

necessarily yield the best values of the virial coefficients, as has been shown by Hanley, McCarty, and Sengers.⁹ These authors found, by fitting series to data subsets of increasing density range, that (for example) a good linear fit could be obtained up to some limiting density ρ_l , beyond which the data deviated from linearity, but that good coefficients for a quadratic fit were not obtained below some density appreciably greater than ρ_l . Most of our isotherm ranges fall in such intermediate regions. We have therefore carried out such subset fits for our data, and the resulting estimates for the best values of a, b, c are given in Table III for N_2 and Ar; the scatter was too great for satisfactory results by this technique for He and H_2 . The values in Table III should thus be taken as our best estimates of these virial coefficients, while those in Table II are best for interpolation over our entire density range.

For N_2 and Ar fits were also made to the series

$$\eta = a + b\rho + \rho^2(c' + d' \ln \rho), \quad (2)$$

which has been proposed on theoretical grounds.³⁸ In each case¹⁰ the precision of the fit was no better or (usually) slightly worse than for the power series (1) with an equal number of coefficients. While this is far from conclusive, our work offers no strong support for the logarithmic-term hypothesis. Hanley, McCarty, and Sengers⁹ found such support in an analysis based primarily on thermal conductivity data; their technique is of limited use to us on this point since our isotherms still have appreciably fewer points (in particular not enough for good linear fits).

In addition to our individual-isotherm fits, further tests were made of the hypothesis¹ that the residual viscosity is a function of density only, i.e., that

$$\eta(T, \rho) = \eta(T, 0) + \Delta\eta(\rho). \quad (3)$$

This is an empirical correlation, the breakdown of which at low temperatures and high densities has been fairly well established.^{4,23} However, where it is valid it not only is quite useful for purposes of estimation, but holds

TABLE III. Best estimates for first three virial coefficients of viscosity, from fits to subsets of the present data.

Gas	T (°C)	a (μP)	b ($\mu\text{P}\cdot\text{cm}^3/\text{g}$)	c ($\mu\text{P}\cdot\text{cm}^6/\text{g}^2$)
N_2	25	176.96	116.5	633
	-50	140.49	111.6	655
	-90	117.52	122.7	603
Ar	25	225.17	116.2	359
	-50	175.19	103.2	363
	-100	137.83	91.0	338

³⁸ A recent review of the theory on this subject is given by J. V. Sengers, *Boulder Lectures in Theoretical Physics* (Gordon & Breach Science Publications, Inc., New York, 1967), Vol. 9C, *Kinetic Theory*, p. 335.

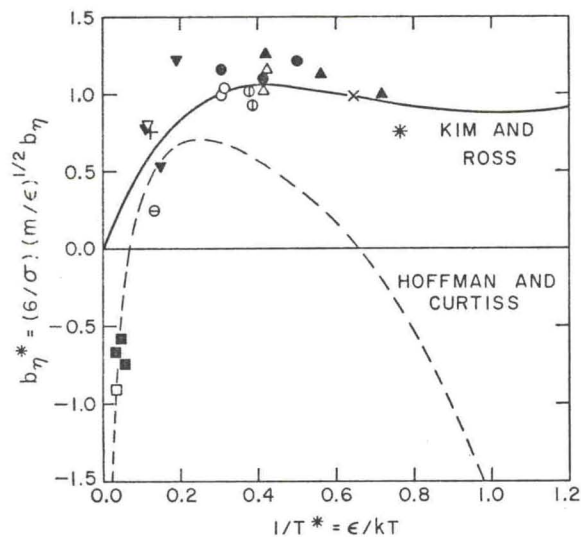


FIG. 5. Comparison of theoretical^{15,8} and experimental values of b_{η}^* , the reduced second virial coefficient of viscosity; present data: \bullet , N_2 ; \blacksquare , He; \blacktriangledown , H_2 ; \blacktriangle , Ar; Kestin and Leidenfrost¹⁸: \circ , N_2 ; \square , He; ∇ , H_2 ; \triangle , Ar; \odot , O_2 ; \ominus , D_2 ; $+$, Ne; \times , Kr; $*$, Xe. See Ref. 8 for the method of calculating b_{η}^* ; the experimental values for the present data are from Table II for N_2 and Ar and from Table III for He and H_2 .

to a remarkable degree of accuracy. Such fits were therefore made, as described in Ref. 1, for each of the gases studied; the standard deviations of the "best" fits are 0.26 μP for N_2 , 0.14 for He, 0.14 for H_2 , 1.41 for Ar (0.46 with -100°C omitted). (See Ref. 10 for the constants in these series and detailed comparison graphs showing to what extent the isotherms are in fact parallel.) Except for Ar, these results are quite consistent with the validity of Eq. (3) for our gases, within our experimental accuracy.

The Ar results, however, are problematical. Even the 25 and -50°C results are definitely not parallel within their own precision (the 25°C data being parallel to Kestin's and Michels' results), but the discrepancy here is only of the order of 1 μP . The -100°C data, in contrast, dip as much as 4% below the values predicted from Eq. (3) and Michels' $\Delta\eta(\rho)$, then rise more steeply at higher densities. (It may be significant that the greatest discrepancy, nearly 10 μP , is at 0.5 g/cm^3 , quite close to the critical density of 0.531 g/cm^3 .) The -50°C deviations, while much smaller, are in the same direction (as are the previous rough results¹ at -78.5°C). As noted above, Eq. (3) is known to fail in the low-temperature liquid-density range, but the previous evidence^{4,23} indicates that the departure is in the direction of *higher* values of $\Delta\eta(\rho)$, the opposite of what we observe here; no effect of either kind appears in the present N_2 data, at similar reduced temperatures and densities. The poor precision of the -100°C data is far too small an effect to account for this discrepancy, and further low-temperature Ar measurements are clearly desirable.

0.12
0.11
0.38
0.06
0.10
0.11
0.04
0.09
0.10
0.11
0.14
0.61

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