5.18 (a) Assume the vapor phase is ideal, and that $\Delta\underline{H}^{\text{vap}}$ is approximately constant (or an average $\Delta\underline{H}^{\text{vap}}$ can be used).

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

$$\Rightarrow \ln\left(\frac{2.026}{1.013}\right) = \frac{-\Delta\underline{H}^{\text{vap}}}{R}\left(\frac{1}{222.0+273.15}-\frac{1}{178.0+273.15}\right)$$

$$\Rightarrow \frac{\Delta\underline{H}^{\text{vap}}}{R} = 3.52\times10^3/\text{K} \qquad \Delta\underline{H}^{\text{vap}} = 2.93\times10^4 \text{ J/mol}$$

(b) $\Delta\underline{H}^{\text{vap}}(T) = \underline{H}(\text{sat. vap}, T) - \underline{H}(\text{sat. liq}, T)$

$$= \left[\underline{H}(\text{sat. vap, } T) - \underline{H}^{\text{IG}}(T)\right] - \left[\underline{H}(\text{sat. liq., } T) - \underline{H}^{\text{IG}}(T)\right]$$

$$\Rightarrow \Delta\underline{H}^{\text{vap}}(T) = T_C\left[\left(\frac{\underline{\underline{H}}-\underline{\underline{H}}^{\text{IG}}}{T_C}\right)_{\text{sat. vap, } T} - \left(\frac{\underline{\underline{H}}-\underline{\underline{H}}^{\text{IG}}}{T}\right)_{\text{sat. liq., } T}\right]$$

(c) $T_r = \dfrac{T}{T_C} = \dfrac{200+273.15}{283.1+273.15} = 0.851$

$$\left(\frac{\underline{\underline{H}}^{\text{IG}}-\underline{\underline{H}}}{T_C}\right)_{\substack{\text{sat. vap}\\ T_r=0.851}} = 5.06 \text{ J/mol K} \quad \text{and} \quad \left(\frac{\underline{\underline{H}}^{\text{IG}}-\underline{\underline{H}}}{T_C}\right)_{\substack{\text{sat. liq.}\\ T_r=0.851}} = 44.69 \text{ J/mol K}$$

$$\Delta\underline{H}^{\text{vap}}(T) = 556.45 \text{ K}[44.69-5.06] = 2.205\times10^4 \text{ J/mol}$$

(d) The reason for the discrepancy is probably not the inaccuracy of corresponding states (since $Z_C = 0.272$ which is close to 0.27) but rather the assumption of an ideal vapor phase in the Clausius-Clapeyron equation. We correct for gas-phase nonideality below.

$$\text{at } T = 178^\circ\text{C},\ T_r = 0.811,\ Z = 0.82$$
$$T = 222^\circ\text{C},\ T_r = 0.890,\ Z = 0.71$$

The average value of the compressibility is

$$\overline{Z} = \frac{1}{2}(0.82+0.71) = 0.765$$

We now replace eqn. 1 with

$$\ln\frac{P_2}{P_1} = \frac{-\Delta\underline{H}^{\text{vap}}}{ZR}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \Rightarrow \Delta\underline{H}^{\text{vap}} = 0.765\times\left(2.93\times10^4 \text{ J/mol}\right)$$
$$= 2.24\times10^4 \text{ J/mol}$$

which is in much better agreement with the result of part (c). A better way to proceed would be to compute the compressibility as a function of temperature, i.e., find $Z = Z(T,P)$ and then integrate

$$\frac{dP}{dT} = \frac{\Delta\underline{H}^{\text{vap}} P}{Z(T,P)RT^2}$$

5.21 (also available as a Mathcad worksheet)

5.21

From Eq. 5.7-4 $\Delta T=\Delta P*\Delta V*T/\Delta H$ $bar := 10^{5}\cdot Pa$

Water

$$\Delta T := \frac{1000\cdot bar\cdot\left(-0.0906\cdot 10^{-6}\cdot\frac{m^{3}}{g}\right)\cdot 273.1\cdot K}{333.8\cdot\frac{joule}{g}} \qquad \Delta T = -7.412\cdot K$$

Acetic acid

$$\Delta T := \frac{1000\cdot bar\cdot\left(0.01595\cdot 10^{-6}\cdot\frac{m^{3}}{g}\right)\cdot 289.8\cdot K}{187\cdot\frac{joule}{g}} \qquad \Delta T = 2.472\cdot K$$

Tin

$$\Delta T := \frac{1000\cdot bar\cdot\left(0.00389\cdot 10^{-6}\cdot\frac{m^{3}}{g}\right)\cdot 505.0\cdot K}{58.6\cdot\frac{joule}{g}} \qquad \Delta T = 3.352\cdot K$$

Bismuth

$$\Delta T := \frac{1000\cdot bar\cdot\left(-0.00342\cdot 10^{-6}\cdot\frac{m^{3}}{g}\right)\cdot 544\cdot K}{52.7\cdot\frac{joule}{g}} \qquad \Delta T = -3.53\cdot K$$

5.22 (also available as a Mathcad worksheet)

5.22

$i := 0..\,10$

$R := 8.314$

$\Delta H(T,a,b,c) := R\cdot\left[c\cdot(T)^{2} + b\cdot T - a\right]$

Ag(s) $Tmax := 1234$ $Tmin := 298$ $a := -14710$ $b := -0.328$ $c := 0$

$$Y_{i} := \frac{Tmax - Tmin}{10}\cdot(i) + Tmin$$

T, K Y_i	ΔHm, J/mol $\Delta H(Y_i, a, b, c)$
298	$1.215\cdot 10^{5}$
391.6	$1.212\cdot 10^{5}$
485.2	$1.21\cdot 10^{5}$
578.8	$1.207\cdot 10^{5}$
672.4	$1.205\cdot 10^{5}$
766	$1.202\cdot 10^{5}$
859.6	$1.2\cdot 10^{5}$
953.2	$1.197\cdot 10^{5}$
$1.047\cdot 10^{3}$	$1.194\cdot 10^{5}$
$1.14\cdot 10^{3}$	$1.192\cdot 10^{5}$
$1.234\cdot 10^{3}$	$1.189\cdot 10^{5}$

Ag(l) $Tmax := 2485$ $Tmin := 1234$ $a := -14260$ $b := -0.458$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K Y_i	ΔHsub, J/mol $\Delta H(Y_i, a, b, c)$
$1.234\cdot10^{3}$	$1.139\cdot10^{5}$
$1.359\cdot10^{3}$	$1.134\cdot10^{5}$
$1.484\cdot10^{3}$	$1.129\cdot10^{5}$
$1.609\cdot10^{3}$	$1.124\cdot10^{5}$
$1.734\cdot10^{3}$	$1.12\cdot10^{5}$
$1.86\cdot10^{3}$	$1.115\cdot10^{5}$
$1.985\cdot10^{3}$	$1.11\cdot10^{5}$
$2.11\cdot10^{3}$	$1.105\cdot10^{5}$
$2.235\cdot10^{3}$	$1.1\cdot10^{5}$
$2.36\cdot10^{3}$	$1.096\cdot10^{5}$
$2.485\cdot10^{3}$	$1.091\cdot10^{5}$

BeO(s) $Tmax := 2800$ $Tmin := 298$ $a := -34230$ $b := -0.869$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K Y_i	ΔHm, J/mol $\Delta H(Y_i, a, b, c)$
298	$2.824\cdot10^{5}$
548.2	$2.806\cdot10^{5}$
798.4	$2.788\cdot10^{5}$
$1.049\cdot10^{3}$	$2.77\cdot10^{5}$
$1.299\cdot10^{3}$	$2.752\cdot10^{5}$
$1.549\cdot10^{3}$	$2.734\cdot10^{5}$
$1.799\cdot10^{3}$	$2.716\cdot10^{5}$
$2.049\cdot10^{3}$	$2.698\cdot10^{5}$
$2.3\cdot10^{3}$	$2.68\cdot10^{5}$
$2.55\cdot10^{3}$	$2.662\cdot10^{5}$
$2.8\cdot10^{3}$	$2.644\cdot10^{5}$

Ge(s) $Tmax := 1210$ $Tmin := 298$ $a := -20150$ $b := -0.395$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K Y_i	ΔHm, J/mol $\Delta H(Y_i, a, b, c)$
298	$1.665 \cdot 10^5$
389.2	$1.662 \cdot 10^5$
480.4	$1.659 \cdot 10^5$
571.6	$1.656 \cdot 10^5$
662.8	$1.654 \cdot 10^5$
754	$1.651 \cdot 10^5$
845.2	$1.648 \cdot 10^5$
936.4	$1.645 \cdot 10^5$
$1.028 \cdot 10^3$	$1.642 \cdot 10^5$
$1.119 \cdot 10^3$	$1.639 \cdot 10^5$
$1.21 \cdot 10^3$	$1.636 \cdot 10^5$

Mg(s) $Tmax := 924$ $Tmin := 298$ $a := -7780$ $b := -0.371$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K Y_i	DHm, J/mol $\Delta H(Y_i, a, b, c)$
298	$6.376 \cdot 10^4$
360.6	$6.357 \cdot 10^4$
423.2	$6.338 \cdot 10^4$
485.8	$6.318 \cdot 10^4$
548.4	$6.299 \cdot 10^4$
611	$6.28 \cdot 10^4$
673.6	$6.261 \cdot 10^4$
736.2	$6.241 \cdot 10^4$
798.8	$6.222 \cdot 10^4$
861.4	$6.203 \cdot 10^4$
924	$6.183 \cdot 10^4$

Mg(l) $Tmax := 1380$ $Tmin := 924$ $a := -7750$ $b := -0.612$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K Y_i	DHm, J/mol $\Delta H(Y_i, a, b, c)$
924	$5.973\cdot10^{4}$
969.6	$5.95\cdot10^{4}$
$1.015\cdot10^{3}$	$5.927\cdot10^{4}$
$1.061\cdot10^{3}$	$5.904\cdot10^{4}$
$1.106\cdot10^{3}$	$5.88\cdot10^{4}$
$1.152\cdot10^{3}$	$5.857\cdot10^{4}$
$1.198\cdot10^{3}$	$5.834\cdot10^{4}$
$1.243\cdot10^{3}$	$5.811\cdot10^{4}$
$1.289\cdot10^{3}$	$5.788\cdot10^{4}$
$1.334\cdot10^{3}$	$5.764\cdot10^{4}$
$1.38\cdot10^{3}$	$5.741\cdot10^{4}$

NaCl(s)

$Tmax := 1074$ $Tmin := 298$ $a := -12440$ $b := -0.391$ $c := -0.46\cdot10^{-3}$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K Y_i	DHm, J/mol $\Delta H(Y_i, a, b, c)$
298	$1.021\cdot10^{5}$
375.6	$1.017\cdot10^{5}$
453.2	$1.012\cdot10^{5}$
530.8	$1.006\cdot10^{5}$
608.4	$1\cdot10^{5}$
686	$9.94\cdot10^{4}$
763.6	$9.871\cdot10^{4}$
841.2	$9.799\cdot10^{4}$
918.8	$9.721\cdot10^{4}$
996.4	$9.639\cdot10^{4}$
$1.074\cdot10^{3}$	$9.552\cdot10^{4}$

Si(s)

$\text{Tmax} := 1683 \qquad \text{Tmin} := 1200 \qquad a := -18000 \qquad b := -0.444 \qquad c := 0$

$$Y_i := \frac{\text{Tmax} - \text{Tmin}}{10} \cdot (i) + \text{Tmin}$$

T, K Y_i	DHm, J/mol $\Delta H(Y_i, a, b, c)$
$1.2 \cdot 10^3$	$1.452 \cdot 10^5$
$1.248 \cdot 10^3$	$1.45 \cdot 10^5$
$1.297 \cdot 10^3$	$1.449 \cdot 10^5$
$1.345 \cdot 10^3$	$1.447 \cdot 10^5$
$1.393 \cdot 10^3$	$1.445 \cdot 10^5$
$1.442 \cdot 10^3$	$1.443 \cdot 10^5$
$1.49 \cdot 10^3$	$1.442 \cdot 10^5$
$1.538 \cdot 10^3$	$1.44 \cdot 10^5$
$1.586 \cdot 10^3$	$1.438 \cdot 10^5$
$1.635 \cdot 10^3$	$1.436 \cdot 10^5$
$1.683 \cdot 10^3$	$1.434 \cdot 10^5$

5.23 (also available as a Mathcad worksheet)

5.23

The metal tin undergoes a transition from a gray phase to a white phase at 286 K at ambier pressure. Given that the enthalpy change of this transition is 2090 kJ/mole and that the volume change of this transition is -4.35 cm3/mole, compute the temperature at which this transition occurs at 100 bar.

From Eq. 5.7-4 $\Delta T = \Delta P * \Delta V * T / \Delta H$ $\quad \text{bar} := 10^5 \cdot \text{Pa}$

$$\Delta T := \frac{99 \cdot \text{bar} \cdot \left(-4.35 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}} \right) \cdot 286 \cdot \text{K}}{2090000 \cdot \frac{\text{joule}}{\text{mole}}} \qquad \Delta T = -5.893 \cdot 10^{-3} \cdot \text{K}$$

5.24 For the solid-liquid transition

$$\left(\frac{\partial P}{\partial T}\right)_{\text{eq}} = \frac{\Delta \underline{H}^{\text{f}}}{T \Delta \underline{V}} \Rightarrow \left(\frac{\partial P}{\partial \ln T}\right)_{\text{eq}} = \frac{\Delta \underline{H}^{\text{f}}}{\Delta \underline{V}} = \frac{127 \text{ J/g}}{0.1317 \text{ cc/g}} = 964.3 \text{ J/cc}$$

$$\left(\frac{\partial P}{\partial \ln T}\right)_{\text{eq}} = 964.3 \text{ J/cc} = 964.3 \times 10^6 \text{ J/m}^3 = 9643 \text{ bar} = 9.643 \times 10^8 \text{ Pa}$$

$$\Rightarrow P_2 = P_1 + 9643 \times \ln \frac{T_2}{T_1}$$

$$\Rightarrow T^{\mathrm{TP}} = T_1 \exp\left\{\frac{P^{\mathrm{TP}} - P_1}{9.643\times 10^8 \text{ Pa}}\right\} = 278.7 \exp\left\{\frac{P^{\mathrm{TP}} - 10^5 \text{ Pa}}{9.643\times 10^8 \text{ Pa}}\right\} \qquad (1)$$

For the solid-vapor transition, assuming an ideal vapor phase

$$\ln\frac{P_2}{P_1} = -\frac{\Delta \underline{H}^{\mathrm{sub}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Rightarrow -\frac{\Delta \underline{H}^{\mathrm{sub}}}{R} = \frac{\ln(P_2/P_1)}{1/T_2 - 1/T_1} = \frac{\ln(26.67/13.33)}{3.696\times 10^{-3} - 3.822\times 10^{-3}} = -5513 \text{ K}$$

$$\Rightarrow \ln\frac{P_2}{P_1} = -5513\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

and

$$T^{\mathrm{TP}} = \left[\frac{1}{T_1} - 0.1814\times 10^{-3}\ln\frac{P^{\mathrm{TP}}}{P_1}\right]^{-1} = \frac{1000}{3.696 - 0.1814\ln\left(P^{\mathrm{TP}}/26.67\right)} \qquad (2)$$

Solving Eqns. (1) and (2) simultaneously gives

$$P^{\mathrm{TP}} = 0.483 \text{ bar} = 4.83 \text{ kPa} \quad \text{and} \quad T^{\mathrm{TP}} = 278.7 \text{ K}$$

[The melting temperature of benzene ~ triple point temperature $= 5.53°\mathrm{C} = 278.7$ K, which agrees exactly with our prediction].

5.25 First, at 298.15 K, lets relate the Gibbs free energy at any pressure to the value given at 1 bar.

$$\underline{G}_{dia}(298.15, P) = \underline{G}_{dia}(298, P = 1\,\text{bar}) + \left(\frac{(P-1)\text{bar}\times 3510\frac{\text{kg}}{\text{m}^3}\times 1000\frac{\text{g}}{\text{kg}}\times\frac{1\text{ mol}}{12\text{ g}}}{8.314\times 10^{-5}\frac{\text{bar m}^3}{\text{mol K}}\times 298.15\text{K}}\right)$$

$$\underline{G}_{g}(29815, P) = \underline{G}_{g}(298, P = 1\,\text{bar}) + \left(\frac{(P-1)\text{bar}\times 2220\frac{\text{kg}}{\text{m}^3}\times 1000\frac{\text{g}}{\text{kg}}\times\frac{1\text{ mol}}{12\text{ g}}}{8.314\times 10^{-5}\frac{\text{bar m}^3}{\text{mol K}}\times 298.15\text{K}}\right)$$

Note that

$$\underline{V}_{dia} = \frac{1}{3510}\frac{\text{m}^3}{\text{kg}}\times\frac{1}{1000}\frac{\text{kg}}{\text{g}}\times 12\frac{\text{g}}{\text{mol}} = 3.4188\times 10^{-6}\frac{\text{m}^3}{\text{mol}}$$

$$\underline{V}_{g} = \frac{1}{2220}\frac{\text{m}^3}{\text{kg}}\times\frac{1}{1000}\frac{\text{kg}}{\text{g}}\times 12\frac{\text{g}}{\text{mol}} = 5.4054\times 10^{-6}\frac{\text{m}^3}{\text{mol}}$$

Therefore

$$\underline{G}_{dia}(298.15, P) - \underline{G}_{g}(29815, P) = \underline{G}_{dia}(298, P = 1\,\text{bar}) - \underline{G}_{g}(298, P = 1\,\text{bar})$$
$$+\left(\frac{(P-1)\text{bar} \times (3.4188 - 5.4054) \times 10^{-6}\,\dfrac{\text{m}^3}{\text{mol}}}{8.314 \times 10^{-5}\,\dfrac{\text{bar m}^3}{\text{mol K}} \times 298.15\,\text{K}}\right)$$

at equilibrium at 298.15 K we have

$$0 = 2900 - 0 \;\; -(P - 1) \times 8.0143 \times 10^{-5}$$

$$P = 1 + \frac{2900}{8.0143 \times 10^{-5}} = 36.185 \times 10^{6}\ \text{bar} \ = \ 36.185\ \text{Mbar}$$

To find the transition pressure at other temperatures we use the Clapeyron equation

$$\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \frac{\Delta S}{\Delta V} = \frac{(2.377 - 5.740)\dfrac{\text{J}}{\text{mol K}}}{(3.4188 - 5.4054) \times 10^{-6}\,\dfrac{\text{m}^3}{\text{mol}}} \times 1\frac{\text{Pa m}^3}{\text{J}}$$

$$= 1.6928 \times 10^{6}\,\frac{\text{Pa}}{\text{K}} = 16.928\,\frac{\text{bar}}{\text{K}}$$

which indicates that for every degree K increase about 298.15 K we need to increase the pressure by 16.928 bar. However, this is a small percentage increase compared to the 36.185 MPa pressure required at 298.15 K. So the transition is essentially (within engineering accuracy) only very weakly dependent on pressure.

5.36 (also available as a Mathcad worksheet)

$$\left(\frac{\P P}{\P T}\right)_{\text{sat}}=\frac{\Delta\underline{H}}{T\Delta\underline{V}}$$

Assume $\underline{V}^{\text{V}}>>\underline{V}^{\text{L}}\Rightarrow\Delta\underline{V}\sim\underline{V}^{\text{V}}=\dfrac{ZRT}{P}$ '

$$\left(\frac{\P P}{\P T}\right)_{\text{sat}}=\frac{\Delta\underline{H}}{ZRT^2/P}\Rightarrow\left(\frac{\P\ln P}{\P T}\right)_{\text{sat}}=\frac{\Delta\underline{H}}{ZRT^2}$$

but

$$\left(\frac{\P\ln P}{\P T}\right)_{\text{sat}}=\frac{\P}{\P T}\left(43.552-\frac{5622.7}{T}-4.70504\ln T\right)$$

$$=+\frac{5622.7}{T^2}-\frac{4.70504}{T}=\frac{1}{T^2}(5622.7-4.70504T)$$

Thus

$$\frac{\Delta\underline{H}}{ZRT^2}=\frac{1}{T^2}(5622.7-4.70504T)$$

or

$$\Delta\underline{H}=ZR(5622.7-4.70504T)=31{,}602\ \text{ J/mol at }75°\text{C}$$

$$Z=\frac{31{,}602}{8.314\times(5622.7-4.70504\times(273.15+75))}=0.9539$$

but

$$\frac{P\underline{V}}{RT}=1+\frac{B}{\underline{V}}=Z=0.9539$$

so

$$\frac{B}{\underline{V}}=0.9539-1=-0.04607\ ;\ B=-0.04607\underline{V}$$

Then $\underline{V}=0.9539\,RT/P$. To find P use

$$\ln P^{\text{vap}}=43.552-\frac{5622.7}{(273.15+75)}-4.70504\ln(273.15+75)$$

$$P^{\text{vap}}=0.8736\text{ bar}$$

$$\underline{V}=\frac{0.9539\times8.314\times10^{-5}\times(273.15+75)}{0.8736}=3.1606\times10^{-2}\ \text{ m}^3/\text{mol}$$

and

$$B=-1.456\times10^{-3}\ \text{ m}^3/\text{mol}$$