

concentration is not. The experimental error in the dew-point and bubble-point pressures is such that the maximum cannot be located along composition axis by inspection. Instead, the weight fraction  $W_c'$  or volume fraction  $\phi_c'$  of polymer at which the system breaks up into two phases of equal volumes can be located approximately from a plot of phase pressure just below the isotherm as a function of composition (Fig. 3). For convenience, this is termed the apparent critical composition. The true critical concentration cannot be very far from the apparent critical concentration for two reasons: relative phase volumes change rapidly with composition (Fig. 3) and only extreme dissymmetry in the pressure-composition diagram close to the critical point could lead to a wide divergence between the two points. Also, although no attempt was made to determine exactly the concentration range in which critical scattering occurred, solutions which were darkest in color by transmitted light generally occurred at concentrations such that the lower phase occupied 30–50% of volume. It seems legitimate to conclude that whereas  $W_c$  might possibly be as much as 30% lower than  $W_c'$ , it cannot greatly exceed the values of  $W_c'$  listed because of the noticeable drop in pressure on the isotherm (pressure-composition section) at concentrations greater than  $W_c'$ .

Table I presents the critical pressures and apparent critical compositions for four fractions of molecular weight 17,000–250,000 at 110°C. The critical points are seen to occur at low polymer concentrations, a situation typical for polymer-solvent systems. The critical pressures converge for high fractions, suggesting the existence of a limiting value for polymer of infinite molecular weight. According to the Flory-Huggins theory,<sup>9</sup> critical concentrations are given approximately by  $x^{-1/2}$ , where  $x$  is the ratio of molecular volumes of polymer and solvent. The apparent critical concentrations are seen to exceed  $x^{-1/2}$ , but the dependence is approximately of the form required.

The existence of a second, and higher, critical pressure at which the system again breaks up into two phases is conceivable. This, according to standard terminology, would be a lower critical solution pressure. No such phenomenon was encountered with the highest molecular weight fraction at pressures up to 2,000 atm. at 130–150°C.

TABLE I

Upper Critical Solution Pressures and Critical Polymer Concentrations for Fractions of Polyethylene in Propane at 110°C.

Designation of fraction	Molecular weight of fraction	Critical pressure, atm.	Apparent critical concentration of polymer		
			Wt. fraction	Vol. fraction	$x^{-1/2}$
2	246,000	582	0.042	0.027	0.017
3	89,000	561	0.072	0.045	0.028
4	37,000	531	0.082	0.054	0.044
5	17,000	449	0.129	0.090	0.066