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

$$\begin{aligned}
dg \;&=\; -sdT + vdP(v,T) \;=\; -sdT + v\frac{\partial P(v,T)}{\partial v}dv + v\frac{\partial P(v,T)}{\partial T}dT \\
dg \;&=\; \Big[-s + v\Big(\frac{\partial P}{\partial T}\Big)_v\Big]dT + v\Big(\frac{\partial P}{\partial v}\Big)_T dv \\
\Rightarrow \;\; \Big(\frac{\partial g}{\partial v}\Big)_T \;&=\; -\frac{RT}{v} + B(T) \;=\; v\Big(\frac{\partial P}{\partial v}\Big)_T \quad \Rightarrow \quad \Big(\frac{\partial P}{\partial v}\Big)_T \;=\; -\frac{RT}{v^2} + \frac{B(T)}{v} \\
\Rightarrow \;\; P \;&=\; RT\Big(\frac{1}{v} - \frac{1}{v_0}\Big) + B(T)\ln\frac{v}{v_0} + \phi(T) \qquad \leftarrow \;\text{eqn. of state}
\end{aligned}$$

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,

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

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

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