

THIRD VIRIAL COEFFICIENTS FOR KRYPTON

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Bobetic, Barker, and Klein¹ have recently constructed a realistic two-body potential function for krypton which has the form

$$u(R) = \epsilon [\exp\{\alpha(1-r)\} \sum_{i=0}^5 A_i(r-1)^i - \sum_{i=0}^2 C_{2i+6}/(\delta+r^{2i+6})]$$

where $r = R/R_m$, with R_m the separation at the minimum of the potential and ϵ the depth at the minimum. This potential function fits the experimental second virial coefficients, gaseous viscosities, and thermal diffusion ratios very well and with the inclusion of the Axilrod and Teller triple-dipole for the non-additive effects fits the Debye parameter, thermal expansion coefficient, and bulk modulus of crystalline krypton.

The gaseous properties calculated all depend on the two-body interaction potential. The solid state properties depend on the many-body forces, but it has been shown² that for krypton and argon the triple-dipole three- and four-body energies virtually cancel one another out. This cancellation of three- and four-body terms does not of course affect the third virial coefficient which depends only on three-body interactions.

It has been noted by two of us³ that for argon third virial coefficients computed using a pair potential of the above form of equation and taking into account non-additive terms up to and including the triple-quadrupole term are in excellent agreement with experiment. We have made similar computations for krypton using the Bobetic, Barker, and Klein¹ potential. The results are shown in Table 1 where they are compared with the experimental values. The only quadrupole polarizability which is available is that due to Bell.⁴ This may not be of high accuracy and in fact for argon Bell's value is considerably lower than the more accurate value of Lahiri and Mukherji.⁵ We have therefore computed third virial coefficients with atomic constants

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¹ Bobetic, M. V., Barker, J. A., and Klein, M. L., *Phys. Rev.*, in press.

² Barker, J. A., Johnson, C. H. J., and Spurling, T. H., *Aust. J. Chem.*, 1972, **25**, 1811.

³ Johnson, C. H. J., and Spurling, T. H., *Aust. J. Chem.*, 1971, **24**, 2205.

⁴ Bell, R. J., *J. Phys. (B)*, 1970, **3**, 751.

⁵ Lahiri, J., and Mukherji, A., *J. phys. Soc. Japan*, 1966, **21**, 1178; *Phys. Rev.*, 1966, **141**, 428; 1967, **153**, 386; 1967, **155**, 24.

derived from Bell's quadrupole polarizability and also from values scaled upwards by the ratio of the two argon values. The computed values in column 5 of Table 1 correspond to the use of Bell's value and those in column 6 to the estimated value. The variation in the virial coefficients represents the uncertainty in the polarizability values.

TABLE 1
EXPERIMENTAL AND CALCULATED VIRIAL COEFFICIENTS FOR KRYPTON
Values of C are in $\text{cm}^6 \text{mol}^{-2}$. D, dipole; Q, quadrupole

T (K)	C (experi- mental)	C (addi- tive)	C (additive+ triple D terms)	C (additive+all D-Q terms) Bell's polarizability	Estimated polarizability
273·16	2757 ^a 3130±125 ^b 2455 ^c	1951	2611	2761	2884
323·16	2260 ^a 3000±120 ^b 2035 ^c	1674	2152	2260	2314
373·16	1942 ^a 2570±90 ^b 1710 ^c	1480	1853	1937	1977
423·16	1759 ^a 1960±85 ^b 1515 ^c	1351	1655	1724	1757
473·16	1583 ^a 1755±75 ^b	1264	1526	1579	1608
573·16	1613 ^a 1355±115 ^b	1163	1363	1404	1425
673·16	1260±150 ^b	1109	1272	1305	1323
773·16	1055±150 ^b	1077	1215	1242	1257
873·16	760±170 ^b	1055	1174	1198	1211

^a Beattie, J. A., Brierly, J. S., and Barriault, R. J., *J. chem. Phys.*, 1952, **20**, 1615.

^b Whalley, C., and Schneider, W. G., *Trans. Am. Soc. mech. Engrs*, 1954, **76**, 1001.

^c Trappeniers, N. J., Wassenaar, T., and Wolkers, G. J., *Physica, 's Grav.*, 1966, **32**, 1503.

As with argon the agreement with experiment is improved by the inclusion of the attractive non-additivity. However, the scatter of the experimental data makes it impossible to comment usefully on the effects of repulsive non-additivity.