5.13 (Also available as a Mathcad worksheet. The Mathcad solution includes graphs.)

(a) Use the Clausius-Clapeyron equation

$$\frac{\Delta \underline{H}^{\text{vap}}}{R} = \frac{\ln(P_2/P_1)}{1/T_1 - 1/T_2}$$

Plotting $\ln P$ vs. $\dfrac{1}{T}$ and graphically taking slope, I find $\Delta \underline{H}^{\text{vap}} \sim 42700 \text{ J/mol}$.

(b) The vapor pressure is low enough that the ideal gas approximation should be valid—thus

$$\frac{d \ln P^{\text{vap}}}{dT} = \frac{\Delta \ln P^{\text{vap}}}{\Delta T} = \frac{\Delta \underline{H}^{\text{vap}}}{RT^2}$$

either graphically or analytically, we find

$$\Delta \underline{H}^{\text{vap}} \sim 313{,}600 \text{ J/mol}$$

5.14 (a) Start with Eqn. (5.4-6)

$$f = P \exp\left\{\frac{1}{RT}\int_0^P \left(\underline{V} - \frac{RT}{P}\right) dP\right\} \Rightarrow \ln\frac{f}{P} = \int_0^P \left(\frac{P\underline{V}}{RT} - 1\right) dP$$

but $\dfrac{1}{P}dP = \dfrac{d(P\underline{V})}{P\underline{V}} - \dfrac{d\underline{V}}{\underline{V}} = \dfrac{dZ}{Z} - \dfrac{d\underline{V}}{\underline{V}}$ so

$$\ln\frac{f}{P} = \int_{Z=1}^{Z} (Z-1)\frac{dZ}{Z} - \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{P\underline{V}}{RT} - 1\right)\frac{d\underline{V}}{\underline{V}} = (Z-1) - \ln\frac{Z}{1} - \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{P}{RT} - \frac{1}{\underline{V}}\right) d\underline{V}$$

or

$$\ln\frac{f}{P} = (Z-1) - \ln Z + \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - P\right) d\underline{V} \qquad \text{(Eqn. 5.4-8)}$$

(b) $Z = 1 + \dfrac{B(T)}{\underline{V}}$ and $P = \dfrac{RT}{\underline{V}}\left(1 + \dfrac{B}{\underline{V}}\right)$

$$\ln\frac{f}{P} = \frac{B}{\underline{V}} - \ln\left(1 + \frac{B}{\underline{V}}\right) + \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left[\left(\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}} - \frac{RT}{\underline{V}}\cdot\frac{B}{\underline{V}}\right)\right] d\underline{V}$$

$$= \frac{B}{\underline{V}} - \ln Z + B\int_{\underline{V}=\infty}^{\underline{V}} \frac{1}{\underline{V}^2} d\underline{V} = \frac{ZB}{\underline{V}} - \ln Z$$

(c) vdW e.o.s.

$$P=\frac{RT}{\underline{V}-b}-\frac{a}{\underline{V}^2}\ ;\ Z^{\text{vdW}}=\frac{P\underline{V}}{RT}=\frac{\underline{V}}{\underline{V}-b}-\frac{a}{\underline{V}^2RT}$$

$$\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}}-P\right)d\underline{V}=\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}}-\frac{RT}{\underline{V}-b}+\frac{a}{\underline{V}^2}\right)d\underline{V}=RT\ln\frac{\underline{V}}{\underline{V}-b}-\frac{a}{\underline{V}}\bigg|_{\underline{V}=\infty}^{\underline{V}}$$

$$=RT\ln\frac{\underline{V}}{\underline{V}-b}-\frac{a}{\underline{V}}\bigg|$$

so

$$\begin{aligned}\ln\frac{f^{\text{vdW}}}{P}&=\ln\frac{\underline{V}}{\underline{V}-b}-\frac{a}{RT\underline{V}}+(Z-1)-\ln Z\\&=\ln Z-\ln\left(Z-\frac{Pb}{RT}\right)-\frac{a}{RT}\cdot\frac{RT}{P\underline{V}}\cdot\frac{P}{RT}+(Z-1)-\ln Z\\&=(Z-1)-\frac{A}{Z}-\ln(Z-B)\end{aligned}$$

where $A=\dfrac{aP}{(RT)^2}$ and $B=\dfrac{Pb}{RT}$.

(d) Peng-Robinson equation of state. Start with

$$\begin{aligned}\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}}-P\right)d\underline{V}&=\int_{\underline{V}=\infty}^{\underline{V}}\left[\frac{RT}{\underline{V}}-\frac{RT}{\underline{V}-b}+\frac{a}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)}\right]d\underline{V}\\&=RT\ln\frac{\underline{V}}{\underline{V}-b}-\frac{a}{2\sqrt{2}b}\ln\left[\frac{\underline{V}+\left(1+\sqrt{2}\right)b}{\underline{V}+\left(1-\sqrt{2}\right)b}\right]\\&=RT\ln\frac{Z}{Z-B}-\frac{a}{2\sqrt{2}b}\ln\left[\frac{\underline{V}+\left(1+\sqrt{2}\right)b}{\underline{V}+\left(1-\sqrt{2}\right)b}\right]\end{aligned}$$

[See solution to Problem 4.2 for integral]. Therefore

$$\begin{aligned}\ln\frac{f^{PR}}{P}&=(Z-1)-\ln Z+\ln\frac{Z}{Z-B}-\frac{a}{2\sqrt{2}bRT}\ln\left[\frac{\underline{V}+\left(1+\sqrt{2}\right)b}{\underline{V}+\left(1-\sqrt{2}\right)b}\right]\\&=(Z-1)-\ln(Z-B)-\frac{a}{2\sqrt{2}bRT}\ln\frac{\underline{V}+\left(1+\sqrt{2}\right)b}{\underline{V}+\left(1-\sqrt{2}\right)b}\end{aligned}$$

5.15 (a) $f^{\text{liq}}_{H_2S}=f^{\text{vap}}_{H_2S}$; $f^{\text{vap}}=P(f/P)$, where the fugacity coefficient, f/P will be gotten from corresponding states.

$$\begin{aligned}&P_{C,\,H_2S}=89.42\text{ bar}\Rightarrow P_r=\frac{20}{89.42}=0.2237\\&T_{C,\,H_2S}=373.2\text{ K}\Rightarrow T_r=\frac{25.5+273.15}{373.2}=0.8002\\&Z_{C,\,H_2S}=0.284,\ \text{which is reasonably close to 0.27}\end{aligned}$$

From Fig. 5.4-1, $\frac{f}{P} = 0.765$, $f_{H_2S} = 20 \times 0.765 = 15.3\ \text{bar}$.

(b) For a liquid, from Eqn. (5.4-18)

$$f = P^{\text{vap}}\left(\frac{f}{P}\right)_{\text{sat}} \exp\left[\int_{P^{\text{vap}}}^{P} \frac{\underline{V}}{RT} dP\right]$$

Since $P^{\text{vap}} = 6.455 \times 10^3$ Pa at the temperature of interest, we will assume that $(f/P)_{\text{sat}} \sim 1$. Also, we will consider the liquid to be incompressible. Thus

$$\int_{P^{\text{vap}}}^{P} \frac{\underline{V}}{RT} dP = \frac{\underline{V}}{RT} \int_{P^{\text{vap}}}^{P} dP = \frac{\underline{V}\left(P - P^{\text{vap}}\right)}{RT}$$

and

$$f_{H_2S} = P^{\text{vap}} \exp\left[\frac{\underline{V}\left(P - P^{\text{vap}}\right)}{RT}\right] = 6455 \exp\left[\frac{0.018(P - 6455)}{8.314 \times 10^3 \times 310.6}\right] \text{Pa}$$

so that

Pressure, Pa	f_{H_2S}, Pa	Reported
$P = 1.0 \times 10^7$	6,921	6,925
5.0×10^7	9,146	9,175
1.0×10^8	12,960	12,967

5.16 (also available as a Mathcad worksheet)

(a) There are (at least) two ways to solve this problem. One way is to start from

$$f = P \exp\left\{\frac{1}{RT} \int_0^P \left(V - \frac{RT}{P}\right) dP\right\}$$

or

$$RT \ln \frac{f}{P} = \int_0^P \left(V - \frac{RT}{P}\right) dP$$

$$\frac{RT}{P} = \frac{8.314 \times 10^{-6}\ \text{MPa} \cdot \text{m}^3/\text{mol K} \times (273.15 + 400)\text{K}}{P(\text{MPa}) \times 18.01\ \text{g/mol} \times 10^{-3}\ \text{kg/g}} = \frac{0.310748}{P}\ \ \text{m}^3/\text{kg}$$

From Steam Tables $T = 400°\text{C}$

P MPa	$\hat{V}$ m^3/kg	$\hat{V} - RT/P$
0.01	31.063	–0.0118
0.05	6.029	–0.00596
0.10	3.103	–0.00448
0.2	1.5493	–0.00444
0.3	1.0315	–0.00433
0.4	0.7726	–0.00427
0.5	0.6173	–0.00420
0.6	0.5137	–0.00421
0.8	0.3843	–0.00413
1.0	0.3066	–0.00415
1.2	0.2548	–0.00416
1.4	0.2178	–0.00416
1.6	0.19005	–0.00417
1.8	0.16847	–0.00417
2.0	0.15120	–0.00417

By numerical integration of this data we find that

$$RT \ln\frac{f}{P} \sim -0.0084 \ \text{MPa}\cdot\text{m}^3/\text{kg}$$

$$\Rightarrow \ln\frac{f}{P} = \frac{-0.0084 \ \text{MPa}\cdot\text{m}^3/\text{kg}}{0.310748 \ \text{MPa}\cdot\text{m}^3/\text{kg}} = -0.027032$$

so $f/P = 0.97333$ and $f = 1.947$ MPa. A second way to use the steam tables is to assume that steam at 400°C and 0.01 MPa is an ideal gas. From the steam tables, at these conditions, we have

$$\hat{H} = 3279.6 \ \text{kJ/kg}; \ \hat{S} = 9.6077 \ \text{kJ/kg K}$$

$$\Rightarrow \hat{G} = \hat{H} - T\hat{S} = 3279.6 - 673.15\times 9.6077 = -3187.8 \ \text{kJ/kg}$$

$$= -57412.7 \ \text{kJ/kmol} = \underline{G}(400°\text{C}, \ 0.01 \text{ MPa}) = \underline{G}^{\text{IG}}(400°\text{C}, \ 0.01 \text{ MPa})$$

Also

$$\underline{G}^{\text{IG}}(T = 400°\text{C}, \ 2 \text{ MPa}) - \underline{G}^{\text{IG}}(T = 400°\text{C}, \ 0.01 \text{ MPa}) = \int_{P=0.01 \text{ MPa}}^{2 \text{ MPa}} \underline{V}^{\text{IG}} dP$$

$$\underline{G}^{\text{IG}}(T = 400°\text{C}, \ 2 \text{ MPa}) = -57412.7 \ \text{kJ/kmol} + \int_{0.01}^{2 \text{ MPa}} \frac{RT}{P} dP$$

$$= -57412.7 + 8.314 \ln 200 = -27760.3 \ \text{kJ/kmol}$$

Also, from steam tables

$$\underline{G}(T = 400°\text{C}, \ 2 \text{ MPa}) = (3247.6 - 673.15\times 7.1271)\times 18.01$$

$$= -27915.63 \ \text{kJ/kmol}$$

$$\frac{f}{P} = \exp\left(\frac{\underline{G} - \underline{G}^{\text{IG}}}{RT}\right) = \exp\left(\frac{-27915.63 + 27760.3}{8.314\times 673.15}\right)$$

$$= 0.9726$$

$$f = 0.9726\times 2 \text{ MPa} = 1.945 \text{ MPa}$$

(b) Corresponding states $(T_C = 647.3\text{ K},\ P_C = 22.048\text{ MPa},\ \ w = 0.344)$

$$T_r = \frac{400 + 273.15}{647.3} = 1.04\,;\ \ P_r = \frac{2}{22.048} = 0.0907$$

From corresponding states chart (actually from Table in Hougen, Watson and Rogatz, Vol. II, p. 601) we have

$$\frac{f}{P} = 0.983 \Rightarrow f = 1.966\text{ MPa}$$

(c) Using the program PR1 we find

$$f = 19.40\text{ bar} = 1.940\text{ MPa}$$

Comment: The steam table results are probably the most accurate, and the corresponding states results the least accurate. Note that with the availability of the computer program PR1, the P-R e.o.s. is the easiest to use. The results would be even more accurate if the PRSV equation was used.