properly taken into account and an effort has been made to obtain an improved model for repulsive interaction in conjunction with the Dymond-Alder potential. After the completion of work on Part I, a new combining rule for the repulsive pair interactions of simple molecules was introduced by Smith,² based on a model of atomic distortion. According to this model, the repulsive potential between unlike molecules $U_{12}^{rep}(R)$ is related to those of the like molecules by

$$U_{12}^{rep}(R) = \frac{1}{2} [U_{11}^{rep}(2r_1) + U_{22}^{rep}(2r_2)], \quad (1)$$

where r_1 and $r_2 = R - r_1$ are the distances satisfying the following condition:

$$[dU_{11}^{rep}(R)/dR]_{R=2r_1} = [dU_{22}^{rep}(R)/dR]_{R=2r_2}. \quad (2)$$

With evidence from theoretical calculations and atomic beam scattering experiments on a few atomic systems, Smith has concluded that the new combining rule is superior to the commonly assumed geometric mean rule:

$$U_{12}^{rep}(R) = [U_{11}^{rep}(R) U_{22}^{rep}(R)]^{1/2}. \quad (3)$$

Lately, a comparative test of the two combining rules, based on the information available from transport properties of noble gases and their mixtures revealed further evidence confirming Smith's conclusion.³

This paper presents a new set of combining rules that can be used for various analytical potential functions representing the effective pair interactions of simple molecules. The proposed rules include Eqs. (1) and (2) and an additional formula for the attractive interactions which is introduced

in this paper. The rules were applied to the Lennard-Jones (12-6) potential and the Morse potential and satisfactory results were obtained in correlating the effective pair interactions of the noble gas atoms

ASSUMPTION ON THE ATTRACTIVE INTERACTIONS

The geometric-mean combining rule for the repulsive potentials was first suggested by Zener⁴ considering the pair interactions of two hydrogen-like atoms at large separation. He noted that if the electron densities of the interacting atoms are given by simple exponential functions, the repulsive potential energy between the two atoms is essentially proportional to the factor $\exp[-(a_1 + a_2)R]$, where a_1 and a_2 are the halves of the respective electron density exponents. The repulsive potential between unlike atoms might therefore be given approximately by Eq. (3). For the same model of atomic interaction, it can be shown that the attractive energy terms also contain the same factor of $\exp[-(a_1 + a_2)R]$ and, hence, it may be assumed that the geometric mean relationship applies to the attractive interactions as well. It may be further suggested that in the interactions of atoms with closed-shell structure, the geometric mean rule will not be entirely satisfactory for the repulsive potentials because of the distortion on the charge distribution caused by the Pauli exclusion principle at smaller separation. This rule is perhaps more appropriate for the attractive interactions because at larger separation the distortion is less intense and the effective charge distributions of the interacting atoms may be safely given by simple exponential functions. Based on these considerations, the following rule is assumed for the attractive interactions: In the intermediate range of molecular separation near the potential minimum, the attractive potential between a pair of unlike molecules $U_{12}^{att}(R)$ is given by the simple geometric mean of the corresponding like-pair potentials

$$U_{12}^{att}(R) = [U_{11}^{att}(R) U_{22}^{att}(R)]^{1/2}. \quad (4)$$

TABLE I. Combining rules for the potential parameters.

L-J (12-6) potential: $U(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$	
$\epsilon_{12}\sigma_{12}^{12} = (\epsilon_{11}\sigma_{11}^{12}/2^{13})[1 + (\epsilon_{22}\sigma_{22}^{12}/\epsilon_{11}\sigma_{11}^{12})^{1/3}]^{13}$	
$\epsilon_{12}\sigma_{12}^6 = (\epsilon_{11}\sigma_{11}^6 \epsilon_{22}\sigma_{22}^6)^{1/2}$	
Morse potential: $U(R) = 4\epsilon\{\exp[2C[1 - (R/\sigma)]] - \exp[C[1 - (R/\sigma)]]\}$	
$(\epsilon_{12}C_{12}e^{2C_{12}/\sigma_{12}})^{\sigma_{12}/C_{12}} = (\epsilon_{11}C_{11}e^{2C_{11}/\sigma_{11}})^{\sigma_{11}/C_{11}}(\epsilon_{22}C_{22}e^{2C_{22}/\sigma_{22}})^{\sigma_{22}/C_{22}}$	
$\sigma_{12}/C_{12} = \frac{1}{2}[(\sigma_{11}/C_{11}) + (\sigma_{22}/C_{22})]$	
$\epsilon_{12}\exp\{\sigma_{12}[(C_{11}/2\sigma_{11}) + (C_{22}/2\sigma_{22})]\} = (\epsilon_{11}e^{C_{11}/\sigma_{11}}\epsilon_{22}e^{C_{22}/\sigma_{22}})^{1/2}$	

Without any further theoretical "justification," the present prescription for the attractive potentials will be simply regarded as an empirical formula whose validity is examined in this paper. A relationship similar to Eq. (4) has been suggested earlier⁵ as a drastic simplification of the well known formula for the long-range dispersion energies and has been used in conjunction with certain analytical potential functions in which $U^{\text{att}}(R)$ are given by an inverse sixth power term of R . In the present consideration of the attractive interactions, Eq. (4) is not intended to disagree with the theory of dispersion energy by extending the formula into the long range separation, neither is it intended to imply any specific analytical expression for $U^{\text{att}}(R)$. The present rule simply states that in the important range of intermediate separation the attractive interactions having great influence on the potential well shape effectively follow the geometric mean relationship regardless of the analytical form assumed for $U^{\text{att}}(R)$.

THE COMBINING RULES

Equation (4) together with Eqs. (1) and (2) gives a complete prescription for the over-all pair potential between unlike molecules, provided that the assumed potential function $U(R)$ does not contain more than three adjustable parameters and can be formally divided into the repulsive and attractive components: $U(R) = U^{\text{rep}}(R) + U^{\text{att}}(R)$. Among the commonly used analytical potential functions,⁶ the Lennard-Jones (12-6) potential and the Morse potential present contrasting forms and provide a convenient testing ground for the proposed combining rules. Applications of the rules to these potentials are straightforward and lead to the formulas shown in Table I. The unlike-pair parameters of each potential for a given molecular pair can be calculated in terms of these formulas simply from a knowledge of the corresponding like-pair parameters.

TEST OF THE COMBINING RULES

Recently, Hogervost⁷ redetermined the L-J (12-6) potential parameters of like-pair inter-

actions for Ne, Ar, Kr, and Xe from accurate viscosity measurements between 100 and 1600 °K. With his parameters, the unlike-pair parameters of the noble gas atoms were calculated by the new combining rules and the results are shown in Table II along with the experimentally deduced values from binary diffusion coefficients of the mixed systems.⁸ The unlike-pair parameters of He-Ar and He-Xe were calculated using the He-He parameters presently estimated from the parameters of Kr-Kr⁷ and He-Kr⁸ pairs with the combining rules. It can be seen that the predicted parameters by the new combining rules are well within the limits of uncertainties attached to the experimental values except for the pairs of Ar-Kr and He-Xe for which the predictions are slightly outside of the limits. When the diffusion coefficients D_{12} were calculated from the predicted parameters, the experimental values⁸ for each mixture were reproduced well within the reported experimental accuracy of $\pm 2\%$ over the entire temperature range of 300-1400 °K, with the exception of those for the Ar-Kr mixture. For this system, the calculated D_{12} values show a maximum deviation of about 2% from the smoothed curve of the experimental data at higher temperatures.

Several combining rules have been suggested

TABLE II. Unlike-pair parameters of the L-J (12-6) potential.

System	ϵ_{12}/k (°K)		σ (Å)	
	Predc.	Expt ^b	Predc.	Expt ^b
Ne-Ar	67.12	64.5 ± 4	3.093	3.09 ± 0.03
Ne-Kr	74.74	71.5 ± 3.5	3.226	3.22 ± 0.03
Ne-Xe	73.38	73.0 ± 4	3.472	3.46 ± 0.03
Ar-Kr	159.6	148 ± 7	3.470	3.51 ± 0.03
Ar-Xe	175.2	178 ± 6	3.665	3.65 ± 0.03
He-Ar ^a	41.50	40 ± 3	2.980	2.98 ± 0.02
He-Xe ^a	40.94	49 ± 5	3.403	3.36 ± 0.03

^aPredictions are made using the He-He parameters presently obtained from the parameters of He-Kr and Kr-Kr pairs with the combining rules.

^bFrom Ref. 8.

TABLE III. Predicted unlike-pair parameters of the Morse potential.^a

System	Combining rules	ϵ_{12}/k (°K)	σ_{12} (Å)	C_{12}
Ne-Ar	new rules	67.20	3.150	5.16
	Saran ^b	79.81	3.065	5.08
	S-G ^c	79.81	3.046	5.0
Ne-Kr	new rules	65.74	3.278	5.02
	Saran ^b	89.65	3.121	4.91
	S-G ^c	89.65	3.072	4.8
Ar-Kr	new rules	160.2	3.455	4.80
	Saran ^b	162.7	3.447	4.80
	S-G ^c	162.7	3.438	4.7

^aPredictions are made using the same like-pair parameters of Ref. 13.

^bCombining rules suggested in Ref. 9.

^cCombining rules suggested in Ref. 10.

for the Morse potential.⁹⁻¹² To test the applicability of the new rules to the Morse potential, the interaction second virial coefficient B_{12} of three binary mixtures Ne-Ar, Ne-Kr, and Ar-Kr were examined in this study. Konowalow and Hirschfelder¹³ have determined the like-pair parameters of the Morse potential for several systems from virial and crystal data. Using their parameters, the unlike-pair parameters of the three mixed systems were calculated and the results are given in Table III. Also included in the table are the values of the unlike-pair parameters predicted by other combining rules previously suggested for the Morse potential. With these parameters, the B_{12} 's of the mixed gases were computed employing the table of reduced virial coefficients¹⁴ and the results are compared with experimental measurements¹⁵⁻¹⁸ in Fig. 1. Although the new combining rules lead to better predictions of B_{12} for the Ar-Kr mixture at lower temperatures, the substantial disagreement between the experimental data reported by different authors at higher temperatures makes it difficult to determine the relative success of the different rules. The results for the other two mixtures, however, clearly show the superior nature of the new combining rules. The combining rules of Saran⁹ have been suggested to be quite satisfactory for correlating the transport properties of several molecular systems and the rules of Saxena and Gambhir¹⁰ were reported as being adequate for predicting B_{12} of Ar-Kr and Ar-CH₄ mixtures.

DISCUSSION

It has been shown that the new set of combining rules given by Eqs. (1), (2), and (4) are satisfactory for correlating the effective pair interactions of noble gas atoms when the interactions are represented by simple analytical potential functions

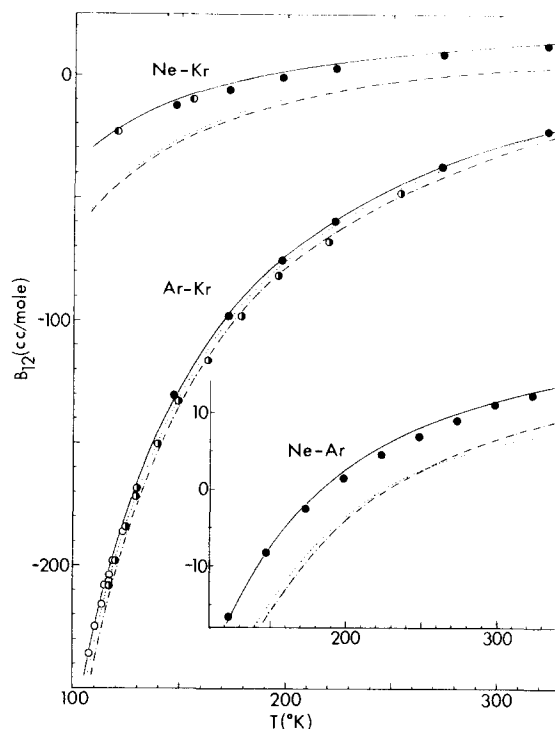


FIG. 1. Comparison of calculated and experimental interaction second virial coefficients B_{12} of noble gas mixtures. Calculated: (—), new combining rules; (---), Saran's rules; (-.-), Saxena-Gambhir's rules. Experimental points: ●, Ref. 18; ○, Ref. 15; ◐, Ref. 17; ○, Ref. 16.

such as the Lennard-Jones (12-6) potential and the Morse potential. For the mixed systems considered here, the new combining rules work without any single case of serious failure. It is noteworthy that the new rules are equally successful for systems like He-Xe and Ne-Xe. It has been pointed out in previous studies^{19,20} that even the best of the previously suggested rules fails to give proper unlike-pair parameters for systems involving molecules with large difference in their "sizes," when the pair interactions are correlated by a two-parameter potential.

In principle, the new combining rules can be applied to other two- or three-parameter potentials. It seems that the new combining rules, as well as the physical models adopted for the repulsive and the attractive interactions in formulating the rules, deserve further examination for their extended application in the study of mixtures.

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