



FIG. 6. Values of c_{η}^* , the reduced third virial coefficient of viscosity, from our data: \bullet , N₂; \blacksquare , He; \blacktriangledown , H₂; \blacktriangle , Ar (from Table II for N₂ and Ar, from Table III for He and H₂).

To return to the individual-isotherm fits, we have reduced the values of the second virial coefficient of viscosity, b (from Table III for N₂ and Ar, Table II for H₂ and He), for comparison with the theories of Kim and Ross³ and Hoffman and Curtiss.⁷ The reduced values b_{η}^* are shown in Fig. 5, along with the two theoretical curves; see Refs. 8 for comparison with several other theoretical models,^{5,6,39} none of which fit the experimental data well. Also shown in Fig. 5 are the values of b_{η}^* from the data of Kestin and Leidenfrost,¹³ to which the parameters in Kim and Ross's theory were fitted; the present values are in general higher, but the shape of the curve remains unchanged.⁴⁰ The theory of Kim and Ross seems reasonably correct, except for its failure to predict the negative values of b for He; on the other hand, that of Hoffman and Curtiss agrees well with the He data but fails at lower reduced temperatures. These results can be explained as due to Kim and Ross's taking inadequate account of repulsive interactions and Hoffman and Curtiss's neglect of orbiting effects important at high and low reduced temperatures, respectively. The plateau predicted by Kim and Ross for $(1/T^*) \gtrsim 0.3$ presumably is related to the nearly temperature-independent residual viscosity discussed above, although the latter appears to apply even at densities where higher virial coefficients are dominant.

In connection with the point just made, a correlation of the *third* virial coefficient should be useful; to our knowledge, this has not been attempted before. While no theory for the value of c exists, the appropriate

reduction is easily made by dimensional analysis: Since we have⁸

$$b_{\eta}^*(T^*) = \frac{(b/\sigma)}{(\epsilon/m)^{1/2}} b_{\eta} \quad (4)$$

where σ and ϵ are Lennard-Jones parameters and $T^* \equiv kT/\epsilon$, it is clear that a dimensionless c_{η}^* should be given by

$$c_{\eta}^*(T^*) \equiv \frac{(1/\sigma^4)}{(\epsilon/m^3)^{1/2}} c_{\eta} \quad (5)$$

If σ is given in angstroms and (ϵ/k) in degrees Kelvin, the reduction factor $\sigma^4(\epsilon/m^3)^{1/2}$ equals $54.92\sigma^4(\epsilon/kM^3)^{1/2} \mu\text{P}\cdot\text{cm}^6/\text{g}^2$, where M is the molecular weight. Values of c_{η}^* were therefore obtained from our data as just described for b_{η}^* , the results being plotted in Fig. 6. Once again a plateau is obtained over most of the temperature range.

ACCURACY

Our previous estimate¹ of experimental precision was 0.001 in. Hg in the pressure difference. Although in our low-temperature work we were frequently restricted (by steady-state considerations) to pressure differences much less than an inch, the reproducibility of the viscosities (Table I) remained better than 0.1% in nearly all cases (even for H₂ at -100°C , where none of the pressure differences exceeded 0.4 in. Hg). The exceptions to the above statement are of course N₂ at -90°C and Ar at -100°C . As mentioned in the previous section, the standard deviations of our isotherm least-squares fits are consistent with these estimates of precision. Our average precision is thus about 0.05% near room temperature, but becomes worse than 0.1% at low temperatures and high densities (perhaps due to lack of thermal equilibrium in the apparatus).

Our accuracy should be somewhat worse than this. For our low-temperature N₂ and He measurements, there is the possibility¹⁰ of errors larger than 0.1% in the density ratios and thus the viscosities, due to our having combined densities from two different sources; the single-source H₂ and Ar density ratios should be good to about 0.02%. Combining this with other known sources of error in the calibrations and measurements, we estimate our accuracy as 0.1%–0.2%.

However, accuracy can be established objectively only by comparison with other work, and the situation in this respect is unsettled. Our agreement with previous work with this apparatus^{1,2} is within the limits just stated, but at -50°C there are some apparently systematic discrepancies¹⁰ at the outer range of these limits. The most precise other work available for comparison is that of Kestin *et al.*,^{18,29} done with oscillating-disk viscometers, and the discussions above have indicated that our results are consistently several tenths of a percent lower than Kestin's; the possibility

³⁹ D. Enskog, Kgl. Sv. Vetenskapskad. Handl. **63**, No. 4 (1922).

⁴⁰ A graph similar to Fig. 5, but including data from many other sources, is given by Hanley, McCarty, and Sengers²; although their analysis of the data was carried out largely by fitting to Eq. (2), the results appear qualitatively the same.