

FIGURE 16. Pressure-density diagram showing isothermal characteristics.

est sensitivity to small variations in pressure or temperature. If the data points in this region are not included, the mean of the absolute values of the density deviations is 0.08 percent for the data of Michels et al. [1]. If the data points in this region are included, the mean deviation in density becomes 0.26 percent for the data of Michels.

Figures 7 and 8 are expanded-scale deviation plots from figures 5 and 6 and correspond to the region near the critical point. Figure 7 is a density deviation plot and shows a systematic trend which can be attributed to the equation of state. The magnitudes of the density deviations in figure 7 are due to the extreme sensitivity of the density in this region. Figure 8 is a pressure deviation plot for the same region. The systematic trend is still present, but the magnitudes of the pressure deviations are significantly smaller than the corresponding density deviations.

Figure 9 illustrates the density deviations for two isotherms from the data of Michels et al. [6]. A total of 94 data points for these two isotherms were fitted to pressures of about 1000 atm. The mean of the absolute values of the density deviations is 0.034 percent for pressures to 1000 atm, and the data appear to be consistent with the data of Michels et al. [1]. In addition, figure 9 shows density deviation plots for the same two isotherms for pressures from 1000 to about 3000 atm. The equation of state was not fitted to any data above 1000 atm, so the latter deviation plots represent an extrapolation of

the equation of state for pressures beyond the fitted data. The density deviations are approximately constant for this pressure range with a mean density deviation of 0.15 percent.

Figure 10 exhibits the density deviations for 41 experimental data points of Michels et al. [1] which are close to the saturation boundary. With the exception of the points close to the critical point the mean density deviation is 0.05 percent. The density deviations for the data close to the critical point are again due to the extreme sensitivity of the density in this region.

Figure 11 is a deviation plot for the saturation line, showing the density deviations between the 23 data points of Michels et al. [1] and the saturation densities calculated by the equation of state. Both saturated liquid and saturated vapor data points are illustrated. With the exception of the saturated liquid data points within about 1.5 K of the critical point, the mean density deviation for the saturated liquid data is 0.03 percent. With the exception of the saturated vapor data points within about 2.5 K of the critical point, the mean density deviation for the saturated vapor data is 0.24 percent.

Figure 12 is the deviation plot for the data of Rogovaya et al. [7]. The mean density deviation is 0.17 percent except for the 90.13 K isotherm. This 90.13 K isotherm appears to be inconsistent with the data of van Itterbeek and Verbeke [8], and van Itterbeek et al. [9], and exhibits a mean density deviation of 0.4 percent. Generally, the data of Rogovaya showed a more random distribution of density deviations than the data from some of the other sources. Rogovaya's data, in general, did not approach the region near the critical point as closely as did Michels et al. [1] and, therefore, no direct comparison of these two data sources is possible in this region where the data are difficult to fit.

Figure 13 illustrates the density deviation plot for the data of van Itterbeek and Verbeke [8]. The mean density deviation for these four isotherms is 0.026 percent. However, the 0.026 percent density deviation of van Itterbeek et al. [8] cannot be directly compared with the deviations of the other data sources since van Itterbeek's data are in the high density-low pressure region of the P - V - T surface where the isothermal derivative $(\partial P/\partial \rho)_T$ is large. In this region small displacements in the isotherms result in small density deviations.

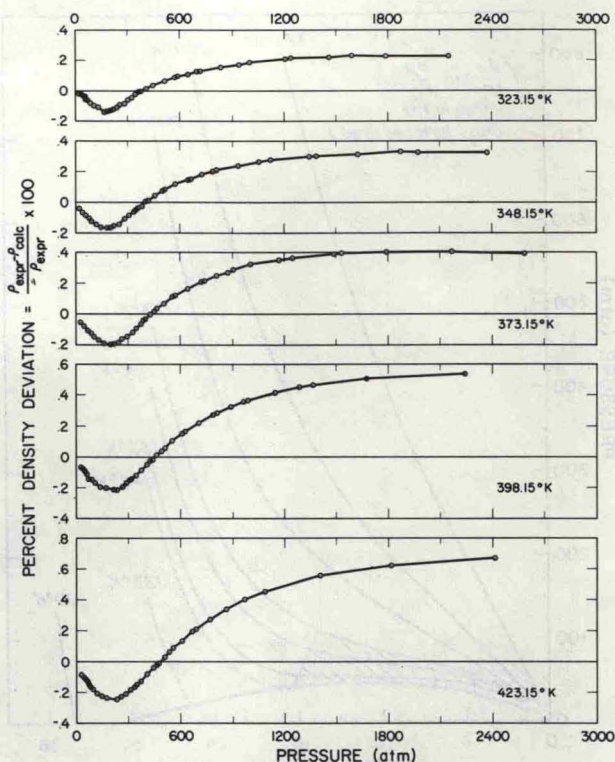
Figures 13 and 14 show the deviation plots for the data of van Itterbeek, Verbeke, and Staes [9]. Comparisons of the deviations for isotherms of increasing temperature show a trend of increasing negative density deviations. This trend is not evident in the deviation plots for Michels et al. [1], figures 5 and 6, or Rogovaya et al. [7], figure 12. The mean density deviation is 0.16 percent with the larger deviations occurring at the higher temperatures.

Figure 15 shows the deviation plot for the data of van Witzenburg [10]. The trend here is opposite that of van Itterbeek, Verbeke, and Staes. The data of van Witzenburg exhibit an increasing negative density deviation for increasing temperatures.

However, the van Witzenburg data extend to higher pressures than most of the other data sources for equivalent isotherms, and direct comparisons of density deviations are difficult to make at these higher pressures. The low temperature, low pressure isotherms may be compared with the data of van Itterbeek, Verbeke, and Staes, where it is noted that the van Witzenburg data exhibit density deviations which are about an order of magnitude greater in the negative direction. The mean density deviation for the data of van Witzenburg is 0.30 percent.

Walker [11] displayed his data by isochores. Comparisons with other data sources were difficult to make since most of the other data were obtained isothermally. Therefore, Walker's data were smoothed to a function of the form $P = q_1 + q_2T + q_3T^2$ where the q 's are constants. (This function was deemed adequate since the isochoric data of Walker was in the liquid region and exhibited only small deviations from straight lines.) These smoothed isochoric P - T values were plotted and compared with other data sources. This plot showed that the slopes from the fitted function were consistent with the slopes from other data, but the values of the isochores assigned by Walker did not agree with others. This disagreement became greater as the critical point was approached. Therefore, the density values of each of the isochores were redetermined by least squaring the experimental data, one isochore at a time, and extrapolating that isochore to the saturated liquid line. Upon comparison, the original data of Walker deviate from the values predicted by the equation of state by about 2 percent in density, with the deviations increasing to about 10 percent as the critical point is approached. However, when comparing the density deviations between the recalculated least square densities and the densities predicted by the equation of state, the mean deviation was 0.25 percent. This latter comparison is, perhaps, a more valid comparison of Walker's data, since he was not able to actually measure the mass of his sample experimentally. Instead, the density values quoted by Walker were estimated by him from an extrapolation of the isochores to the coexistence line. Private communication from Walker [13] indicated that there were errors in the original values quoted for the densities, especially near the critical point. The new values given to us by Walker [13] agreed much more closely with the values predicted by the equation of state.

Figure 17 illustrates the density deviations for the data of Michels et al. [6]. These data include temperatures above 300 K for pressures to about 2600 atm. Since the equation of state was not fitted to the data in this region, these deviation plots represent an extrapolation of the equation of state for temperatures and pressures beyond the fitted data. The mean density deviation for these data is 0.15 percent for temperatures to 423 K and pressures to 2600 atm, which includes a total of 247 data points. The mean density deviations for



NOTE: These Deviation Plots are for Temperatures and Pressures which are Extrapolations Beyond the Fitted Data Points.

FIGURE 17. Density deviations for data at temperatures and pressures extrapolated beyond the fitted data points.

temperatures from 323 to 423 K for pressures to 1000 atm is 0.11 percent. The deviation plots of figures 5 through 17 display varying amounts of systematic deviations between the equation of state and the experimental data. Most of the systematic deviations are small except for the region near the critical point where they become quite marked, as shown in figures 7 and 8. It should be noted that these systematic deviations, although quite small in most cases, are magnified in their contribution to the calculated derivatives.

Although not used for the final fit, the 112 data points of Onnes and Crommelin [26] were compared to the density values predicted by the equation of state. In general, the data of Onnes et al. exhibited a greater scatter than the other data sources, with a mean density deviation of 1.05 percent from the equation of state. Although the Onnes data were limited to pressures below 60 atm, some of the experimental isotherm data overlapped portions of the experimental range investigated by Michels et al. [1]. Generally, the Onnes data showed the same characteristics as the Michels data except for lesser precision. In almost all cases where comparisons could be made, the magnitude of the density quoted by Onnes was smaller than the experimental density of Michels. In a few instances, the Onnes data could be compared with the data of Rogovaya et al. [7]. Again, the densities quoted by Onnes were