

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 welldefined 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 We have adopted the Redlich-Kwong equation of state. state (1) with certain alterations. The Redlich-Kwong equation is

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

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

$$a = \frac{\Omega_a R^2 T_c^{23}}{P_c}$$
(6)  
$$b = \frac{\Omega_b R T_c}{P_c}$$
(7)

The dimensionless constants  $\Omega_a$  and  $\Omega_b$  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

Vol. 13, No. 6

temperature and density, it is best to determine the dimensionless parameters  $\Omega_a$  and  $\Omega_b$  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  $\Omega_b$  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  $\Omega_b$  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  $\Omega_b$  may be represented by a function of the acentric factor  $\omega$  (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,  $\Omega_a$  is determined by the experimental critical temperature, pressure, and volume of that component according to

$$\Omega_{a} = \left(\frac{RT_{c}}{v_{c} - b} - P_{c}\right) \frac{P_{c} v_{c} (v_{c} + b)}{(RT_{c})^{2}}$$
(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

$$a = \sum_{i} \sum_{j} x_{i} x_{j} a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii} a_{jj}})$$
(10)

$$b = \sum_{i} x_i b_i \tag{11}$$

where

а

h

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

$$_{i} = \frac{\Omega_{b_{i}} R T_{c_{i}}}{P_{c_{i}}}$$
(13)

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





**AIChE Journal** 

967

LING

action of a

(4)

of the

es of

se for

diffi-

meter

data

on (4)

on of

itical

is of

as a  $v_{c_2}^{\frac{2}{3}}$ .

mical

timat-

data

iy be

and

vol-

one

pres-

vious

itical

inear

nent i