from the equation of state (39). Such comparisons were made in all regions of the *P-V-T* surface except the compressed liquid region where the continuous expressions were not possible. The differences in the specific heats obtained by the two methods were on the order of 10^{-5} of the total value.

Both the C_v and the C_p diagrams omit the isobars above 100 atm between 130 and 150 K, i.e., areas enclosed by dashed boxes (figs 21, 22). The specific heats calculated from the equation of state in this range of temperature and pressure exhibited erratic behavior inconsistent with the rest of the surface. This behavior is probably caused by the adjustments made to the entropy and enthalpy values for the saturated liquid (see sec. 10).

Comparisons were made between experimental specific heat data and values calculated from the equation of state. With the exception of the low temperature compressed liquid region and the critical region the agreement was good. The deviations were usually less than 5 percent and averaged about 1 percent. Experimental C_v specific heat data near the critical point such as the data of

Voronel et al. [54] disagree with the values calculated from the equation of state by as much as 53 percent with an average deviation of 40 percent. The only experimental specific heat data available for the compressed liquid region below 110 K were those of van Itterbeek et al. [9]. The agreement between these data and values calculated from the equation of state was poor, the average deviation being about 15 percent, in C_v and 5 percent in C_p. However, these experimental data appear to have some internal inconsistency, and it is difficult to assess their reliability. Unfortunately no other experimental data exist in this region, leaving it somewhat in doubt. Good agreement was obtained between the calculated specific heats and the experimental data of Lestz [55]. These data were taken at temperatures of 273.15 and 303.7 K at pressures to 12 atm. The maximum deviation between calculated values and these data for both C_p and C_v is 0.37 percent. The data of Michels et al. [47] and Michels et al. [48] cover a temperature range from 133.15 to 423.15 K with pressures to 2423 atm. Excluding the critical region and the compressed liquid where deviations ranged to 9
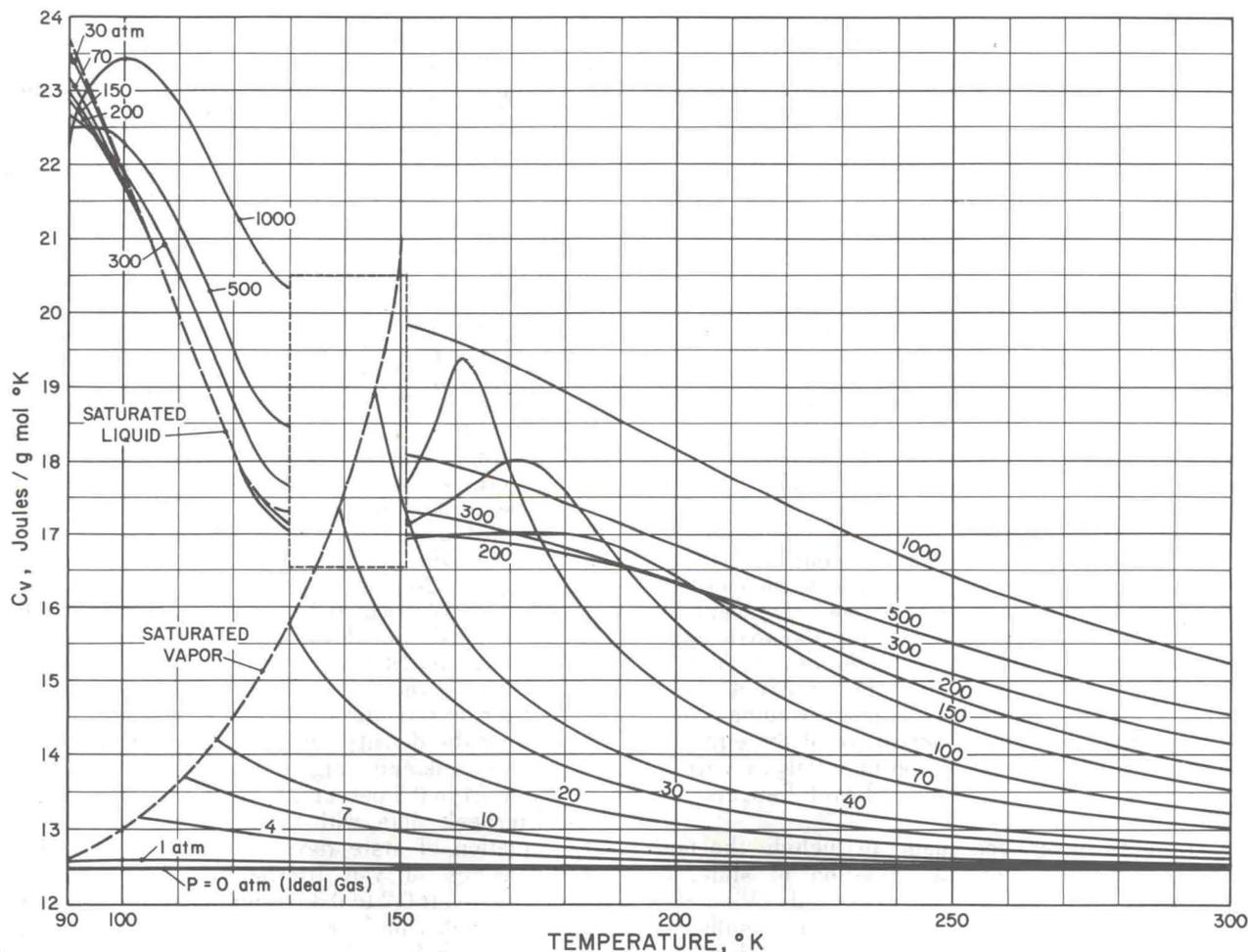
FIGURE 22. *Specific heat at constant volume calculated by numerical method.*

25

percent, the maximum deviation between experimental and calculated C_v's was 6.4 percent at 2423 atm and 398.15 K. The maximum C_p deviation for this group of data was 5.8 percent at 163.15 K and 70 atm. The specific heat data of Walker [11] were also compared with values calculated from the equation of state. The agreement between these data and the calculated values was slightly worse than the agreement obtained with Michels' data. However, the reliability of these data is believed to be less than that of Michels.

Comparison of the specific heats calculated here and those tabulated by two other correlations revealed satisfactory agreement. The C_p's tabulated by Hilsenrath et al. [27] for temperatures of 240 K and above agree with the values calculated here to better than one percent. However, the C_p's tabulated by Hilsenrath et al. [27] for temperatures below 240 K do not agree as well, especially at the high pressures. For example, at 200 K and 100 atm, the disagreement is about 10 percent in C_p while the

value tabulated by Din [31] for this temperature and pressure agrees with this report to within 1.5 percent. The average deviation in C_p between this report and Din [31] is about 1.5 percent, which is much greater than the average deviation between this report and Hilsenrath et al. [27].

It is difficult to formulate a single equation of state which predicts valid P-V-T values over the liquid, vapor and critical point regions, and which also permits accurate calculation of specific heats. The specific heat of a fluid is a function of the second derivative of the equation of state. As pointed out in section 8, slight systematic deviations between the experimental P-V-T surface and the equation of state become magnified when derivatives are taken. The effect of these deviations becomes greater as higher order derivatives are taken and, in the region of the critical point where the equation of state has the largest systematic deviations, the second order derivatives contribute large errors to the specific heats.

15. Conclusions

An equation of state has been developed which represents the experimental P-V-T data for both the liquid and vapor phases, with a consistent transition from the low temperature-high density region to the low density region. Since some of multiple data sources are inconsistent where they overlap, it is difficult to assign an overall "figure of merit" for the adequacy of the equation of state as compared to an experimental P-V-T surface. In general, the equation of state represents the different sources of experimental data to within the accuracy of the data except in the region of the critical point. Numerous deviation plots have been presented so that direct comparisons between the equation of state and each source of experimental data can be made.

In the region of the critical point, the equation of state has a mean density deviation of about one percent and shows a systematic trend which can be attributed to the form of the equation of state. The critical point region has isotherms which undergo large changes in their first and second derivatives. Therefore, it is difficult to represent this critical point region and, at the same time, represent the liquid and vapor regions with a single analytic equation of state. The difficulty near the critical point is magnified when considering the apparent divergence of the specific heat at constant volume (which is related to the second derivative of the equation of state) which was found experimentally by Voronel et al. [54] and discussed by Levelt-Sengers and Vicentini-Missoni [56].

Attempts have been made to include the non-analytic character of the equation of state, as discussed by Levelt-Sengers and Vicentini-Missoni [56]. However, at the present, insufficient progress has been made in including this non-analytic behavior in equations of state which are

explicit in pressure or density and cover a large range of the P-V-T surface.

Recent comments by Heller [57] and Pings and Teague [58] indicate that the critical temperature (and hence the critical pressure) stated earlier in this work may be slightly in error. However, definitive experimental verification of these comments is not yet available and the values for the critical temperature and pressure stated in this work appear to be the best estimate which is available at this writing.

Since the development of the equation of state, some new data on the P-V-T measurements of liquid argon have been published by van Witzenburg and Stryland [59]. These data cover the region from about 95 to 150 K at pressures from about 100 to 1900 atm. A comparison was made between these data and the values of density predicted by the equation of state. For the 38 points at 115 K and below, the mean density deviation was 0.15 percent, with one point having a maximum deviation of 0.5 percent. For the 126 points from 120 to 150 K, the mean density deviation was 0.3 percent with three points having a maximum deviation of 0.5 percent. Van Witzenburg and Stryland state that there were two small regions where their data could be compared with other investigators. One of these comparisons shows that the density values of van Itterbeek et al. [9] were consistently higher than van Witzenburg by about 0.4 to 0.5 percent. Comparison of the same van Itterbeek data with the values predicted by the equation of state developed here shows that the densities of van Itterbeek are consistently higher by about 0.2 to 0.3 percent. The second comparison which could be made shows that six data points of Michels et al. [1] had densities which were about 0.25 percent lower than van Witzenburg.

26