

## LETTERS

### 電子氣體 理論으로 計算한 分子間 퍼텐셜을 利用한 結合法則에 關한 研究\*

金永植 · 李熙天

서울대학교 自然科學大學 化學科

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### Study of the Combining Rules Using the Electron Gas Model Intermolecular Forces\*

Yung Sik Kim and Hee Chun Lee

Department of Chemistry, College of Natural Sciences,

Seoul National University, Seoul, Korea

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Recently, Smith<sup>1</sup> proposed a combining rule that can be used for estimating the repulsive interaction potential,  $V_{AB}$ , of the unlike pair of closed shell atoms or ions when those of the like pairs  $V_{AA}$ ,  $V_{BB}$  are known. The rule is based on the ideas that the electron densities of the two atoms or ions are distorted as they approach each other and that the repulsive energy is the sum of the distortion energies of the two atoms or ions. According to this rule the unlike pair interaction is represented by

$$V_{AB}(R) = 1/2 V_{AA}(2r_A) + 1/2 V_{BB}(2r_B) \quad (1)$$

or

$$V_{AB}(R, r_A) = 1/2 V_{AA}(2r_A) + 1/2 V_{BB}(2(R-r_A)), \quad (2)$$

where the relation  $r_A + r_B = R$  is used. Here,  $V_{AB}$  depends on  $r_A$ , the distance of the imaginary boundary plane from the nucleus  $A$ , as well as on  $R$ . To choose appropriate values for  $r_A$ , Smith assumed that the boundary plane settles at a distance which minimizes the total interaction energy, or at  $r_A$  which satisfies the following condition:

$$\frac{\partial V(R, r_A)}{\partial r_A} = 0 \quad (3)$$

Smith himself checked the accuracy of this rule using the Hartree-Fock repulsive potentials of  $\text{He}_2$ ,  $\text{Ne}_2$ ,  $\text{Ar}_2$ ,  $\text{HeNe}$ ,  $\text{HeAr}$  and  $\text{NeAr}$  and showed its superiority over the geometric mean rule,

$$V_{AB}(R) = [V_{AA}(R) V_{BB}(R)]^{1/2} \quad (4)$$

Other investigators<sup>2</sup> have since put this rule to more extensive tests using empirical potentials

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and have also found more accurate estimates of the potential parameters than those obtained from the geometric mean rule.

However, these latter checks are significant only for the potential values at the attractive well, and thus cannot be counted as proper tests of the Smith rule which is supposed to hold among the repulsive potentials. Smith's own check is not adequate, either, because he used the Hartree-Fock values which, especially the ones including Ar, were not accurate enough. In addition, what has to be compared with the Smith rule is not the geometric mean rule, but really the arithmetic mean rule,

$$V_{AB}(R) = 1/2V_{AA}(R) + 1/2V_{BB}(R), \quad (5)$$

because the Smith rule is reduced to the arithmetic mean rule in the limiting case where  $r_A = R - r_B = 1/2R$ . Furthermore, as can easily be seen from the comparison of equations (2) and (5), what the Smith rule does is to incorporate to the arithmetic mean rule the fact that the two atoms or ions in the pair  $AB$  are different. Thus, any improvement that it brings about should be checked in comparison with the arithmetic mean rule. The purpose of this letter is to point out the above point and suggest a way to amend the situation.

One of the problems that Smith faced was the scarcity of the reliable repulsive potentials. What were available to him were only the Hartree Fock repulsive potentials for the pairs containing He, Ne and Ar atoms. With the subsequent success of the electron gas model<sup>3</sup>, the situation is now vastly different: we have reliable repulsive potentials for many systems containing the closed shell atoms and ions, notably the rare gas atoms, alkali and halide ions.<sup>3,4</sup> While these potentials will doubtless involve some errors, it has been shown<sup>3</sup> that these values are much more accurate than

the Hartree-Fock values. And what is more important, the potentials were the ones obtained from a single method and thus should be consistent with each other.

We have used these electron gas model repulsive potentials in our work to compare the accuracy of the Smith rule with that of the arithmetic mean rule. The results are given in Table 1 for several systems and are plotted in Fig. 1 for the  $\text{Na}^+\text{-Cl}^-$  repulsion as an example.

Comparison of the values in Table 1 shows the general superiority of the Smith rule over the geometric mean rule. However, when the Smith rule is compared with the arithmetic mean rule we find the opposite situation: more often than not the estimate of the arithmetic mean rule is better than that of the Smith rule. This could be expected from the fact that the estimated values of the arithmetic mean rule are usually lower than the calculated values. The Smith rule, by trying to lower this estimate by varying  $r_A$ , makes the deviation even larger. Fig. 1 illustrates this very well for  $\text{Na}^+\text{-Cl}^-$  repulsion.

A better method of incorporating the difference of the constituent atoms or ions in the unlike pairs is to use their size difference. Of course the Smith rule does this to some degree as can be seen from the  $r_A$  values obtained by the Smith rule variation given in Table 1: in most cases, the  $r_A$  value,  $A$  being the smaller atom or ion of the pair  $AB$ , is smaller than  $1/2R$ . However, these  $r_A$  values do not completely reflect the size differences. Usually, the  $r_A : r_B$  ratios are greater than what their relative sizes would predict. In some cases, notably in  $\text{K}^+\text{F}^-$ ,  $\text{K}^+\text{Cl}^-$ ,  $\text{Rb}^+\text{Cl}^-$  and  $\text{Rb}^+\text{Br}^-$ , the  $r_A$  values have come out to be larger than  $1/2R$ .

We can improve the situation greatly by taking the ratios of the ionic radii<sup>5</sup> for the ionic pairs and the covalent radii<sup>6</sup> for the atomic

Table 1. Comparison of the estimated potentials using various combining rules.\*

System	R	Calculated values	Geo. mean (error, %)	Arith. mean (error, %)	Smith rule $V_{AB}(\text{error, \%})r_A$	Eq. (6) $V_{AB}(\text{error, \%})r_A$
Na <sup>+</sup> F <sup>-</sup>	2.5	0.3712	0.2338(37)	0.2589(30)	0.2542(32) 1.214	0.3592( 3) 1.028
K <sup>+</sup> F <sup>-</sup>	3	0.2548	0.2278(11)	0.2496( 2)	0.2249(12) 1.630	0.2567(0.5) 1.483
Na <sup>+</sup> Cl <sup>-</sup>	3	0.3500	0.0874(75)	0.1411(60)	0.1176(66) 1.360	0.2996(14) 1.033
NeAr	3	0.2488	0.1885(24)	0.2424( 3)	0.2151(14) 1.372	0.2527( 2) 1.218
K <sup>+</sup> Cl <sup>-</sup>	3.5	0.2202	0.1218(45)	0.1221(45)	0.1192(46) 1.817	0.2129( 3) 1.482
F <sup>-</sup> Rb <sup>+</sup>	3	0.3585	0.3277( 9)	0.4376(22)	0.3275( 9) 1.288	0.3811( 6) 1.437
Na <sup>+</sup> Br <sup>-</sup>	3.5	0.2025	0.0389(81)	0.1413(30)	0.0668(67) 1.432	0.1521(25) 1.147
NeKr	3	0.3432	0.2665(22)	0.4394(28)	0.3150( 8) 1.284	0.3873(13) 1.115
Rb <sup>+</sup> Cl <sup>-</sup>	3.5	0.2931	0.1821(38)	0.2021(31)	0.1737(41) 1.917	0.3098( 6) 1.574
K <sup>+</sup> Br <sup>-</sup>	3.5	0.2855	0.1895(34)	0.2034(29)	0.1935(32) 1.670	0.2797( 2) 1.419
ArKr	3.5	0.2398	0.2436( 2)	0.2561( 7)	0.2427( 1) 1.653	0.2435( 2) 1.622
Rb <sup>+</sup> Br <sup>-</sup>	3.5	0.3906	0.2833(27)	0.2834(27)	0.2833(27) 1.762	0.4078( 4) 1.510

\*All the numbers except the percentages are in atomic units.

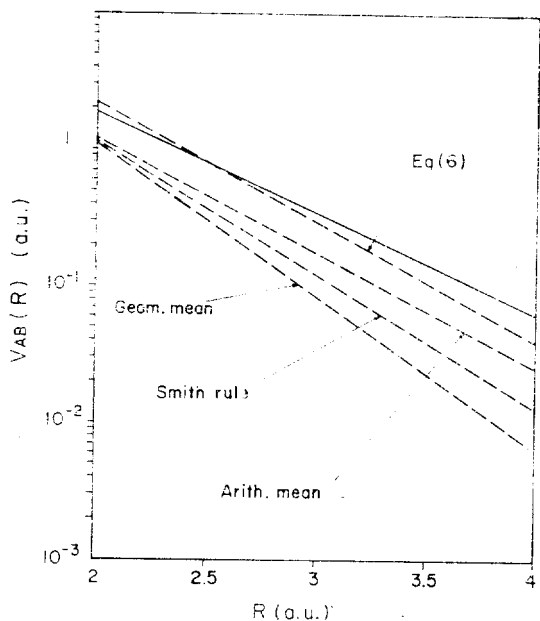


Fig. 1. Na<sup>+</sup>-Cl<sup>-</sup> repulsive potentials. —: Calculated curve, ---: estimated curve using combining rules.

pairs. The unlike pair interaction then becomes

$$V_{AB}(R) = 1/2 \left[ V_{AA} \left( \frac{2\rho_A R}{\rho_A + \rho_B} \right) + V_{BB} \left( \frac{2\rho_B R}{\rho_A + \rho_B} \right) \right] \quad (6)$$

where  $\rho_A$  and  $\rho_B$  are the ionic (or covalent) radii of A and B. The last column of Table 1 gives the  $V_{AB}$  values and the  $r_A$  values estimated in this manner. In all the cases, the result represents an improvement over the Smith rule estimates. In many cases the improvement is very impressive and the estimated values are very close to the calculated ones, within a few percent of them. The great improvement can also be seen in Fig. 1 for the Na<sup>+</sup>Cl<sup>-</sup> repulsion.

Similar examination is being carried out with more systems, and further aspects of the size dependence in the use of combining rules are being studied, by the present authors.

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