

Problem 7-5 solution

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

F-la (7-20):

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

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

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

Problem 7-7 solution

Eq. (7-27):

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

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

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

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

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

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

where $\phi(T)$ is an undetermined function of T .To fix $\phi(T)$, one can measure for example the expansivity $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$, then

$$\left(\frac{\partial P}{\partial T} \right)_v = - \frac{\left(\frac{\partial v}{\partial T} \right)_P}{\left(\frac{\partial v}{\partial P} \right)_T} = \frac{\beta}{\kappa}$$

Since we know the compressibility

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

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

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

Next,

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

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

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

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

Problem 7-10 solution

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

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

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

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