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Vapor-Liquid Equilibria at High Pressures: Calculation of Critical Temperatures, Volumes, and Pressures of Nonpolar Mixtures

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An analysis of critical data for a large number of binary mixtures of normal fluids shows that the critical temperature and the critical volume can each be expressed as quadratic functions of the surface fraction. Each of these functions requires one adjustable parameter characteristic of the binary pair; for any family of chemical components, these parameters, upon suitable reduction, follow definite trends. It was shown that the surface fraction gives much better correlation than any other size-weighted variable. For the critical pressure, however, no quadratic function was adequate. To calculate critical pressures, the correlations for critical temperature and critical volume were used in conjunction with a slightly altered version of the Redlich-Kwong equation.

Generalizations to systems containing more than two components follow without additional assumptions. The methods presented in this paper provide good estimates for critical constants of multicomponent mixtures. These are particularly useful for analyzing and correlating vapor-liquid equilibria in the critical region.

The critical properties of pure fluids have received much attention and as a result of much experimental work, dating back nearly 100 years (3, 6), as well as semiempirical correlations (56), it is now possible to make good estimates of the critical temperature, pressure, and volume of most pure fluids encountered in typical chemical engineering

work. The critical properties of mixtures, however, are not known nearly as well, although experimental data are available for a surprisingly large number of binary mixtures (58).

Critical properties of mixtures are required in petroleum and natural gas engineering and for rational design of separation equipment and chemical reactors at high pressures.