Problem 7-5 solution

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

F-la (7-20):

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

$$s \;=\; -\Big(\frac{\partial f}{\partial T}\Big)_v \;=\; c_v\ln\frac{T}{T_0} + R\ln\frac{v-b}{v_0-b} + s_0$$

$$\Rightarrow\; u \;=\; f + Ts \;=\; c_v(T-T_0) - a\big(\frac{1}{v}-\frac{1}{v_0}\big) + f_0 + Ts_0 \;=\; c_vT + \frac{a}{v} + \text{const}$$

Problem 7-7 solution

Eq. (7-27):

$$\Big(\frac{\partial g}{\partial T}\Big)_P \;=\; -S, \qquad \Big(\frac{\partial g}{\partial P}\Big)_T \;=\; v \qquad \Rightarrow\quad dg \;=\; -SdT + vdP$$

If $g \;=\; -RT\ln\frac{v}{v_0} + vB(T) = g(v,T)$

$$dg \;=\; -sdT + vdP(v,T) \;=\; -sdT + v\frac{\partial P(v,T)}{\partial v}dv + v\frac{\partial P(v,T)}{\partial T}dT$$

$$dg \;=\; \Big[-s + v\Big(\frac{\partial P}{\partial T}\Big)_v\Big]dT + v\Big(\frac{\partial P}{\partial v}\Big)_T dv$$

$$\Rightarrow\;\Big(\frac{\partial g}{\partial v}\Big)_T \;=\; -\frac{RT}{v} + B(T) \;=\; v\Big(\frac{\partial P}{\partial v}\Big)_T \quad\Rightarrow\quad \Big(\frac{\partial P}{\partial v}\Big)_T \;=\; -\frac{RT}{v^2} + \frac{B(T)}{v}$$

$$\Rightarrow\; P \;=\; RT\Big(\frac{1}{v}-\frac{1}{v_0}\Big) + B(T)\ln\frac{v}{v_0} + \phi(T) \qquad\leftarrow\;\text{eqn. of state}$$

where $\phi(T)$ is an undetermined function of T.

To fix $\phi(T)$, one can measure for example the expansivity $\beta \;=\; \frac{1}{v}\Big(\frac{\partial v}{\partial T}\Big)_P$, then

$$\Big(\frac{\partial P}{\partial T}\Big)_v \;=\; -\frac{\big(\frac{\partial v}{\partial T}\big)_P}{\big(\frac{\partial v}{\partial P}\big)_T} \;=\; \frac{\beta}{\kappa}$$

Since we know the compressibility

$$\kappa \;=\; -\frac{1}{v}\Big(\frac{\partial v}{\partial P}\Big)_T \;=\; \frac{v}{RT - vB(T)}$$

the expansivity will give us $\Big(\frac{\partial P}{\partial T}\Big)_v$ which fixes the form of $\phi(T)$ since

$$\phi'(T) \;=\; \beta\Big(\frac{RT}{v} - B(T)\Big) - R\big(\frac{1}{v}-\frac{1}{v_0}\big) - B'(T)\ln\frac{v}{v_0}$$

Next,

$$\Big(\frac{\partial g}{\partial T}\Big)_v \;=\; -R\ln\frac{v}{v_0} + vB'(T) \;=\; -s + v\Big(\frac{\partial P}{\partial T}\Big)_v \;=\; -s + R\big(1-\frac{v}{v_0}\big) + B'(T)v\ln\frac{v}{v_0} + v\phi'(T)$$

$$\Rightarrow\; s \;=\; R\big(1-\frac{v}{v_0} + \ln\frac{v}{v_0}\big) + B'(T)v\big(\ln\frac{v}{v_0} - 1\big) + v\phi'(T)$$

and since $u \;=\; g + Ts - Pv$ we get

$$u \;=\; v\big(\ln\frac{v}{v_0} - 1\big)[TB'(T) - B(T)] + v[T\phi'(T) - \phi(T)]$$

Problem 7-10 solution

$$\Phi \equiv S - \frac{U + PV}{T} \quad \Rightarrow \quad d\Phi = dS - \frac{1}{T}(dU + PdV + VdP) + \frac{dT}{T^2}(U + PV)$$

$$TdS = dU + PdV \quad \Rightarrow \quad d\Phi = -\frac{V}{T}dP + \frac{dT}{T^2}(U + PV) \quad \Rightarrow \quad \left(\frac{\partial \Phi}{\partial P}\right)_T = -V$$

$$\left(\frac{\partial \Phi}{\partial P}\right)_T = -V, \quad \left(\frac{\partial \Phi}{\partial T}\right)_P = \frac{U + PV}{T^2} \quad \Rightarrow \quad T\left(\frac{\partial \Phi}{\partial T}\right)_P + P\left(\frac{\partial \Phi}{\partial P}\right)_T = \frac{U}{T}$$

$$T\left(\frac{\partial \Phi}{\partial T}\right)_P + \Phi = \frac{U + PV}{T^2} + S - \frac{U + PV}{T} = S$$