

and the data to be reported were obtained with the four center fractions. The heterogeneity of the fractions was not determined. Molecular weights were measured osmotically for the two high fractions and obtained from intrinsic viscosities<sup>6</sup> for the two low fractions. Ethane, *n*-propane, and *n*-butane were obtained from the Matheson Company, ethane at 99%, and *n*-propane and *n*-butane at 99.5% purity. *n*-Pentane was obtained from the Phillips Petroleum Company at 98.5% purity.

### Procedure

A known weight of polymer and a steel ball,  $\frac{5}{8}$  in. in diameter, were placed in the bomb which was then evacuated. Solvent was then compressed into the bomb (the pump chamber had to be cooled when ethane was used) such that, upon bringing it to the desired temperature, the system was at a pressure slightly greater than the anticipated dew-point or bubble-point pressure. When the desired temperature had been approached, the bomb was rocked. After the system had reached equilibrium in the one-phase region, it was vented slowly through valve C. Upon approaching the phase boundary, the transmitted light intensity diminished sharply, and a phase boundary became visible. The pressure interval over which these phenomena took place varied from barely resolvable (2 atm.) to as much as 30 atm. with the lowest molecular weight fraction at low polymer concentrations. Where the interval was relatively broad, the pressure at which the sharpest intensity change took place was taken as the dew-point or bubble-point pressure. Prior to phase separation the solution sometimes showed a dark orange color by transmitted light, indicating the occurrence of critical scattering. This generally happened at concentrations where the solution, upon lowering the pressure, separated such that the lower phase occupied 30–50% of the volume. The phase volume at a pressure as close as possible to that at which the phases separated was determined by means of a prior calibration of bomb angle versus phase volumes. During a run valve H was closed and, strictly speaking, the experimental system extended to that point. However, there was very little diffusion of polymer out of the bomb, and none into the coil. The volume between the bomb and the valve C was only about 1 cc., and the concentration change due to venting was always small. Concentration changes due to diffusion and venting were therefore ignored in the calculation.

The amount of solvent charged into the bomb was not measured. It was calculated for propane from the data of Reamer, Sage, and Lacey,<sup>7</sup> assuming no volume change of mixing. Since a negative volume change of mixing is, in fact, likely, this introduces an error into the calculation of weight per cent polymer. The isotherms, however, are reported at low polymer concentrations only, and judging from other experiments carried out in this laboratory, the error is not believed to exceed 10% at the highest polymer concentrations reported, and should be considerably less at the critical concentration. The critical conditions are also reported as volume fraction polymer, defined here as volume of pure polymer at the