4.3 Start with eqn. (4.2-21): $d\underline{U} = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V}$. Thus $\left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = C_V$;

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P = C_V + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_P \text{ and}$$

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P - \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_P .$$

(a) Ideal gas $P\underline{V} = RT$

$$T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = 0 \Rightarrow \left(\frac{\partial \underline{U}}{\partial T}\right)_P = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}}$$

(b) van der Waals gas

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2};\ \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V} - b};\ \Rightarrow \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right] = \frac{a}{\underline{V}^2}$$

Also: $dP = \frac{RdT}{\underline{V} - b} - \frac{RT}{(\underline{V} - b)^2}d\underline{V} + \frac{2a}{\underline{V}^3}d\underline{V}$

$$\Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{R/(\underline{V}-b)}{RT/(\underline{V}-b)^2 - 2a/\underline{V}^3} = \left[\frac{T}{(\underline{V}-b)} - \frac{2a(\underline{V}-b)}{R\underline{V}^3}\right]^{-1}$$

$$\Rightarrow \left(\frac{\partial \underline{u}}{\partial T}\right)_P - \left(\frac{\partial \underline{u}}{\partial T}\right)_{\underline{V}} = \frac{a}{\left[\underline{V}^2 T/(\underline{V}-b)\right] - \left[2a(\underline{V}-b)/R\underline{V}\right]}$$

$$= \frac{aR\underline{V}(\underline{V}-b)}{RT\underline{V}^3 - 2a(\underline{V}-b)^2}$$

(c) The Virial Equation of State

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \cdots = 1 + \sum_{i=1} \frac{B_i}{\underline{V}^i}$$

or $P = \dfrac{RT}{\underline{V}} + \sum_{i=1} \dfrac{B_i RT}{\underline{V}^{i+1}}$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}} + \sum_{i=1} \frac{B_i R}{\underline{V}^{i+1}} + \sum_{i=1} \frac{RT}{\underline{V}^{i+1}} \left(\frac{dB_i}{dT}\right) \leftarrow$$

Note: This is a total derivative, since B_i is a function of only temperature

$$\Rightarrow T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \sum_{i=1} \frac{RT}{\underline{V}^{i+1}} \frac{dB_i}{d\ln T}$$

Also need $(\partial \underline{V}/\partial T)_P$, but this is harder to evaluate alternatively. Since

$$\left(\frac{\partial \underline{V}}{\partial T}\right)_P \left(\frac{\partial P}{\partial \underline{V}}\right)_T \left(\frac{\partial T}{\partial P}\right)_{\underline{V}} = -1 \Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_{\underline{V}}}{(\partial P/\partial \underline{V})_T}$$

$\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}}$ is given above.

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = -\frac{RT}{\underline{V}^2} - \sum_{i=1} \frac{(i+1)B_i RT}{\underline{V}^{i+2}}$$

$$\Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{\underline{V}\left(RT/\underline{V} + \sum_{i=1}\left[B_i RT/\underline{V}^{i+1}\right] + \sum\left(RT/\underline{V}^{i+1}\right)(dB_i/d\ln T)\right)}{T\left(RT/\underline{V} + \sum_{i=1}\left[(i+1)B_i RT/\underline{V}^{i+1}\right]\right)}$$

Using $\dfrac{RT}{\underline{V}} = P - \sum_{i=1} \dfrac{B_i RT}{\underline{V}^{i+1}}$, we get

$$\left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{\underline{V}\left[P + \sum\left(RT/\underline{V}^{i+1}\right)(dB_i/d\ln T)\right]}{T\left[P + \sum (iB_i RT)/\underline{V}^{i+1}\right]}$$

and

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P - \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = \sum \frac{R}{\underline{V}^i}\frac{dB_i}{d\ln T}\left[\frac{P+\sum\left(RT/\underline{V}^{i+1}\right)(dB_i/d\ln T)}{P+\sum iB_i RT/\underline{V}^{i+1}}\right]$$

4.4 (a) Start from

$$\mu = -\frac{1}{C_\mathrm{P}}\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right] \Rightarrow C_\mathrm{P} = -\frac{1}{\mu}\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]$$

but $\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right] = -T^2\left(\frac{\partial(\underline{V}/T)}{\partial T}\right)_P$ and $C_\mathrm{P} = \frac{T^2}{\mu}\left(\frac{\partial(\underline{V}/T)}{\partial T}\right)_P$.

(b) $\left(\frac{\partial(\underline{V}/T)}{\partial T}\right)_P = \frac{\mu C_\mathrm{P}}{T^2}$; integrate $\left(\frac{\underline{V}}{T}\right)_{T_2,P} - \left(\frac{\underline{V}}{T}\right)_{T_1,P} = \int_{T_1,P}^{T_2,P}\frac{\mu C_\mathrm{P}}{T^2}dT$.

Thus $\underline{V}(T_2,P) = \underline{V}(T_1,P)\frac{T_2}{T_1} + T_2\int_{T_1,P}^{T_2,P}\frac{\mu C_\mathrm{P}}{T^2}dT$.

4.8

$$\left(\frac{\partial T}{\partial P}\right)_{\underline{S}} = \frac{\partial(T,\underline{S})}{\partial(P,\underline{S})} = \frac{\partial(T,\underline{S})}{\partial(P,T)}\cdot\frac{\partial(P,T)}{\partial(P,\underline{S})} = -\frac{\partial(\underline{S},T)/\partial(P,T)}{\partial(\underline{S},P)/\partial(T,P)}$$

$$= \frac{-(\partial \underline{S}/\partial P)_T}{(\partial \underline{S}/\partial T)_P} = \frac{(\partial \underline{V}/\partial T)_P}{C_P/T} = \frac{\underline{V}\alpha T}{C_P}$$

and

$$\frac{\kappa_S}{\kappa_T} = \frac{(1/\underline{V})(\partial \underline{V}/dP)_{\underline{S}}}{(1/\underline{V})(\partial \underline{V}/dP)_T} = \frac{\partial(\underline{V},\underline{S})/\partial(P,\underline{S})}{\partial(\underline{V},T)/\partial(P,T)} = \frac{\partial(\underline{V},\underline{S})}{\partial(\underline{V},T)}\cdot\frac{\partial(P,T)}{\partial(P,\underline{S})}$$

$$= \frac{\partial(\underline{S},\underline{V})}{\partial(T,\underline{V})}\cdot\frac{\partial(T,P)}{\partial(\underline{S},P)} = \left(\frac{\partial \underline{S}}{\partial T}\right)_{\underline{V}}\cdot\left(\frac{\partial T}{\partial \underline{S}}\right)_P = \frac{C_V}{T}\cdot\frac{T}{C_P} = \frac{C_V}{C_P}$$

4.9 (a)

$$\left(\frac{\partial \underline{H}}{\partial \underline{V}}\right)_T = \frac{\partial(\underline{H},T)}{\partial(\underline{V},T)} = \frac{\partial(\underline{H},T)}{\partial(P,T)}\cdot\frac{\partial(P,T)}{\partial(\underline{V},T)} = \left(\frac{\partial \underline{H}}{\partial P}\right)_T\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

Since $\left(\frac{\partial P}{\partial \underline{V}}\right)_T \neq 0$ (except at the critical point)

$$\left(\frac{\partial \underline{H}}{\partial \underline{V}}\right)_T = 0 \text{ if } \left(\frac{\partial \underline{H}}{\partial P}\right)_T = 0$$

(b)

$$\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P = \frac{\partial(\underline{S},P)}{\partial(\underline{V},P)} = \frac{\partial(\underline{S},P)}{\partial(T,P)}\cdot\frac{\partial(T,P)}{\partial(\underline{V},P)} = \left(\frac{\partial \underline{S}}{\partial T}\right)_P\cdot\left(\frac{\partial T}{\partial \underline{V}}\right)_P$$

$$= \frac{C_P}{T}\cdot\frac{1}{\underline{V}}\cdot\underline{V}\left(\frac{dT}{d\underline{V}}\right)_P = \frac{C_P/T\underline{V}}{(1/\underline{V})(\partial \underline{V}/\partial T)_P} = \frac{C_P}{T\underline{V}\alpha} \Rightarrow \left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P \sim \alpha^{-1}$$