

SHORT COMMUNICATIONS

THE ZERO-PRESSURE JOULE-THOMSON COEFFICIENT OF QUADRUPOLEAR GASES*

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The product of the zero-pressure Joule-Thomson coefficient (μ^0) and the zero-pressure molar specific heat (c_p^0) of a gas is related to its second virial coefficient $B(T)$ by the equation^{1a}

$$\phi^0(T) = \mu^0 c_p^0 = T \frac{dB(T)}{dT} - B(T) \quad (1)$$

where T is the absolute temperature. ϕ^0 has been calculated for a number of spherically symmetric intermolecular potential functions^{1b} but the only orientation-dependent functions for which ϕ^0 has been calculated are the 12-6-3^{1c} and the 18-6-3² Stockmayer potentials. In this note we show how ϕ^0 can be calculated for any orientation-dependent potential function with a Lennard-Jones (12-6), (18-6), or (28-7) central component using existing tabulated functions, and illustrate the procedure by calculating ϕ^0 for the four quadrupolar gases nitrogen, ethylene, carbon dioxide, and nitrous oxide.

The second virial coefficient, $B(T)$, for an orientation-dependent potential with a Lennard-Jones (12-6) central component can be expressed as an infinite series of functions³ defined by the equation

$$\int_0^\infty r^{-k} \exp(-\phi(r)/kT) r^2 dr = \frac{1}{12} \sigma_0^{3-k} y^{-4} H_k(y) \quad (2)$$

in which

$$y = 2(\epsilon_0/kT)^{1/2} \quad \text{and} \quad \phi(r) = 4\epsilon_0\{(\sigma_0/r)^{12} - (\sigma_0/r)^6\}$$

The $H_k(y)$ values have been tabulated by Buckingham and Pople³ for k in the range $6 \leq k \leq 17$ and y in the range $0.6 \leq y \leq 3.2$. For $k > 15$ the $H_k(y)$ values are defined by the equation

$$H_k(y) = \frac{k-15}{12y^2} H_{k-12}(y) + \frac{1}{2} H_{k-6}(y) \quad (3)$$

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¹ Hirschfelder, J. O., Curtis, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids." (a) p. 232; (b) p. 173; (c) p. 217. (John Wiley: New York 1954.)

² Saxena, S. C., Joshi, K. M., and Ramaswamy, S., *Indian J. pure appl. Phys.*, 1953, **1**, 420.

³ Buckingham, A. D., and Pople, J. A., *Trans. Faraday Soc.*, 1955, **51**, 1173.

Differentiating equation (2) with respect to y leads to the equation

$$dH_k(y)/dy = 4y^{-1}H_k(y) - 2yH_{k+12}(y) + 2yH_{k+6}(y) \quad (4)$$

Equations similar to equations (2)–(4) can be written for any Lennard–Jones (n – m) potential. H-type functions have been tabulated for n – m having the values 18–6 and 28–7.⁴ Equation (1), with y as the variable instead of T , becomes

$$\phi^0(y) = -b_0 \left\{ \frac{y}{2} \frac{dB^*(y)}{dy} + B^*(y) \right\} \quad (5)$$

where $b_0 = \frac{2}{3}N\pi\sigma_0^3$ and $B^*(y) = B(y)/b_0$.

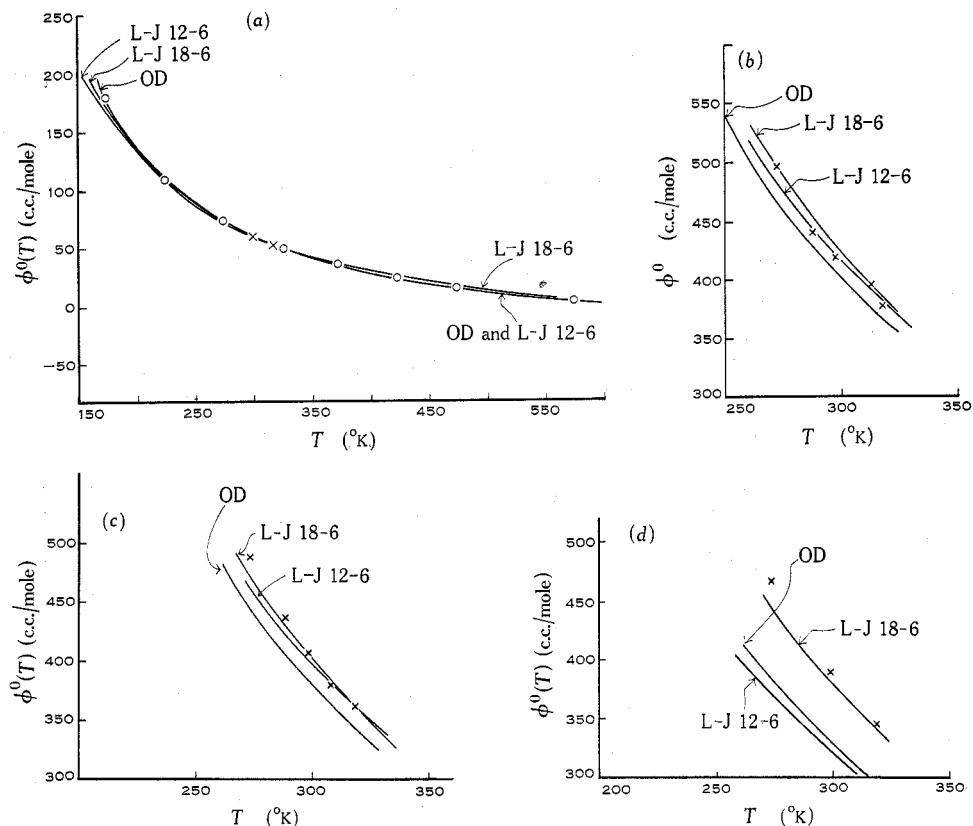


Fig. 1.—Comparison of calculated and experimental values of $\phi^0(T)$ for (a) nitrogen, (b) ethylene, (c) nitrous oxide, (d) carbon dioxide. Experimental values: $\times$, Charnley, A., Isles, G. L., and Townley, J. R., *Proc. R. Soc. A*, 1953, **218**, 133; $\circ$, Roebuck, F. R., and Osterberg, F., *Phys. Rev.*, 1935, **48**, 450.

Recently⁵ an intermolecular potential function, consisting of a Lennard–Jones (12–6) central component together with various orientation-dependent contributions, has been fitted to experimental viscosity and second virial coefficient data for nine

⁴ Bottomley, G. A., and Spurling, T. H., *Aust. J. Chem.*, 1966, **19**, 1331.

⁵ Spurling, T. H., and Mason, E. A., *J. chem. Phys.*, 1967, **46**, 322.

quadrupolar gases. These include nitrogen, ethylene, carbon dioxide, and nitrous oxide for which experimental Joule-Thomson data are available. The function used can be summarized as follows:

$$\begin{aligned}\phi(r, \theta_1, \theta_2, \phi) = & \phi(\text{L-J 12-6}) + \phi(\text{quadrupole}) + \phi(\text{quadrupole-induced dipole}) \\ & + \phi(\text{anisotropy}) + \phi(\text{shape})\end{aligned}\quad (6)$$

where θ_1, θ_2 , and ϕ are angles describing the relative orientation of two linear molecules, $\phi(\text{quadrupole})$ and $\phi(\text{quadrupole-induced dipole})$ are terms due to the classical electrostatic interaction of permanent polarizable quadrupoles, $\phi(\text{anisotropy})$ is a term arising from the anisotropy of the quantum mechanical dispersion forces and $\phi(\text{shape})$ is a term due to the anisotropy of the repulsive part of the potential. Further details of the function, expressions for the second virial coefficient according to it, and the parameters derived for the four gases under study can be found in ref.⁵

Values of ϕ^0 calculated from equation (6) using equations (4) and (5) for the four gases are compared to experimental values in Figure 1. Also included in the figures are values calculated by Saksena and Saxena⁶ for Lennard-Jones 18-6 and 12-6 potentials with parameters derived solely from second virial coefficients.

For nitrogen (Fig. 1(a)) the orientation-dependent potential (OD) fits the data equally as well as do the other two models but seems to be slightly better at the lowest temperature where the effect of the orientation-dependent terms is the greatest. Since the potential also fits the gas viscosity and second virial coefficient data it is a very satisfactory model for nitrogen. None of the models seems wholly adequate for ethylene (Fig. 1(b)) although the Lennard-Jones 12-6 potential is slightly better than the other two. However, for both nitrous oxide and carbon dioxide (Figs. 1(c) and 1(d)) the Lennard-Jones 18-6 potential is clearly better than the orientation-dependent potential. This suggests that for these two gases a potential function to fit both equilibrium and transport data should probably be equation (2) with the spherically symmetric component replaced by a Lennard-Jones 18-6 potential.

⁶ Saksena, M. P., and Saxena, S. C., *Proc. natn. Inst. Sci. India A*, 1966, **32**, 177.