

242 Unit II Generalized Analysis of Fluid Properties

The other departure functions can be derived from these. Note the mathematical similarity between P in the pressure dependent formulas and ρ in the density-dependent formulas.

Example 7.5 Application of pressure-dependent formulas in compression of methane

Methane gas undergoes a continuous throttling process from upstream conditions of 40°C and 20 bars to a downstream pressure of 1 bar. What is the gas temperature on the downstream side of the throttling device? An expression for the molar heat capacity of methane in the ideal gas state is

$$C_p = 19.25 + 0.0523 T + 1.197E-5 T^2 - 1.132E-8 T^3; T [\equiv] \text{K}; C_p [\equiv] \text{J/mol-K}$$

The virial equation of state may be used for methane at these conditions:

$$Z = 1 + BP/RT = 1 + (B^0 + \omega B^1)P_r/T_r$$

$$\text{where } B^0 = 0.083 - 0.422/T_r^{1.6} \text{ and } B^1 = 0.139 - 0.172/T_r^{4.2}$$

Solution: Since a throttling process is isenthalpic, the enthalpy departure will be used to calculate the outlet temperature.

$$\Delta H = 0 = H_2 - H_1 = (H_2 - H_2^{ig}) + (H_2^{ig} - H_1^{ig}) - (H_1 - H_1^{ig})$$

The enthalpy departure for the first and third terms in parenthesis on the right hand side can be calculated using Eqn. 7.31. For the integrand, the temperature derivative of Z is required. Recognizing B is a function of temperature only, performing the integrations,

$$\left(\frac{\partial Z}{\partial T}\right)_P = 1 + \frac{P}{R} \left[\frac{\partial(B \cdot (1/T))}{\partial T} \right]_P = \frac{P}{R} \left[\left(\frac{1}{T}\right) \frac{dB}{dT} - \left(\frac{B}{T^2}\right) \right]$$

Inserting the derivative into Eqn 7.31

$$\left(\frac{H - H^{ig}}{RT}\right) = \int_0^P \frac{1}{R} \left[\left(\frac{B}{T}\right) - \frac{dB}{dT} \right] dP$$

$$\left(\frac{H - H^{ig}}{RT}\right) = \frac{P}{R} \left(\frac{B}{T} - \frac{dB}{dT} \right)$$

$$\left(\frac{S - S^{ig}}{R}\right) = -\frac{P}{R} \frac{dB}{dT}$$

We can easily show

$$\frac{dB^0}{dT_r} = \frac{0.6752}{T_r^{2.6}} \quad \frac{dB^1}{dT_r} = \frac{0.7224}{T_r^{5.2}}$$

Example 7.5 Application of pressure-dependent formulas in compression of methane (Continued)

Substituting the relations for B^0 and B^1 into the formulas for the departure functions for a pure fluid, we get

$$\left(\frac{H - H^{ig}}{RT}\right) = -P_r \left[\frac{1.0972}{T_r^{2.6}} - \frac{0.083}{T_r} + \omega \left(\frac{0.8944}{T_r^{5.2}} - \frac{0.139}{T_r} \right) \right] \quad 7.33$$

$$\left(\frac{S - S^{ig}}{R}\right) = -P_r \left[\frac{0.675}{T_r^{2.6}} + \omega \frac{0.722}{T_r^{5.2}} \right] \quad 7.34$$

For the initial state, 1

$$\left(\frac{H - H^{ig}}{RT}\right) = -0.110$$

$$(H - H^{ig})_1 = -287 \text{ J/mole}$$

Assuming a small temperature drop the heat capacity will be approximately constant over the interval, $C_p \approx 36 \text{ J/mole-K}$

For a throttle, $\Delta H = 0 \Rightarrow (H - H^{ig})_2 + 36(T_2 - 40) + 287 = 0$

Trial and error at state 2 where $P = 1 \text{ bar}$, $T_2 = 35^\circ\text{C} \Rightarrow -13 + 36(35 - 40) + 287 = 94$

$$T_2 = 30^\circ\text{C} \Rightarrow -13 + 36(30 - 40) + 287 = -87$$

Interpolating, $T_2 = 35 + (35 - 30)/(94 + 87)(-94) = 32.4^\circ\text{C}$

7.7 REFERENCE STATES

If we wish to calculate state changes in a property, then the reference state is not important, and all reference state information drops out of the calculation. However, if we wish to generate a chart or table of thermodynamic properties, or compare our calculations to a thermodynamic table/chart, then designation of a reference state becomes essential. Also, if we need to solve unsteady-state problems, the reference state is important because the answer may depend on the reference state as shown in Example 2.13 on page 72. The quantity $H_R - U_R = (PV)_R$ is non-zero, and although we may substitute $(PV)_R = RT_R$ for an ideal gas, for a real fluid we must use $(PV)_R = Z_R RT_R$, where Z_R has been determined at the reference state. We also may use a real fluid reference state or an ideal gas reference state. Whenever we compare our calculations with a thermodynamic chart/table, we must take into consideration any differences between our reference state and that of the chart/table. Therefore, to specify a reference state for a real fluid, we need to specify:

Pressure