HW #1 solutions

1. Chandler 1.8

Consider $\left(\frac{\partial C_p}{\partial p}\right)_{T,n} = T\left(\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_{p,n}\right)_{T,n} =$

$$= T\left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial S}{\partial p}\right)_{T,n}}_{-\left(\frac{\partial V}{\partial T}\right)_{p,n}}\right)_{p,n} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{p,n}.$$

2. Chandler 1.12

$$dE = TdS + fdL + \mu dn$$

Since E is extensive, we have

$E = TS + fL + \mu n$ and thus

$$dE = \underline{TdS} + SdT + \underline{fdL} + Ldf + \underline{\mu dn} + nd\mu,$$

or

$$SdT + Ldf + nd\mu = 0$$

GD equation

3. Chandler 1.13

Eq. of state: $$E = \frac{\overset{\text{const}}{\theta} S^2 L}{n^2}.$$

Then $$\mu = \left(\frac{\partial E}{\partial n}\right)_{S,L} = -\frac{2\theta S^2 L}{n^3} \qquad (*)$$

To compute $\mu = \mu(T, L, n)$, use

$$T = \left(\frac{\partial E}{\partial S}\right)_{L,n} = \frac{2\theta S L}{n^2} \Rightarrow S = \frac{n^2 T}{2\theta L}.$$

Substitute into $(*)$:

$$\mu = -\frac{2\theta L}{n^3}\left(\frac{n^2 T}{2\theta L}\right)^2 = -\frac{T^2}{2\theta (L/n)} = \mu\left(T, \frac{L}{n}\right).$$

as requested

GD equation:

$$S dT + L df + n d\mu = 0 \qquad (**)$$

Consider $$dT \overset{T=T(S,L,n)}{=} \left(\frac{\partial T}{\partial S}\right)_{L,n} dS + \left(\frac{\partial T}{\partial L}\right)_{S,n} dL + \left(\frac{\partial T}{\partial n}\right)_{S,L} dn =$$

$$= \frac{2\theta L}{n^2} dS + \frac{2\theta S}{n^2} dL + \left(-\frac{4\theta S L}{n^3}\right) dn$$

Next, consider

$$f = \left(\frac{\partial E}{\partial L}\right)_{S,n} = \frac{\theta S^2}{n^2} = f(S,n).$$

Then $$df = \frac{2\theta S}{n^2}\,dS + \left(-\frac{2\theta S^2}{n^3}\right)dn.$$

Finally, $\mu = \mu(S, L, n)$:

$$d\mu = \left(-\frac{4\theta S L}{n^3}\right)dS + \left(-\frac{2\theta S^2}{n^3}\right)dL + \underline{\underline{\frac{6\theta S^2 L}{n^4}\,dn}}.$$

Substitute dT, df, $d\mu$ into $(**)$:

$$\left[\frac{2\theta L S}{n^2} + \frac{2\theta S L}{n^2} - \frac{4\theta S L}{n^2}\right]dS +$$

$$+ \left[\frac{2\theta S^2}{n^2} - \frac{2\theta S^2}{n^2}\right]dL +$$

$$+ \left[-\frac{4\theta S^2 L}{n^3} - \frac{2\theta S^2 L}{n^3} + \frac{6\theta S^2 L}{n^3}\right]dn = 0$$

since each $[\ldots] = 0$ separately.

(4.) Chandler 1.14

p-V-n system, $r=1$

Recall the GD equation:

$$-SdT + Vdp - nd\mu = 0, \text{ or}$$

$$d\mu = -\underbrace{\left(\frac{S}{n}\right)}_{s} dT + \underbrace{\left(\frac{V}{n}\right)}_{v} dp$$

per mole

Hence $$\left(\frac{\partial \mu}{\partial v}\right)_T = -s\cancel{\left(\frac{\partial T}{\partial v}\right)_T} + v\left(\frac{\partial p}{\partial v}\right)_T =$$

$$= v\left(\frac{\partial p}{\partial v}\right)_T, \text{ as requested.}$$