The rising use of high pressures in chemical technology calls for increased knowledge of fluid phase behavior in the critical region. Since our primary aim is to establish thermodynamic methods for calculating vapor-liquid equilibria at high pressures, including the critical region (see preceding paper), it is essential to have available methods for estimating the critical conditions wherein the vapor phase and the liquid phase become identical.

In this work we present correlations for the critical temperatures and volumes of binary mixtures, and we present an equation-of-state method for calculating critical pressures using critical temperatures and volumes. In a very straightforward way, we generalize our results for estimating critical properties of mixtures containing any number of components. Our attention is restricted to normal fluids [as defined by Pitzer (*47*)]; that is to molecules which have zero (or small) dipole moments, no tendency to associate by hydrogen bonding or similar chemical forces, and which have sufficiently large mass to permit neglect of quantum corrections.

Several authors (*1, 14, 17, 19, 21, 22, 34, 36, 44, 45, 63, 64*) have reported correlations of the critical temperature or critical pressure of mixtures but these, by and large, have been confined to a particular chemical class of substances (usually paraffins). Very little work has been reported on the correlation of critical volumes of mixtures (*22*). While the critical volume seldom enters directly into engineering calculations, it is of more fundamental significance than the critical pressure, and it is needed to provide estimates of the very large effect of pressure on liquid phase activity coefficients in the critical region.

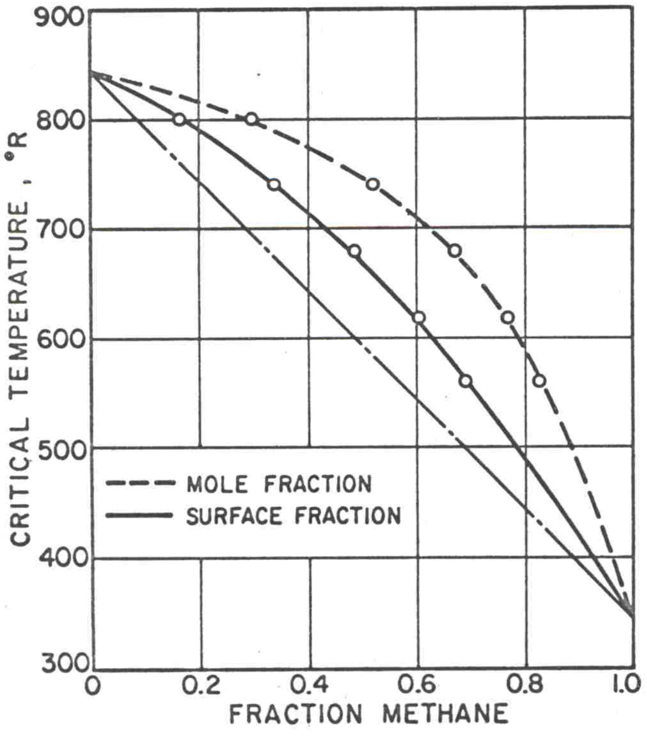

Fig. 1. Critical temperatures of the methane–*n*-pentane system as a function of mole fraction and of surface fraction.

CRITICAL TEMPERATURES

Rowlinson (*58*) has shown that for a binary mixture of components 1 and 2, the critical temperature of the mixture is, to a good approximation, a simple quadratic function of the mole fraction, provided components 1 and 2 consist of simple, spherically symmetric molecules of nearly the same size. Rowlinson writes

$$T_{cT} = x_1 T_{c_1} + x_2 T_{c_2} + 2x_1 x_2 \Delta T_{12} \tag{1}$$

where ΔT_{12} is a known function of T_{c_1}, T_{c_2}, v_{c_1} and v_{c_2}, and a parameter which depends on the two exponents used in the potential function for describing the intermolecular forces. In addition, ΔT_{12} depends on the energy characteristic of the 1–2 interaction; it is common to assume that this characteristic energy is given by the geometric mean of the pure-component characteristic energies, but this assumption, unfortunately, can often lead to appreciable error. The important simplifying element of Rowlinson's treatment lies in his assumption of pairwise additivity of intermolecular energies; the potential energy of a multibody assembly is given by the sum of the potential energies of all nearest neighbor pairs. As a result, the critical temperature of the mixture is a quadratic function of the mole fractions. Rowlinson's treatment is not useful for mixtures whose components differ appreciably in molecular size. For such mixtures, the thermodynamic properties are quadratic functions of the mole fraction only at moderate densities (second virial coefficients); at liquid-like densities, it has been common practice to express the thermodynamic properties of such mixtures in terms of volume fractions. The critical density is intermediate between that of liquids and that wherein the second virial coefficient gives a sufficiently good approximation. We propose, therefore, to correlate experimentally determined critical temperatures as a quadratic function of the surface fraction θ defined by

$$\theta_i = \frac{x_i v_{c_i}^{2/3}}{\sum_i x_i v_{c_i}^{2/3}} \tag{2}$$

For a binary mixture, the critical temperature is given by

$$T_{cT} = \theta_1 T_{c_1} + \theta_2 T_{c_2} + 2\theta_1 \theta_2 \tau_{12} \tag{3}$$

where τ_{12} is a parameter characteristic of the 1–2 interaction. Equation (3) is a one-parameter equation. By expressing the mixture's critical temperature as a function of surface fraction, we find that the quadratic term $2\theta_1\theta_2\tau_{12}$ makes a comparatively small contribution. For mixtures whose components differ very much in molecular size, the contribution of the quadratic term is smaller when surface fractions are used; it is significantly larger if the critical temperature is expressed by quadratic functions in mole fraction. To illustrate, Figure 1 shows that the critical temperatures of the methane–*n*-pentane system are more nearly linear and symmetric when plotted against surface fraction rather than mole fraction. As a result, the correlating parameter τ_{12} in Equation (3) is smaller than ΔT_{12} in Equation (1); uncertainties in τ_{12}, therefore, lead to smaller error than comparable uncertainties in ΔT_{12}. For the methane–*n*-pentane system the experimental data (*62*) are correlated by Equation (3) (using $\tau_{12} = 78.8$°K.) with an average error of 0.73%. On the other hand, the optimum fit of the data with Equation (1) (using $\Delta T_{12} = 127.8$°K.) produces an average error of 4.08%.

Equation (3) has been used to correlate the critical temperatures of sixty-five binary systems; Table 1 gives the parameters τ_{12} in reduced form for these systems. The average deviation of all experimental and fitted critical temperatures is 0.4%.

For a given family of chemical systems, the reduced parameters follow a trend which can form the basis for interpolation and cautious extrapolation. For example, for paraffin-paraffin systems (for which experimental data are most plentiful) the reduced parameter is a smooth function of the absolute value of $(T_{c_1} - T_{c_2})/(T_{c_1} + T_{c_2})$ as illustrated in Figure 2. Paraffin-olefin systems follow the same