4. Solve the cubic polynomial for the compressibility factor. If there are more than one positive roots, choose according to the phase of the mixture:[12] for a liquid mixture choose the smallest root; for gas mixture, choose the largest.

5. Use the compressibility factor to calculate the residual enthalpy and entropy according to the equations in Table 5-3.

In working with eqs. (9.38)–(9.43) we follow the convention: a single subscript refers to pure component, whereas no subscript refers to *mixture*.

9.7 Mixture Properties from Equations of State

Residual properties are defined in the same manner as for pure components:

$$F = F^{\mathrm{igm}} + F^R, \tag{9.44}$$

where F is the molar property of the mixture at a given state, F^{igm} is the same property in the hypothetical ideal-gas state, and F^R is the residual property. All terms in eq. (9.44) are at the same pressure, temperature, and composition. For the enthalpy of the mixture, this equation becomes

$$\boxed{H = \sum_i x_i H_i^{\mathrm{ig}} + H^R.} \tag{9.45}$$

Here we have substituted for H^{igm} the expression from eq. (9.26), which gives the ideal-gas enthalpy of the mixture in terms of the ideal-gas enthalpy of the pure components. For entropy we obtain a similar result,

$$\boxed{S = \sum_i x_i S_i^{\mathrm{ig}} - R \sum_i x_i \ln x_i + S^R.} \tag{9.46}$$

Here, the ideal-gas entropy of mixture is given by eq. (9.27) and includes the ideal entropy of mixing. Equations (9.45) and (9.46) reduce the calculation of mixture properties into a two-step calculation, one for the ideal-gas contributions, and one for the residual corrections.

To calculate the absolute enthalpy and entropy of mixture we need ~~to~~ the absolute properties of the pure components, H_i^{ig} and S_i^{ig}. These must be calculated

12. The phase must be known ahead of time. We will learn in Chapter 10 that it is possible to determine the phase from the equation of state itself.

based on a reference state. We must specify one reference state for each component, not necessarily the same for all components, though this choice is convenient. If the reference state for component i is at temperature T_{0i} and pressure P_{0i}, its ideal-gas properties at temperature T and pressure P are

$$H_i^{\mathrm{ig}} = H_{0i}^{\mathrm{ig}} + \int_{T_{0i}}^{T} C_{P,i}^{\mathrm{ig}}\, dT, \tag{9.47}$$

$$S_i^{\mathrm{ig}} = S_{0i}^{\mathrm{ig}} + \int_{T_{0i}}^{T} C_{P,i}^{\mathrm{ig}} \frac{dT}{T} - R \ln \frac{P}{P_{0i}}, \tag{9.48}$$

where H_{i0}^{ig} and S_{i0}^{ig} are the ideal-gas enthalpy of the component at its reference state. The value of these constants depends on the reference state adopted:

- *Actual enthalpy and entropy at P_0, T_0, are set to zero.* For this reference state we use,

Right-hand side should have a minus in both equations

$$H_{0i}^{\mathrm{ig}} = -H_{0i}^{R}, \quad S_{0i}^{\mathrm{ig}} = -S_{0i}^{R}, \tag{9.49}$$

  where H_{0i}^{R} and S_{0i}^{R} are the residual properties of pure component at its reference state.[13]

- *Ideal-gas enthalpy and entropy at P_0, T_0, are set to zero.* In this case,

$$H_{0i}^{\mathrm{ig}} = 0, \quad S_{0i}^{\mathrm{ig}} = 0. \tag{9.50}$$

Once the reference state for each component is selected, H_{0i}^{ig} and S_{0i}^{ig} become numerical constants and the calculation proceeds as usual. Table 9-2 summarizes all the equations needed for the calculation of the enthalpy and entropy of a binary mixture based on the Soave-Redlich-Kwong equation of state. The calculation is somewhat involved but completely straightforward. Except for the calculation of the ideal-gas integrals, everything else involves serial algebraic calculations. The entire procedure can be coded easily for computer calculation. The required inputs are the critical properties, the ideal-gas heat capacities as functions of temperature, and the numerical values of the reference state values H_{01}^{ig} and S_{0i}^{ig} of all components. The calculation should then be set up so that enthalpy and entropy are calculated for any user input of temperature, pressure, mol fractions and phase of the mixture. The phase is needed in order to select the proper root of the compressibility equation, if more than one real root is found.

13. Using $H_i = H_i^{\mathrm{ig}} + H_i^{R}$ you should be able to confirm that this above reference state leads to $H_0 = 0$ and $S_0 = 0$.

Table 9-2: Properties of binary mixture using the Soave-Redlich-Kwong equation of state. Subscript $_i$ refers to pure component 1 or 2; the values of H_{0i}^{ig} and S_{0i}^{ig} are fixed by the reference state.

$$H = x_1 H_1^{\mathrm{ig}} + x_2 H_2^{\mathrm{ig}} + H^R \quad [9.45]$$

$$S = x_1 S_1^{\mathrm{ig}} + x_2 S_2^{\mathrm{ig}} - R(x_1 \ln x_1 + x_2 \ln x_2) + S^R \quad [9.46]$$

$$H_i^{\mathrm{ig}} = H_{0i}^{\mathrm{ig}} + \int_{T_{0i}}^{T} C_{P,i}^{\mathrm{ig}}\, dT \quad [9.47]$$

$$S_i^{\mathrm{ig}} = S_{0i}^{\mathrm{ig}} + \int_{T_{0i}}^{T} C_{P,i}^{\mathrm{ig}} \frac{dT}{T} - R \ln \frac{P}{P_{0i}} \quad [9.48]$$

$$H^R = RT(Z-1) + \frac{T(da/dT) - a}{b} \ln \frac{Z+B'}{Z} \quad [5.55]$$

$$S^R = R \ln(Z - B') + \frac{da/dT}{b} \ln \frac{Z+B'}{Z} \quad [5.56]$$

$$Z^3 - Z^2 + (A' - B' - B'^2)Z - A'B' = 0 \quad [2.44]$$

$$A' = \frac{aP}{(RT)^2}, \qquad B' = \frac{bP}{RT} \quad [2.36]$$

$$b = x_1 b_1 + x_2 b_2 \quad [9.41]$$

$$a = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 (1 - k_{12})\sqrt{a_1 a_2} \quad [9.42]$$

$$\frac{da}{dT} = x_1^2 \left(\frac{da_1}{dT}\right) + x_2^2 \left(\frac{da_2}{dT}\right) + x_1 x_2 (1 - k_{12})\sqrt{a_1 a_2} \left(\frac{1}{a_1}\frac{da_1}{dT} + \frac{1}{a_2}\frac{da_2}{dT}\right) \quad [9.43]$$

$$b_i = 0.08664 \frac{R T_{ci}}{P_{ci}} \quad [2.41]$$

$$a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + \Omega_i \left(1 - \sqrt{T_{ri}}\right)\right]^2 \quad [2.42]$$

remove square power

$$\frac{da_i}{dT} = -0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \frac{\left(1 + \Omega_i \left(1 - \sqrt{T_{ri}}\right)\right) \Omega_i}{\sqrt{T_{ri}}} \quad [5.57]$$

$$\Omega_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \quad [2.43]$$