164

the pycnometric will be described

164

e that have been s only discussed vostat is shown nprovement over or elements were nechanically) and other so that the ng frequency was more than ± 0.2 temperature and de it possible to art in 106. This in h the λ line to a ie molar volume terval of this size were $\frac{1}{10}$ -W Allen shown in Fig. 1. itor was the main attached to the .6°K, and a 64- Ω ed to detect the ed by the sample vere measured on evel of about 10^{-8} this gave a resoluhermometer. The and fed into a ctor in turn fed a ontinuous display

nt to ± 0.1 mm of solute accuracy to ed with the meaor pressures up to as used. In runs I with a pressure a Heise bourdon 01 atm was used. d against a dead the resolution to of the gauges was pressure control e capacitor by a hat had an 0.008hor at 4.2°K and influx along the pressures below between pressure n. Thus there was

roceedings of the Fifth re Physics, Madison, University of Wiscon-

and tabulation of all by D. L. Elwell, Duke somewhat more scatter in the high resolution data at low pressures than elsewhere.

Resistance and sample frequency were recorded automatically on IBM punch cards. The 14 MHz signal was amplified and mixed with a 10-MHz standard (from the counter) and the resultant beat frequency was counted on a Hewlett-Packard 5245L solid-state scaler. The reading of this counter fed on command directly to the key punch. Resistance values were read both as dial settings on the standard decade box which was one arm of the Wheatstone bridge, and as the voltage imbalance from the phase-sensitive detector. This recording system was designed and built by Dr. J. Jarvis of this laboratory and has been described by him in detail elsewhere.¹²

At the beginning of an experimental run the emptycell frequency of the oscillator and the resistance of the thermometers were measured as a function of the vapor pressure of the He⁴ in the pot and thus of temperature on the T_{58} scale. The resistance calibration showed a scatter of ± 0.5 mdeg, and in addition there was a small drift in the resistance of the thermometers over periods of several days which introduced other uncertainties, so that we estimate the total uncertainty in the absolute temperature to be ± 1 mdeg on the T_{58} scale. The empty-cell frequency calibration scattered by about ± 2 Hz. Additional shifts as large as ± 50 Hz (over a total range of 400 Hz) were often induced by shaking the apparatus while filling the helium pot and were compensated for by maintaining reference points at various pressures. It should be noted that these shifts were avoided during the data-taking periods, and therefore the high-resolution data were not affected.

Once helium was introduced into the density cell, the calibration constants in Eq. (1) were determined from a fitting of our frequency results to the densities given by Lounasmaa¹³ along the 1.75°K isotherm. The uncertainty in Lounasmaa's data and hence in the absolute value at our molar volumes was estimated to be about 0.1% Relative values along a given isobar are of course known to a much greater precision. After calibration of the apparatus, volume measurements were made at constant pressure over the whole temperature range available to us, and in this process the approximate location of the transition was determined. Successively higher resolution passes were then made over decreasing intervals of temperature both while warming and cooling the density cell through the transition. The last three to five such passes would cover an interval of about 2 mdeg and take around 2 h with readings punched every 20 sec. The data for one such pass at 13 atm are shown in Fig. 2, and we emphasize that most of the other passes were parallel and of similar quality. We take this parallelism to indicate that thermal equilibrium was maintained in the sample. This is of course important, because even a small disequilibrium would

¹¹ J. F. Jarvis, thesis, Duke University, 1967 (unpublished).
¹² O. V. Lounasmaa, Cryogenics 1, 1 (1961).



Fig. 2. High-resolution data at 13.0 atm in the neighborhood of the λ transition.

smear the transition badly. The cell was particularly suitable from this point of view, since the sample was always within 0.05 mm of a copper wall and since there was a large surface-to-volume ratio and heat could be exchanged rapidly. A further potential source of broadening was the hydrostatic pressure head in the sample. However the 1-cm height of our sample corresponded to a shift in T_{λ} of only about 10^{-70} K and since this was considerably less than the available resolution it did not effect the validity of the results.

Finally, the raw data were converted by computer, without smoothing or fitting, into molar volume-versustemperature points, and these were plotted on large graphs. Curves were drawn through the data by hand and slopes obtained graphically. In this way we have avoided prejudicing the shape of the α_P singularity in favor of any particular mathematical form and consider that the data we present in the next section give a good representation of the equation of state near the λ transition.

III. RESULTS AND DISCUSSION

For convenience we divide this section into two parts; the first one gives our data over the broad temperature range and a comparison with other such data, and the

247