

eters usually used to represent variables in reduced form. The best set of scale factors was found to be 1.931 for the temperature and 0.633 for the density, with which a 1% agreement of the isotherms in the range of overlap was obtained.

Since it had been previously found<sup>2</sup> that the ratio of reduction factors in terms of the molecular parameters of the Kihara potential were much closer to the ideal ones than those of the Lennard-Jones potential, it could be predicted that if the isotherms of argon and xenon were reduced with our set of parameters they would come much closer to each other than when reduced with L-J parameters. In this article the results of this calculation are presented using the data of Tables I and IV of Levelt's paper, where  $PV/RT$  values of argon and xenon are listed in terms of the reduced temperature and the reduced density based on the L-J parameters. For example

$$T_{LJ}^* = T \frac{k}{\epsilon_{LJ}}; \quad T_K^* = T_{LJ}^* \frac{\epsilon_{LJ}}{\epsilon_K}$$

where  $T_{LJ}^*$  and  $T_K^*$  are the reduced temperatures in terms of the Lennard-Jones and Kihara potential parameters  $\epsilon_{LJ}$  and  $\epsilon_K$ , respectively, and  $k$  is the Boltzmann constant. Numerical values for the ratio of the  $\epsilon$ 's are 0.868 for argon and 0.847 for xenon. Correspondingly, we obtain for the reduced density  $d^*$

$$d_{LJ}^* = \frac{N\sigma_{LJ}^3}{V_m}; \quad d_K^* = d_{LJ}^* \frac{\sigma_K^3}{\sigma_{LJ}^3}$$

where  $\sigma_{LJ}$  and  $\sigma_K$  are the distances between molecular centers when the potentials are zero.  $V_m$  is the molar volume, and  $N$  is Avogadro's number. Numerical values for the ratio of the  $\sigma$ 's are 0.978 for argon and 0.900 for xenon. The collision diameter  $\sigma$  is obtained from  $\sigma = 2^{-1/4}\rho_0 + d$ , where  $\rho_0$  is the potential parameter in eq 1. The diameter of the spherical core  $d$  is not an extra, adjustable parameter but is independently fixed<sup>4a</sup> by the simple relationship  $d = 0.08\rho_0$ , so that  $\sigma = \rho_0(2^{-1/4} + 0.08) = 0.971\rho_0$ . We thus obtained a two-parameter potential function as required by the theory of corresponding states.<sup>4b</sup> The molecular parameters we used are shown in Table I. They have been obtained by simultaneous fitting of both

second virial coefficient and viscosity coefficient.<sup>5</sup> Values of the parameters for xenon differ somewhat from those of ref 5 because recent viscosity measurements by Rigby and Smith<sup>6</sup> have been included in determining  $\epsilon/k$  and  $\sigma$ ; Lennard-Jones parameters are, of course, the same ones Levelt used.

We have performed a two-variable polynomial interpolation on the xenon data thus obtaining the  $PV/RT$  surface in the  $(PV/RT, T_K^*, d_K^*)$  space by automatic computation. We used the least-squares program 1007 on the Mercury computer of this university. The resulting polynomial  $Z(T_K^*, d_K^*)$  is of the sixth degree in  $d^*$  and the fifth degree in  $T^*$ , six being the maximum power of any term. This function gives a sum of the squares of the differences between the calculated and the observed value of  $PV/RT$  of xenon of  $1.73 \times 10^{-4}$  for the 136 data points used. We then calculated from the polynomial  $Z$  the values of  $PV/RT$  of xenon at values of  $T_K^*$  and  $d_K^*$  corresponding to those available from the actual measurements on argon. These values of  $PV/RT$  of xenon and argon for the same values of the reduced variables illustrate how well corresponding states are followed. Results of the calculations are shown in Table II where we list the differences ( $PV/RT$  of argon -  $PV/RT$  of xenon) reduced in terms of the Kihara potential parameters. Differences in terms of the Lennard-Jones parameters as taken from Levelt's paper are also included for comparison in Table III.

It can be observed that the differences are now significantly reduced in almost the entire range of overlap which extends from 1.17 to 1.56 in reduced temperature and from 0.098 to 0.685 in reduced density. The sum of the squares of the differences is  $4.15 \times 10^{-3}$  (standard deviation  $6.32 \times 10^{-3}$ ) for the Kihara potential and 1.437 (standard deviation 0.126) for the Lennard-Jones potential. In Table II there are two more columns than in Table III, *i.e.*, reduced densities 0.562 and 0.611. These correspond to densities 0.575 and 0.625, respectively, for the L-J case and do not appear in Table III because there are no experimental values of  $PV/RT$  for xenon reported for these densities. These results were in fact expected from a comparison of the values of the scale factors. The scale factor for temperature is simply the ratio  $\epsilon_K$  of xenon/ $\epsilon_K$  of argon. The scale factor for density is  $(\sigma_K \text{ of argon})^3/(\sigma_K \text{ of xenon})^3 \times V_s$  of xenon/ $V_s$  of argon where  $V_s$  is the

Table I: Parameters for the Kihara Potential

	$\epsilon/k$ , °K	$\sigma$ , Å	$d$ , Å
Argon	138.0	3.381	0.279
Xenon	266.0	3.932	0.324

(4) (a) F. Danon and K. S. Pitzer, *J. Chem. Phys.*, **36**, 425 (1962);  
(b) K. S. Pitzer, *ibid.*, **7**, 583 (1939).

(5) J. C. Rossi and F. Danon, *Discussions Faraday Soc.*, **40**, 97 (1965).

(6) M. Rigby and E. B. Smith, *Trans. Faraday Soc.*, **62**, 54 (1966).

(7) Numerical values of the coefficients will be furnished on request.