Noting that the parameter a is a function of temperature, the partial derivative of pressure with respect to T is,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{da/dT}{V(b+V)},$$

from which we obtain,

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{a - T(da/dT)}{V(b+V)}.$$

Inserting into eq. (5.50), the residual enthalpy is

$$H^R = PV - RT + \frac{a - T(da/dT)}{b} \underset{(\text{const. } T)}{\int_\infty^V} \frac{dV}{V(V+1)} \qquad \text{V+b}$$

$$= PV - RT + \frac{a - T(da/dT)}{b} \ln \frac{V}{V+b}.$$

The result may be expressed in the alternative form,

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

where we have used $V = ZRT/P$ to eliminate V in favor of Z, and $B' = Pb/RT$ is the dimensionless parameter previously defined in eq. (2.36). This streamlines the calculation of the residual enthalpy since working with the compressibility form of the equation of state is generally preferable. The reduced entropy is obtained in the same manner, and the final result is

$$\boxed{S^R = R\ln(Z-B') + \frac{da/dT}{b} \ln \frac{Z+B'}{Z}.} \tag{5.56}$$

The derivative da/dT, which is needed for the calculation, is

$$\frac{da}{dT} = -0.42748 \frac{R^2 T_c}{P_c} \frac{\left(1 + \Omega\left(1 - \sqrt{T_r}\right)\right)\Omega}{\sqrt{T_r}}. \tag{5.57}$$

These results are summarized in Table 5-3, which also includes results for the van der Waals and the Peng-Robinson equation. In all cases, B' is defined as $B' = Pb/RT$, where b is the corresponding parameter in the equation of state.

The important conclusion is that residual properties can be calculated from the equation of state. The general procedure is this: at given T and P, first solve for Z, then apply the equations for the residual enthalpy and entropy. If the cubic equation for Z has three positive roots, the proper root must be selected based on the phase of the system. The calculation is demonstrated in the examples that follow.

Second printing corrections for Matsoukas, Fundamentals of Chemical Engineering Thermodynamics (9780132693066).
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