Standard forms of the equation are:

$$(P + a/V^2)(V - b) = RT, \tag{1}$$

$$z = PV/RT = V/(V - b) - a/RTV. \tag{2}$$

Polynomial forms are:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0, \tag{3}$$

$$z^3 - \left(\frac{bP}{RT} + 1\right)z^2 + \frac{aP}{(RT)^2}z - \frac{abP^2}{(RT)^3} = 0. \tag{4}$$

Virial form:

$$z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \cdots. \tag{5}$$

Reduced form:

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \tag{6}$$

The parameters in terms of critical properties:

$$a = 3P_cV_c^2 = 27R^2T_c^2/64P_c, \tag{7}$$

$$b = V_c/3 = RT_c/8P_c, \tag{8}$$

$$R = 8P_cV_c/3T_c, \tag{9}$$

$$z_c = 0.375. \tag{10}$$

The value of R given by Eq. 9 is not the same as the true gas constant, 8.314 joules/gmol-K; the true value should be used for evaluation of the parameters a and b from Eqs. 7 & 8.

Derivation of the formulas for a and b:

Method 1: At the critical condition, the first and second derivatives with respect to V at constant T are zero. Performing these differentiations,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0, \tag{11}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0. \tag{12}$$

Also,

$$\left(P_c + \frac{a}{V_c^2}\right)(V_c - b) = RT_c. \tag{13}$$

Eqs. 11–13 are solved simultaneously to obtain the results of lines 7–9.

Method 2: At the critical point, the three roots of the polynomial, Eq. 3, are equal.

$$(V - V_c)^3 = V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0. \tag{14}$$

Comparison of coefficients of like powers of Eqs. 3 and 14 will lead to the same results for the parameters as by method 1.

For mixtures, the parameters are expressed in terms of the pure component parameters by the *combining rules:*

$$a = (\Sigma y_i\sqrt{a_i})^2 = \Sigma\Sigma y_iy_j\sqrt{a_ia_j} = \Sigma\Sigma y_iy_ja_{ij}; \tag{15}$$

$$b = \Sigma y_ib_i. \tag{16}$$

Fugacity equations are in tables 3.3 and 3.4. Residual property equations are in Table 11.3.

From Walas, Phase Equilibria in Chemical Engineering