Problem 6-5 solution

Eqn of state: $(P+b)v \;=\; RT$

From Eq. (6-16) $\left(\frac{\partial c_v}{\partial v}\right)_T \;=\; T\left(\frac{\partial^2 P}{\partial T^2}\right)_v \;=\; 0 \;\;\Rightarrow\; c_v = c_v(T)$. Next, $c_P = c_v + T\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P \;=\; c_v + R$

$$\left.\begin{aligned} du &= c_v dT + \left[T\left(\tfrac{\partial P}{\partial T}\right)_v - P\right]dv, \\ ds &= \tfrac{c_P}{T}dT - \left(\tfrac{\partial v}{\partial T}\right)_P dP, \\ dh &= c_P dT + \left[v - T\left(\tfrac{\partial v}{\partial T}\right)_P\right]dP \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} u &= u_0 + \textstyle\int_{T_0}^{T} dT\ c_v + \int_{v_0}^{v} dv\ \left[T\left(\tfrac{\partial P}{\partial T}\right)_v - P\right] \;=\; u_0 + \int_{T_0}^{T} dT\ c_v + b(v-v_0), \\ s &= s_0 + \textstyle\int_{T_0}^{T} dT\ \tfrac{c_P}{T} - \int_{P_0}^{P} dP\ \left(\tfrac{\partial v}{\partial T}\right)_P \;=\; s_0 + \int_{T_0}^{T} dT\ \tfrac{c_v}{T} + R\ln\tfrac{v}{v_0}, \\ h &= h_0 + \textstyle\int_{T_0}^{T} dT\ c_P + \int_{P_0}^{P} dP\ \left[v - T\left(\tfrac{\partial v}{\partial T}\right)_P\right] \;=\; h_0 + \int_{T_0}^{T} dT\ c_P \end{aligned}\right.$$

Need $c_v(T)$ (or $c_P(T)$) to determine u, s and h.

Problem 6-16 solution

(a):

If we know $c_v(T,v)$, $\left(\frac{\partial P(T,v)}{\partial T}\right)_v$, and $P(T,v) \Rightarrow$ we know $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$, $\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$ and $c_P = c_v + \frac{\beta^2 T v}{\kappa}$.

$$\begin{aligned} u &= u_0 + \textstyle\int_{T_0}^{T} dT\ c_v + \int_{v_0}^{v} dv\ \left[T\left(\tfrac{\partial P}{\partial T}\right)_v - P\right], \\ s &= s_0 + \textstyle\int_{T_0}^{T} dT\ \tfrac{c_P}{T} - \int_{P_0}^{P} dP\ \left(\tfrac{\partial v}{\partial T}\right)_P, \\ h &= h_0 + \textstyle\int_{T_0}^{T} dT\ c_P + \int_{P_0}^{P} dP\ \left[v - T\left(\tfrac{\partial v}{\partial T}\right)_P\right] \end{aligned}$$

(b)

If we know $P(T,v)$ we can find $\left(\frac{\partial P(T,v)}{\partial T}\right)_v$.

Problem 7-5 solution

We know

$$f \;=\; c_v(T-T_0) - c_v T\ln\frac{T}{T_0} - a\Big(\frac{1}{v} - \frac{1}{v_0}\Big) - RT\ln\frac{v-b}{v_0-b} - s_0(T-T_0) + f_0$$

F-la (7-20):

$$P \;=\; -\Big(\frac{\partial f}{\partial v}\Big)_T \;=\; -\frac{a}{v^2} + \frac{RT}{v-b}$$

$$\begin{aligned} s \;&=\; -\Big(\frac{\partial f}{\partial T}\Big)_v \;=\; c_v\ln\frac{T}{T_0} + R\ln\frac{v-b}{v_0-b} + s_0 \\ \Rightarrow\; u \;&=\; f + Ts \;=\; c_v(T-T_0) - a\Big(\frac{1}{v} - \frac{1}{v_0}\Big) + f_0 + Ts_0 \;=\; c_v T + \frac{a}{v} + \text{const} \end{aligned}$$