

Fig. 4. Pressure-composition section for polyethylene-*n*-propane at 110°C.: (\odot) fraction 2; (\triangle) fraction 3; (\heartsuit) fraction 4; (\boxdot) fraction 5. Bubble-point and dew-point pressures by direct observation (unprimed symbols); by calculation from phase volumes in two-phase region primed symbols. Vertical lines indicate apparent critical composition.

The effect of temperature on the UCSP is small. Several of the fractions were investigated up to 150 °C., and although UCSP's at that temperature appeared to be lower, the effect was only slightly greater than the experimental error. In none of the systems studied was the UCSP lowered by more than 15 atm. in going from 110 to 150 °C. In going to the higher temperature, the critical point appeared to shift only very slightly toward higher polymer concentrations.

At polymer concentrations less than critical the pressure on the phase boundary (dew-point pressure) was found to be very close to the critical pressure down to extremely low polymer concentrations. Thus, for fraction 2, dew-point pressures within experimental error of the UCSP were found for polymer concentrations down to 0.3, and possibly 0.15 wt.-% (0.2 and 0.1 vol.-%). On the low concentration side, the phase boundary runs along the pressure axis up to pressures closely approaching the UCSP. This makes it possible to estimate the phase diagram at pressures below the UCSP by determining the location of the meniscus and by assuming the critical composition to occur with the meniscus at 50 vol.-% bomb contents. The pressure-composition diagrams are shown in Figure 4. Points obtained by the less reliable method just described fall on the same plots as those obtained by the direct measurement of dew-point and bubblepoint pressures.

3223