SHORT COMMUNICATIONS

ON THE ($N-6$) POTENTIAL FOR THE INERT GASES*

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In the course of a general program devoted to determining intermolecular forces between pairs of similar inert gas atoms we have been led to consider potentials whose functional form involves inverse power terms. In this note we give the results of fitting a simple ($N-6$) inverse power potential to these gases using only the experimental values of the second virial coefficient and independently determined values of C, the coefficient of r^{-6} in the potential $\phi(r)$ which we write

$$\phi(r) = \alpha\epsilon[(r/\sigma)^{-N}-(r/\sigma)^{-6}] \tag{1}$$

so that $C = \alpha\epsilon\sigma^6$, where $\alpha = [N/(N-6)][N/6]^{6/(N-6)}$.

The coefficient C is not completely arbitrary and must be determined independently. The most precise way of doing this is to use oscillator strengths obtained from absorption spectra. Values for C for the inert gases have recently been calculated in this way by Barker and Leonard[1] and these values were used in the present calculations.

The method of fitting the potential (Equation (1)) was as follows: For a given gas an integral value of N was assumed and σ, and hence ϵ, was varied to give the minimum mean of the squared differences between the experimental and calculated values of the second virial coefficient as computed from the gamma-function series (see, e.g., Hirschfelder *et al.*[2], p. 163). N was then varied through integral values and the process repeated until finally a combination of N and σ which minimized the mean of the squared differences was found. The detailed results follow (p. 2150). The units for the virial coefficients are cm^3 $mole^{-1}$ so that the mean of differences has the same units while the mean of squared differences has units cm^6 $mole^{-2}$.

The results for helium have been included for comparison but they are not satisfactory since quantum effects will be very important. When quantum corrections are taken into account for the other gases the results are much the same as the present ones.

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[1] Barker, J. A., and Leonard, P. J., *Phys. Lett.*, 1964, **13**, 127.

[2] Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids." (John Wiley: New York 1954).

Gas: Helium

$C = 1 \cdot 39 \times 10^{-60}$ erg cm^6

No. of data: 149

Temperature range: 1·59–1473·16°K

Best potential $= 4 \cdot 13 \times 10^{-16}\{(\sigma/r)^8 - (\sigma/r)^6\}$ erg

N	7	8	9	12
σ (Å)	2·351	2·662	2·831	3·078
ϵ/k (°K)	3·387	2·992	2·905	2·967
Mean of differences	−3·2	−0·2	+2·2	+7·7
Mean of abs. differences	6·2	4·5	3·7	8·9
S.D. of differences	6·8	6·6	6·9	7·9
Mean of squared differences	55·6	43·8	51·8	121·7

Gas: Neon

$C = 6 \cdot 14 \times 10^{-60}$ erg cm^6

No. of data: 57

Temperature range: 40·0–973·16°K

Best potential $= 61 \cdot 54 \times 10^{-16}\{(\sigma/r)^{16} - (\sigma/r)^6\}$ erg

N	12	15	16	17
σ (Å)	2·579	2·638	2·650	2·661
ϵ/k (°K)	37·80	43·01	44·58	45·95
Mean of differences	−1·3	−0·3	−0·03	+0·2
Mean of abs. differences	2·3	0·9	0·7	0·7
S.D. of differences	2·1	1·2	1·1	1·2
Mean of squared differences	6·0	1·5	1·3	1·4

Gas: Argon

$C = 61 \cdot 0 \times 10^{-60}$ erg cm^6

No. of data: 101

Temperature range: 84·21–873·16°K

Best potential $= 236 \cdot 07 \times 10^{-16}\{(\sigma/r)^{20} - (\sigma/r)^6\}$ erg

N	12	19	20	21
σ (Å)	2·993	3·188	3·203	3·22
ϵ/k (°K)	153·5	169·0	171·0	171·6
Mean of differences	−4·1	−0·4	−0·02	+1·1
Mean of abs. differences	6·2	1·4	1·2	1·7
S.D. of differences	5·5	2·1	2·0	2·1
Mean of squared differences	46·8	4·4	4·1	5·4

Gas: Krypton

$C = 126 \times 10^{-60}$ erg cm^6

No. of data: 50

Temperature range: 107·55–873·16°K

Best potential $= 326 \cdot 77 \times 10^{-16}\{(\sigma/r)^{18} - (\sigma/r)^6\}$ erg

N	12	17	18	19
σ (Å)	3·174	3·354	3·376	3·395
ϵ/k (°K)	222·8	234·4	236·7	238·9
Mean of differences	−4·7	−0·8	−0·2	+0·3
Mean of abs. differences	6·7	2·3	2·0	1·8
S.D. of differences	6·0	2·9	2·8	2·9
Mean of squared differences	58·0	9·1	8·0	8·4

Gas: Xenon

$C = 258 \times 10^{-60}$ erg cm^6

No. of data: 44

Temperature range: 273·16–973·16°K

Best potential $= 525\cdot 71 \times 10^{-16}\{(\sigma/r)^{28} - (\sigma/r)^6\}$ erg

N	12	18	27	28	29
σ (Å)	3·409	3·589	3·686	3·692	3·698
ϵ/k (°K)	297·5	336·9	377·4	380·8	384·2
Mean of differences	−2·1	−1·0	−0·1	+0·02	+0·1
Mean of abs. differences	5·8	2·9	1·1	1·1	1·1
S.D. of differences	6·7	3·3	1·8	1·8	1·8
Mean of squared differences	48·9	12·1	3·3	3·3	3·4

On comparing the present results with those obtained by fitting the Kihara potential, for example, it was found that the $(N-6)$ potential with independently determined values of C gave a better fit to the experimental second virial coefficients for neon and argon but the results for krypton and xenon were much the same. However, the Kihara potential gives a better overall fit to both second virial coefficients and transport properties. Even so, a more general potential function is needed if a more comprehensive description of the effects of intermolecular forces for inert gases is to be given.