b. *Example 2*

The fundamental relation for the entropy of an electron gas can be approximated as

$$S(U,V,N) = B\ N^{1/6}\ V^{1/3}\ U^{1/2}, \text{ where} \tag{A}$$

$$B = 2^{3/2}\pi^{4/3}k_B m^{1/2}N_{avag}^{1/6}/(3^{1/3}h_P). \tag{B}$$

Here, k_B denotes the Boltzmann constant that has a value of $\overline{R}/N_{Avag} = 1.3804\times10^{-26}$ kJ K^{-1}, h_P is the Planck constant that has a value of 6.62517×10^{-37} kJ s, m denotes the electron mass of 9.1086×10^{-31} kg, N the number of kmoles of the gas, V its volume in m^3, and U its energy in kJ. Determine $\bar{s}$, T, and P when $\bar{u} = 4000$ kJ k $mole^{-1}$, and $\bar{v}$ = 1.2 m^3 $kmole^{-1}$.

Solution

The value of $B = 5.21442$ $kg^{1/2}$ k $mole^{1/6}$ s K^{-1}. From Eq. (A),

$$\bar{s} = S/N = (B/N)\ N^{1/6}(\bar{v}N)^{1/3}(\bar{u}N)^{1/2} = B\ \bar{v}^{1/3}\ \bar{u}^{1/2}, \text{ i.e.,} \tag{C}$$

$$\bar{s} = 5.21442\ (kg^{1/2}\ K^{-1}\ Kmole^{1/6}\ s)(1.2\ m^3\ k\ mole^{-1})^{1/3}\ (4000\ kJ\ kmole^{-1})^2.$$

Recalling that the units kg (m/s^2) m $\equiv$ J.

$$\bar{s} = 350\ kg^{1/2}\ m\ kJ^{1/2}\ kmole^{-1}\ K^{-1}. = 350.45\ kJ\ kmole^{-1}\ K^{-1}.$$

From the entropy fundamental equation

$$1/T = (\partial\bar{s}/\partial\bar{u})\ \bar{v}.$$

Differentiating Eq. (C) with respect to $\bar{u}$ and using this relation,

$$1/T = (1/2)\ B\ \bar{v}^{1/3}/\bar{u}^{1/2} = 0.04381\ \text{or } T = 22.8\ K. \tag{D}$$

Similarly, since

$$P/T = (\partial\bar{s}/\partial\bar{v})_u,$$

Upon differentiating Eq. (C) and using the above relation,

$$P/T = (1/3)\ B\ \bar{u}^{1/2}/\bar{v}^{2/3} = 94.35\ kPa\ K^{-1}. \tag{E}$$

Using the value for T = 22.83 K, the pressure P = 2222.4 kPa.. The enthalpy

$$\bar{h} = \bar{u} + P\bar{v} = 4000 + 2222.4 \times 1.2 = 6666.9\ kJ\ kmole^{-1}.$$

h. Example 8

Obtain a relation for ds for an ideal gas. Using the criterion for an exact differential show that for this gas c_v is only a function of temperature.

Solution

For an ideal gas

$$P = RT/v. \tag{A}$$

Using Eq. (A) and Eq. (32), we obtain

$$ds = R \,(dv/v) + c_v \,(dT/T). \tag{B}$$

Comparing Eq. (B) with the relation $dZ = Mdx + Ndy$, and using the criterion for an exact differential we obtain

$$\partial\{(c_v/T)/\partial v\}_T = \partial\,\{(R/v)/\partial T\}_v = 0.$$

since at constant volume (R/v) is not a function of temperature (or pressure). Therefore, the term $\partial\{(c_v/T)/\partial v\}_T$ is not a function of v and, at most, is a function of temperature alone.

j. Example 10

A VW gas is used as the working fluid in an ideal power cycle. A relation between T and v is required for an isentropic process (data for $c_{vo}(T)$ is available). If $v_1 = 0.006$ $m^3\,kg^{-1}$, $T_1 = 200$ K, the compression ratio $v_1/v_2 = 3$, determine the values of T_2 and P_2 if the gas is air.

Solution

Recall that

$$ds = c_v dT/T + (\partial P/\partial T)v\,dv, \text{ i.e., } ds = cv\,dT/T + R\,dv/(v{-}b) \tag{A}$$

$$P = RT/(v - b) - a/(T^n \, v \, (v + c))$$

where n=1/2, c= b for a RK fluid, n=0, c=0 for VW fluids, and n=1, c=0 for Berthelot fluids.

Using the criterion for an exact differential,

$$(\partial c_v/\partial v)_T = \partial \, [\{R/(v-b)\}/\partial T]_v = 0.$$

This implies that c_v is not a function of volume and is a function of temperature alone, i.e., $c_v = c_{vo}(T)$. Since $ds = 0$ for the ideal cycle, upon integrating Eq. (A),

$$\int c_{vo} \, dT/T = -R \ln(v-b) + C. \tag{B}$$

Since, $s^o = \int c_{p,o}dT/T$, we define

$$(s')^o(T) = \int c_{vo}dT/T = \int(c_{p,o} - R)dT/T = s^o - R \ln T. \tag{C}$$

We use Eqs. (B) and (C) to obtain the relation

$$(s')^o = -R \ln \{(v-b)\} + C'.$$

Therefore,

$$(s_2')^o - (s_1')^o = R \ln((v_1 - b)/(v_2 - b)). \tag{D}$$

Simplifying,

$$\exp ((s_2')^o/R - (s_1')^o/R) = (\exp (s_2^o/R)/T_2)/(\exp(s_1^o/R)/T_1) = (v_2 - b)/(v_1 - b). \tag{E}$$

Upon defining $v_r = \exp (s^o/R)/T$, Eq. (E) can be written in the form

$$v_{r2}/v_{r1} = (v_2 - b)/(v_1 - b). \tag{F}$$

Values of v_r are usually tabulated. Once the volume ratio v_2/v_1 is specified, T_2 can be determined from Eq. (F). Using the VW equation of state, we can then determine P_2. Since, $v_1 = 0.006$ m³ kg⁻¹ at $T_1 = 200$ K, the VW equation yields
$$P_1 = 0.08314 \times 200 \div (0.006 \times 28.97 - 0.0367) - 1.368 \div (0.006 \times 28.97)^2$$
$$= 121.3 - 45.3 = 76 \text{ bar.}$$
At $T = 200$ K, $v_{r1} = 1707$. We will use the relation

$$v_{r2}/v_{r1} = (v_2 - b)/(v_1 - b),$$

and the values $v_1 = 0.006$ m³ kg⁻¹, $b = 0.0367 \div 28.97 = 0.00127$ m³ kg⁻¹.
Therefore,
$v_2 = 0.006 \div 3 = 0.002$ m³ kg⁻¹, and
$v_{r2}/v_{r1} = (0.002 - 0.00127) \div (0.006 - 0.00127) = 0.154$, so that
$v_{r2} = 1707 \times 0.154 = 262.9$.
The tabulated values indicate that at $v_{r2} = 263$, $T_2 = 423$ K.
Finally, using the VW equation of state
$$P_2 = 0.08314 \times 423 \div (0.002 \times 28.97 - 0.0367) - 1.368 \div (0.002 \times 28.97)^2$$
$$= 1656 - 408 = 1248 \text{ bar.}$$

k. *Example 11*

Derive an expression for the sound speed ($c^2 = -v^2(\partial P/\partial v)_s = v/\beta_s$) in terms of the measurable properties of a simple compressible substance.

Show that $c_p/c_v = k = \beta_T/\beta_s$.

Determine a relation for the sound speed for an ideal gas.
Determine a relation for the sound speed for a VW gas.

Solution

Recall that the speed of sound

$$c^2 = -v^2(\partial P/\partial v)_s = v/\beta_s$$

$$ds = 0 = c_v \, dT/T + (\partial P/\partial T)_v \, dv, \text{ and} \tag{A}$$

$$ds = 0 = c_p dT/T - (\partial v/\partial T)_P \, dP. \tag{B}$$

We multiply Eq. (A) by (T/c_v) and Eq. (B) by (T/c_p) and then subtract one of the resulting relations from the other to obtain

$$(\partial P/\partial T)_v \, (T/c_v) \, dv_s + (\partial v/\partial T)_P \, (T/c_p) \, dP_s = 0, \text{ or} \tag{C}$$

$$(\partial P/\partial v)_s = -k \, (\partial P/\partial T)_v/(\partial v/\partial T)_P, \text{ where} \tag{D}$$

$$k(T,v) = c_p(T,v)/c_v(T,v). \tag{E}$$

Applying the expression for the speed of sound $c^2 = -v^2(\partial P/\partial v)_s = v/\beta_s$ in Eq. (D),

$$c^2 = v^2 \, k(T,v)(\partial P/\partial T)_v/(\partial v/\partial T)_P. \tag{F}$$

Using the cyclical rule

$$(\partial P/\partial v)_T(\partial v/\partial T)_P(\partial T/\partial P)_v = -1 \tag{G}$$

we obtain

$$(\partial v/\partial T) = -(\partial P/\partial T)/(\partial P/\partial v) \tag{H}$$

Substituting from Eq. (H) in Eq. (F),

$$c^2 = -k(T,v) \, v^2 \, (\partial P/\partial v)_T = k(T,v) \, v/\beta_T \tag{I}$$

With $c^2 = v/\beta_s$, in Eq. (I)

$$v/\beta_s = k(T,v) \, v/\beta_T, \text{ or } k(T,v) = \beta_T/\beta_s.$$

In the case of ideal gases,

$$k = -(c^2/v^2)/(-RT/v^2) = c^2/RT \text{ or } c^2 = kRT. \tag{J}$$

Typically we denote c as c_0 for ideal gases.

For a VW gas,

$$\partial P/\partial v = -RT/(v-b)^2 + 2a/v^3 \tag{K}$$

Thereafter, combining Eqs. (I) and (K)

$$c^2 = k(T,v) \, v^2 \, (RT/(v-b)^2 + a/v^3) \tag{L}$$

o. *Example 15*

Obtain an expression for the enthalpy change dh in a Clausius I fluid that follows the relation

$$P = RT/(v-b), \tag{A}$$

and show that c_p is a function of T alone.

Solution

Using Eq. (A)

$$v = b + RT/P, \text{ and} \tag{B}$$

using Eq. (43),

$$dh = c_p\, dT + (v - T\,R/P)\, dP = c_p\, dT + b\,dP, \text{ i.e., } h = h(T,P). \tag{C}$$

Using the criterion for an exact differential we can show that

$$dc_p/dP = db/dT = 0. \tag{D}$$

Therefore, c_p is a function of temperature alone.
Integrating Eq. (C),

$$h = \int c_p\, (T)\, dT + bP + \text{constant}. \tag{E}$$

s. **Example 19**

Assume that

$$a(T,v) = a_o(T,v) + RT\, \ln(v/(v-b)) + (a/(bT^{1/2}))\, \ln\,(v/(v+b)).$$

Determine an expression for the pressure.

$$da = -s\, dT - P\,dv$$

$$h_2 - h_1 = (h_2 - h_1)_{\text{ideal}} - RT_{cr}(Z_{h_2} - Z_{h_1}) \tag{12–59}$$

12-88 Using the cyclic relation and the first Maxwell relation, the other three Maxwell relations are to be obtained.

12-90 It is to be shown that

$$c_v = -T\left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial P}{\partial T}\right)_v \quad \text{and} \quad c_p = T\left(\frac{\partial P}{\partial T}\right)_s\left(\frac{\partial v}{\partial T}\right)_P$$

Analysis Using the definition of c_v,

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial P}\right)_v\left(\frac{\partial P}{\partial T}\right)_v$$

Substituting the first Maxwell relation $\left(\frac{\partial s}{\partial P}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_s$,

$$c_v = -T\left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial P}{\partial T}\right)_v$$

Using the definition of c_p,

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_P = T\left(\frac{\partial s}{\partial v}\right)_P\left(\frac{\partial v}{\partial T}\right)_P$$

Substituting the second Maxwell relation $\left(\frac{\partial s}{\partial v}\right)_P = \left(\frac{\partial P}{\partial T}\right)_s$,

$$c_p = T\left(\frac{\partial P}{\partial T}\right)_s\left(\frac{\partial v}{\partial T}\right)_P$$

12-91 It is to be proven that for a simple compressible substance $\left(\frac{\partial s}{\partial v}\right)_u = \frac{P}{T}$.

Analysis The proof is simply obtained as

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{-\left(\frac{\partial u}{\partial v}\right)_s}{\left(\frac{\partial u}{\partial s}\right)_v} = -\frac{-P}{T} = \frac{P}{T}$$

12-75 Methane is compressed adiabatically by a steady-flow compressor. The required power input to the compressor is to be determined using the generalized charts.

Assumptions **1** Steady operating conditions exist. **2** Kinetic and potential energy changes are negligible.

Analysis The steady-flow energy balance equation for this compressor can be expressed as

$$\dot{E}_{in} - \dot{E}_{out} = \Delta \dot{E}_{system}^{\nearrow 0 \,(steady)} = 0$$

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{W}_{C,in} + \dot{m}h_1 = \dot{m}h_2$$

$$\dot{W}_{C,in} = \dot{m}(h_2 - h_1)$$

The enthalpy departures of CH_4 at the specified states are determined from the generalized charts to be (Fig. A-29)

$$\left. \begin{array}{l} T_{R1} = \dfrac{T_1}{T_{cr}} = \dfrac{263}{191.1} = 1.376 \\[4mm] P_{R1} = \dfrac{P_1}{P_{cr}} = \dfrac{2}{4.64} = 0.431 \end{array} \right\} \longrightarrow Z_{h1} = 0.21$$
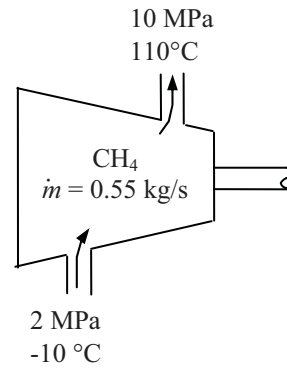
and

$$\left. \begin{array}{l} T_{R2} = \dfrac{T_2}{T_{cr}} = \dfrac{383}{191.1} = 2.00 \\[4mm] P_{R2} = \dfrac{P_2}{P_{cr}} = \dfrac{10}{4.64} = 2.155 \end{array} \right\} \longrightarrow Z_{h2} = 0.50$$

Thus,

$$\begin{aligned} h_2 - h_1 &= RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{ideal} \\ &= (0.5182)(191.1)(0.21 - 0.50) + 2.2537(110 - (-10)) \\ &= 241.7 \text{ kJ/kg} \end{aligned}$$

Substituting,

$$\dot{W}_{C,in} = (0.55 \text{ kg/s})(241.7 \text{ kJ/kg}) = \textbf{133 kW}$$

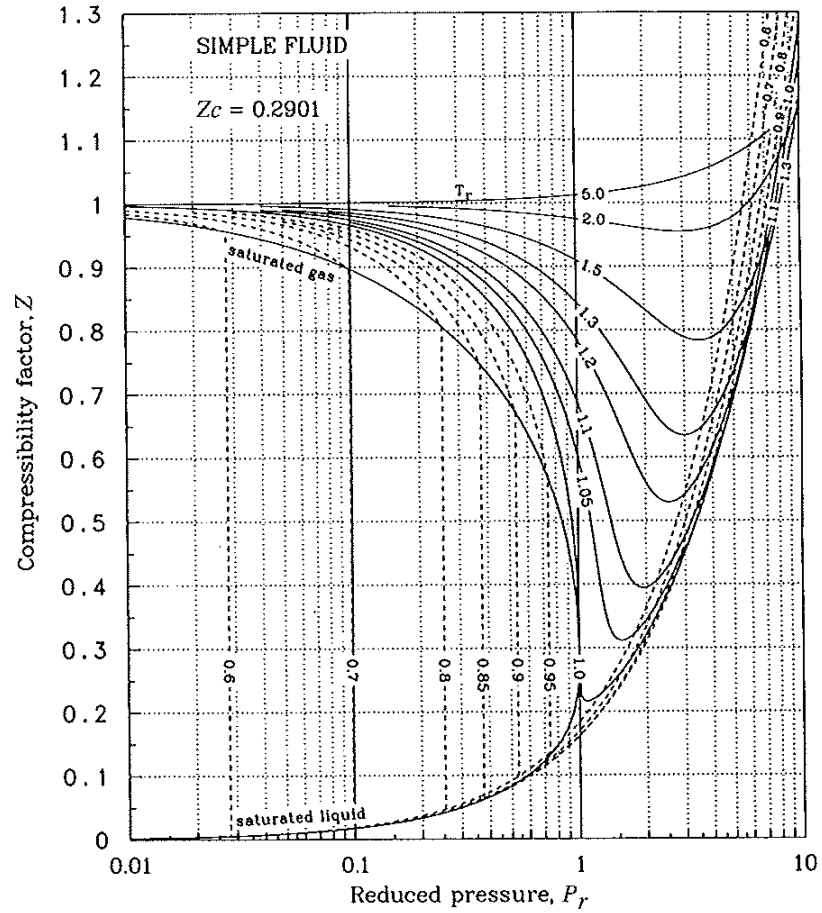Diagram annotations:
10 MPa
110°C

CH_4
$\dot{m} = 0.55$ kg/s

2 MPa
-10 °C

FIGURE D.1 Lee–Kesler Simple Fluid Compressibility Factor.