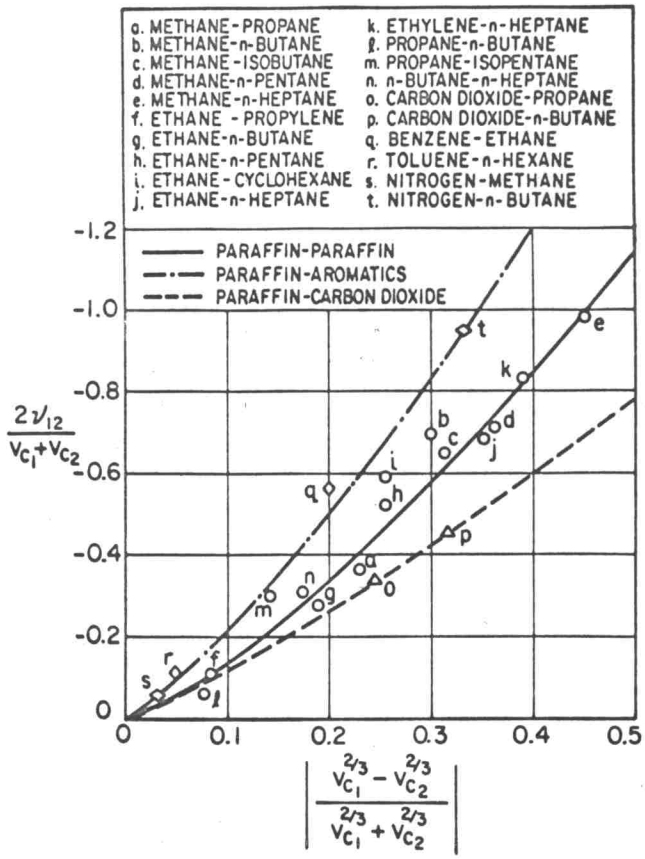

Fig. 4. Correlating parameter v_{12} for critical volumes of some binary systems.

than that of the critical temperature and the critical volume; in many systems a plot of critical pressure vs. mole fraction shows a sharp maximum and a point of inflection. The more complicated behavior of the critical pressure follows from its nonfundamental nature; subject to well-defined assumptions, both critical temperatures and critical volumes can be related directly to the intermolecular potential, but the critical pressure can be related to the intermolecular potential only indirectly through the critical temperature and critical volume.

To express the critical pressure as a function of composition, we propose to use our correlations for critical temperature and critical volume coupled with an equation of state. We have adopted the Redlich-Kwong equation of state (*1*) with certain alterations. The Redlich-Kwong equation is

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \tag{5}$$

For a pure component, the constants a and b are related to the critical temperature and pressure of that component by

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \tag{6}$$

$$b = \frac{\Omega_b R T_c}{P_c} \tag{7}$$

The dimensionless constants Ω_a and Ω_b may be found (as is commonly done) by equating to zero the first two isothermal derivatives of pressure with respect to volume at the critical point. This procedure gives $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. To do so, however, puts a severe strain on the equation of state, leading to a value of z_c which is too large. Since any two-parameter equation of state is necessarily approximate when applied to a wide range of temperature and density, it is best to determine the dimensionless parameters Ω_a and Ω_b from experimental data available in the region of temperature and density where the equation of state is to be used. Toward that end, we have previously (7, 9) evaluated the parameter Ω_b for a variety of fluids from pure-component volumetric data, once for saturated liquids and once for saturated vapors. For our present purpose, we use for Ω_b for each substance the arithmetic mean of the two values obtained from saturated liquid and saturated vapor volumes. For a variety of normal fluids, this Ω_b may be represented by a function of the acentric factor ω (47, 9):

$$\Omega_b = 0.0867 - 0.0125\,\omega + 0.011\,\omega^2 \quad (0 \le \omega < 0.6) \tag{8}$$

To force agreement for each pure component at the critical point, Ω_a is determined by the experimental critical temperature, pressure, and volume of that component according to

$$\Omega_a = \left(\frac{RT_c}{v_c - b} - P_c\right)\frac{P_c v_c (v_c + b)}{(RT_c)^2} \tag{9}$$

where b is given by Equations (7) and (8).

To apply Equation (5) to mixtures, we require mixing rules for a and b. We propose, as before (9), to use

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii}a_{jj}}) \tag{10}$$

$$b = \sum_i x_i b_i \tag{11}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{12}$$

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{13}$$

$$a_{ij} = \frac{\frac{1}{4}(\Omega_{a_i} + \Omega_{a_j}) R T_{c_{ij}}^{1.5} (v_{c_i} + v_{c_j})}{0.291 - 0.04(\omega_i + \omega_j)} \tag{14}$$

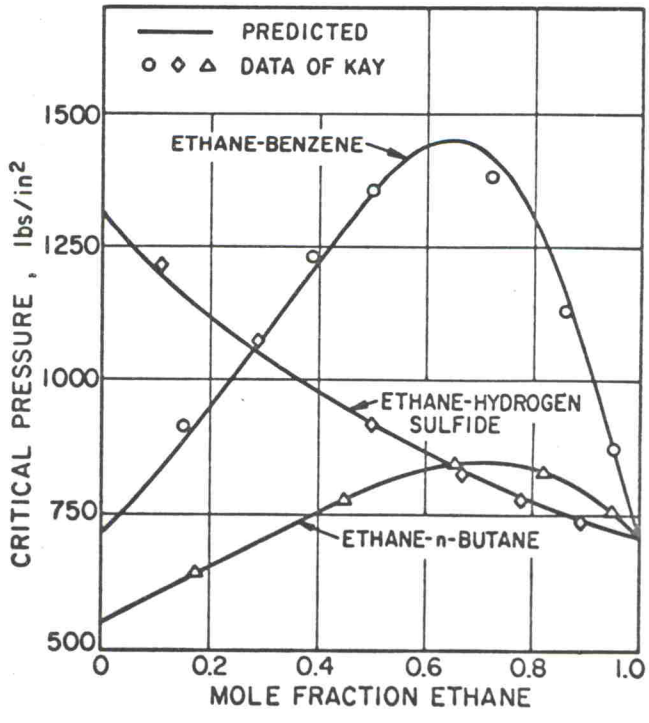

Fig. 5. Critical pressures of three binary systems containing ethane.