a free energy, too. It seems therefore not unreasonable to discuss critical mixing in terms of the critcal conditions derived from the Flory-Huggins theory ($\chi_c = 0.5$ for polymer of infinite molecular weight), and to expect χ_c to be given approximately by the solubility parameter term.

Assuming the volume of change of mixing not to be excessive, the solubility parameter for a gas can be calculated by substituting its energy of compression, ΔE_1, for the energy of vaporization[1] of the standard treatment. The solubility parameter for the solvent, δ_1, is then taken to be the square root of the cohesive energy density, $\Delta E_1/V_1$, where V_1 is the molar volume of the solvent. Table II lists the solubility parameters at the UCSP, calculated by means of a reduced variable correlation.[16] δ_1 is seen to vary with temperature, but to be nearly constant at a given temperature for all alkanes studied, although a slight drop with the size of the solvent molecule seems indicated. If one uses the value of Allen et al.[17] for an amorphous linear polyethylene (δ_2 is 8.37 cal.$^{1/2}$ cc.$^{-1/2}$ at a density of 0.855 g. cc.$^{-1}$), and allows δ_2 to vary as $a^{1/2}/V_2^{-1}$ (van der Waals fluid behavior), one obtains values of χ in the range of 0.4–0.8. Positive deviations from 0.5 increase with the size of the solvent molecule and with temperature. The data are, therefore, not quantitatively consistent with the approach outlined. A very rough estimate of the UCSP from the thermodynamic properties of the components is, however, possible. In the *n*-alkane–polyethylene systems investigated, furthermore, the UCSP for a given solvent at a given temperature is evidently calculable with reasonable accuracy from that of another by assuming critical mixing to occur at a fixed value of δ_1. Note, however, that at least equally successful a calculation could be made in terms of reduced densities (Table II).

The critical locus of binary alkane systems whose components differ only moderately in size is a continuous unbroken line joining the critical points of the pure components. Katz and Rzasa[5] in a detailed optical study of methane with an oil fraction containing mostly C_{20} paraffin, have shown that, as the size difference between the components increases, the maximum pressure on the critical locus rises and is shifted toward the component of low molecular weight. Freeman and Rowlinson,[3] however, found that solutions of hydrocarbon polymers in hydrocarbon solvents, upon heating under their own vapor pressures, break up into two liquid phases at a LCST which can be well below the critical point of the solvent. This LCST must also be the lower critical end point (LCEP) of the critical locus which, if closed along the pressure axis, must change gradually from a liquid–liquid to a gas–liquid boundary.[4] This lack of sharp distinction between liquid and gaseous solvents is demonstrated in this study which shows sections of the critical locus of polyethylene with solvents which are above, below, and close to their critical temperatures. The slope of the critical locus at a given temperature differs in sign and magnitude (Table II, Fig. 5); it is close to zero, but slightly negative, with propane just above its own critical point of 97°C. This suggests that the critical