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## Intermolecular Potential Energy Functions for Simple Molecules

THE development of an intermolecular potential energy function for simple molecules based solely on an investigation of properties arising from two-body interactions<sup>1</sup> may prove more valuable than the alternative approach which considers also the properties of solids<sup>2</sup>. The latter approach involves the assumption of the pair-wise additivity of potential energy, the validity of which must be regarded as unproven. Unfortunately, the second virial coefficient, which is the most convenient two-body property to analyse, is not capable of defining a unique potential energy function<sup>3</sup>. However, recent low-temperature data provide a valuable test of the adequacy of potential energy functions and illustrate clearly the failure of many widely-used potentials<sup>4</sup>. Although some evidence points to a more complex form of the potential function, it seems appropriate to examine first simple two-term functions of the (n-6) type, which may be written:

$$U(r) = \varepsilon \left[ \left( \frac{6}{n-6} \right) \left( \frac{r_m}{r} \right)^n - \left( \frac{n}{n-6} \right) \left( \frac{r_m}{r} \right)^6 \right]$$

when  $r_m$  is the separation of the molecular centres at the potential minimum. The collision diameter  $\sigma$  is related to  $r_m$  by:

$$\sigma = r_m \left(\frac{6}{n}\right)^{\frac{1}{n-6}}$$

An analysis of the second virial coefficients of a number of simple gases shows that, as expected, many potentials of this type are capable of interpreting the experimental data for relatively high temperatures. However, analysis of the low-temperature results leads to the definite conclusion that, of the (n-6) potentials, only those with n in the range  $16 \leq n \leq 20$  are acceptable. (It is of interest to note that the shape of the (16-6) potential is similar to that of the Kihara function as applied to the inert gases<sup>5</sup>). This is illustrated for the very-low-temperature ranges in Fig. 1. Further evidence in favour of such values of n may be obtained from investigations of the transport properties of gases. It has been shown that an (n-6) potential with n > 12 is superior to the traditional (12-6) potential when applied to such properties<sup>6</sup>, and a quantitative investigation is in progress. Of the potentials we have considered, the (18-6) potential has previously been used to interpret the properties of globular molecules and found to be as good as the (28-7) potential which was expressly developed for this purpose<sup>7</sup>.

On the basis of all the foregoing considerations we conclude that the (18-6) potential will provide a much more useful basis for the description of second virial coefficients and the transport properties of gases than any of the simple potential functions<sup>11</sup> in general use.



Fig. 1. The second virial coefficients at low reduced temperatures. The reduction procedure used was based on the Boyle temperature of the gases,  $TB.B_o$  is defined as the second virial coefficient at T = 0.7 T B. Results are available for three classical gases in this region:  $\bullet$ , argon, refs. 4, 8, 9; O, krypton, refs. 4, 10;  $\Theta$ , oxygen, ref. 8. The solid curves a, b, c and d represent the theoretical values for (n-6) potentials when nhas the values 12, 16, 18, 20, respectively

We have calculated values of the reduced third virial coefficient over a range of reduced temperatures on the basis of the (18-6) potential by direct numerical integration, making the assumption of pair-wise additivity of the potential energy. The results are given in Table 1

Table 1. REDUCED THIRD VIRIAL COEFFICIENT FOR THE (18-6) POTENTIAL

$T^*$	$C^*$	$\Delta C^*/\alpha$
0.7	-0.640	
0.9	+0.513	
1.0	+0.572	8.71
$1 \cdot 2$	+0.535	5.73
1.5	+0.448	3.69
$2 \cdot 0$	+0.373	2.27
3.0	+0.339	1.28
5.0	+0.338	0.69

 $T^* = kT/\epsilon$ ,  $C^* = C/b_0^2$  where  $b_0 = \frac{2\pi}{3} N\sigma^3$ .  $a^* = a/\sigma^3$  where a is the polarizability.  $\Delta C^*/a^*$  is correction factor for non-additivity.

and are accurate to better than 0.5 per cent. A comparison with the rather uncertain experimental data shows the agreement to be reasonable, but in no way superior to that given by the (12-6) potential. However, if correction is made for non-additivity of the potential energy<sup>12</sup>, the agreement is considerably improved.

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