3. The equation of state (40) predicts the critical pressure when the critical density and temperature are substituted into it.

In addition, provisions were made to account for the different uncertainties in the experimental data from the different data sources. The weighting function described by eqs (18) and (23) was used in conjunction with the equation of state (40), where

$$Y=Z-1=\frac{P}{\rho RT}-1 \tag{41}$$

$$\sigma_Y^2=\left(\frac{\Delta Y}{2}\right)^2=\frac{Z^2}{4}\left(\frac{\Delta P}{P}+\frac{\Delta\rho}{\rho}+\frac{\Delta T}{T}\right)^2 \tag{42}$$

$$\left(\frac{\partial f}{\partial x_1}\right)=\left(\frac{\partial(Z-1)}{\partial T}\right)_\rho=\left(\frac{\partial Z}{\partial T}\right)_\rho \tag{43}$$

$$\left(\frac{\partial f}{\partial x_2}\right)=\left(\frac{\partial(Z-1)}{\partial \rho}\right)_T=\left(\frac{\partial Z}{\partial \rho}\right)_T \tag{44}$$

$$2\sigma_T=\Delta T;\ 2\sigma_\rho=\Delta_\rho. \tag{45}$$

Substituting eqs (42) through (45) into eq (18), and simplifying,

$$W=\frac{4}{Z^2\left[\frac{\Delta P}{P}+\frac{\Delta\rho}{\rho}+\frac{\Delta T}{T}\right]^2+\left[T\left(\frac{\partial Z}{\partial T}\right)_\rho\frac{\Delta T}{T}\right]^2+\left[\rho\left(\frac{\partial Z}{\partial \rho}\right)_T\frac{\Delta\rho}{\rho}\right]^2}. \tag{46}$$

The uncertainties in the P-V-T data were estimated from the statements of the investigators, from a knowledge of the experimental apparatus, and from preliminary examinations of the data. The estimated uncertainties associated with the various data are given in table 7.

The uncertainties from table 7 were substituted into eq (46) and weights were calculated for each P-V-T data point. These weights were then substituted into the generalized normal least squares equations with constraints as shown by Hust and McCarty [20].

TABLE 7. *Estimated uncertainties of the experimental data*

% Density	% Pressure	% Temperature	Source
0.05	0.02	0.02	[1]
.05	.02	.02	[6]
.1	.1	.1	[7]
.2	.02	.02	[8]
.2	.02	.02	[9]
.2	.2	.2	[10]

Since the normal equations are linear in the coefficients, the coefficient n_{16} in eq (40) had to be determined before the remaining 15 coefficients were evaluated. A systematic search for the optimum value of n_{16} was performed on the digital computer so that a minimum in the sum of the squares of the deviations was obtained. In order to have a realistic range in the search for n_{16}, an approximate value was obtained by corresponding states with nitrogen. A modified corresponding states method, proposed by Kamerlingh Onnes, was used. This method suggests that the reduced density is

$$\rho_r=\frac{\rho RT_c}{P_c}. \tag{47}$$

The difference between eq (47) and eq (1) is discussed by Gosman [22]. In eq (40), n_{16} appears as the coefficient of a squared density term. From eq (47), a corresponding states expression for a squared density term was obtained:

$$\rho_N^2=\left(\frac{P_c}{T_c}\right)_N^2\left(\frac{T_c}{P_c}\right)_A^2\rho_A^2, \tag{48}$$

where the subscripts N and A represent nitrogen and argon, respectively. Equation (48) was substituted into the exponential term in eq (40). From Strobridge, the n_{16} for nitrogen was also substituted into the exponential term of eq (40). The resulting approximate value of the coefficient n_{16} for argon from corresponding states was calculated to be 0.0039. The range of the systematic search for n_{16} was thus determined to be 0.0039 ± 0.0015. The systematic search was accomplished by incrementing 0.0039 by small values and performing a linear least squares fit for each consecutive value of n_{16}. As the search proceeded, it was found that the sum of the squares of the deviations were not much affected by the current value of n_{16}. However, the fit of the equation of state in the region of the critical point was moderately affected by the different trial values of n_{16}. The resulting value of n_{16} and the least square estimates of the remaining 15 coefficients for eq (40) are given in table 8.

TABLE 8. *Least squares estimates of coefficients for equation of state (40)*[a]

Coefficient	Least squares estimate	Standard deviation of coefficient	Significance level %[b]
n_1	0.25978374×10^{-2}	4.927×10^{-5}	99.5+
n_2	$-.89735867$	3.002×10^{-2}	99.5+
n_3	$-.67273638\times10^{2}$	2.939×10	99.5+
n_4	$-.26494177\times10^{4}$	2.475×10^{2}	99.5+
n_5	$.97631231\times10^{7}$	7.133×10^{5}	99.5+
n_6	$.70478556\times10^{-4}$	1.814×10^{-6}	99.5+
n_7	$-.46767764\times10^{-2}$	1.323×10^{-4}	99.5+
n_8	$.22640765\times10^{-5}$	6.177×10^{-8}	99.5+
n_9	$.48141071\times10^{3}$	8.442×10	99.5+
n_{10}	$.64565346\times10^{5}$	3.152×10^{4}	95.0
n_{11}	$-.11485282\times10^{8}$	2.495×10^{6}	99.5+
n_{12}	$-.64835488$	1.942×10^{-1}	99.5+
n_{13}	$.46524812\times10^{3}$	7.373×10^{2}	25.0
n_{14}	$.10933578\times10^{5}$	1.287×10^{3}	99.5+
n_{15}	$.69439530\times10^{-6}$	4.064×10^{-9}	99.5+
n_{16}	$.48\times10^{-2}$	.....	.....

[a] Where P is in atm, T is in degrees K, ρ is in g-mol/l, and $R=0.0820535$ atm l/g-mol K.

[b] These parameters are significant at the level indicated when applying the standard F test.

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8. Analysis of *P-V-T* Data

Using the coefficients shown in table 8, the equation of state (40) was used to calculate the densities which corresponded to each of the experimental *P-V-T* data points. Percent density deviations between the points calculated by the equation of state and the individual experimental data points which were used in the fit are illustrated in figures 5 through 15. These deviation plots permit the identification of the maximum deviations corresponding to each region of the *P-V-T* surface as well as the specific deviations from each data source.

The deviation plots for the data of Michels et al. [1] and Michels et al. [6] are shown by figures 5 through 11. Inspection of figures 5 and 6 shows that the largest density deviations occur in the vicinity of the 153.15 K isotherm. For this isotherm, the largest deviations occur in the region of the critical point. The same phenomenon occurs for the 163.15 K and 150.65 K isotherms and, to a lesser extent, for the 173.15 K and 148.15 K isotherms. This behavior is illustrated in figures 7 and 8.

Figure 16 illustrates the characteristics of the different isotherms as they range over the pressure-density coordinate system. It is seen that the high and low temperature isotherms have relatively large

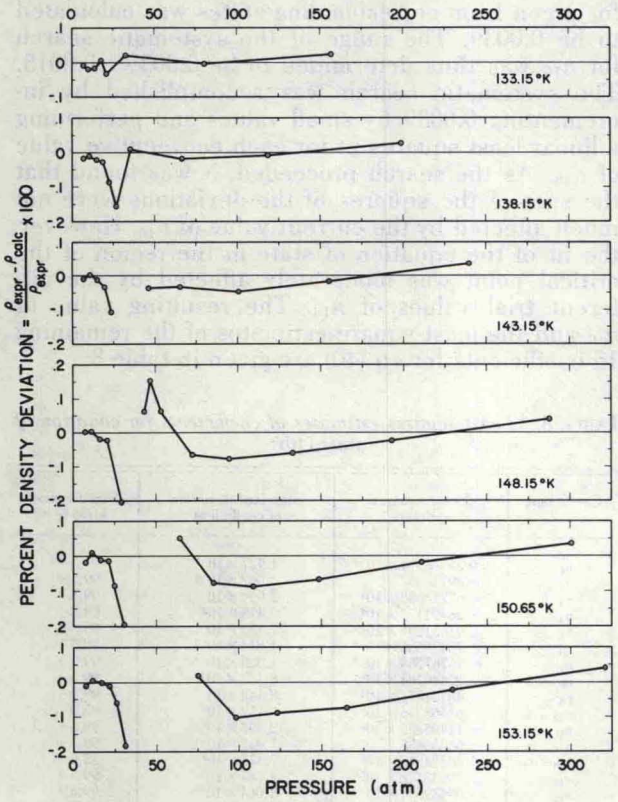

FIGURE 5. *Low temperature density deviations of data by Michels et al. [1] from the equation of state (40).*

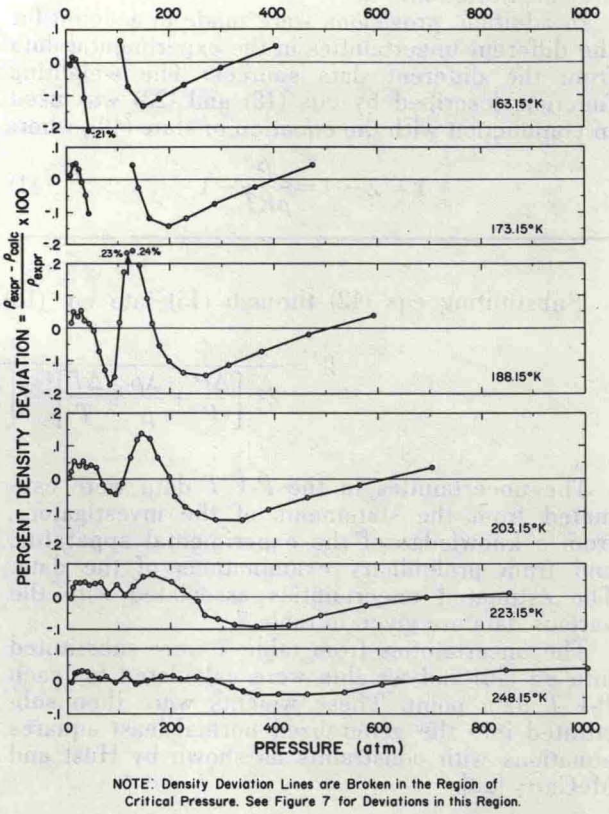

FIGURE 6. *High temperature density deviations of data by Michels et al. [1] from the equation of state (40).*

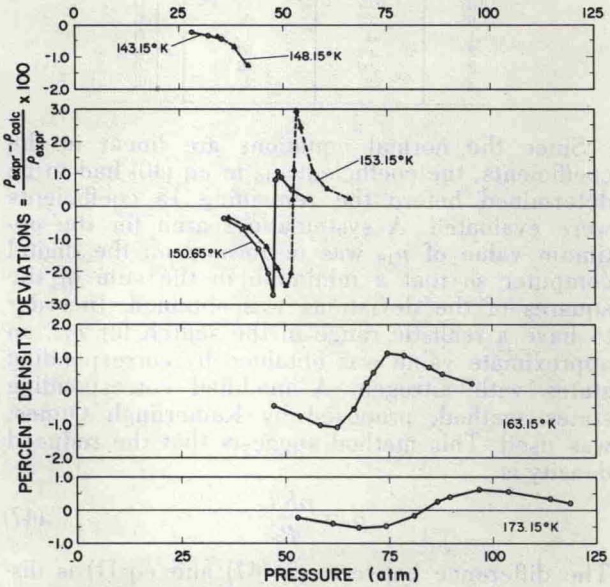

FIGURE 7. *Density deviations in the region of the critical point.*