

6 Physical transformations of pure substances

Solutions to exercises

Discussion questions

- E6.1(b)** Refer to Fig. 6.8. The white lines represent the regions of superheating and supercooling. The chemical potentials along these lines are higher than the chemical potentials of the stable phases represented by the colored lines. Though thermodynamically unstable, these so-called metastable phases may persist for a long time if the system remains undisturbed, but will eventually transform into the thermodynamically stable phase having the lower chemical potential. Transformation to the condensed phases usually requires nucleation centers. In the absence of such centers, the metastable regions are said to be kinetically stable.
- E6.2(b)** At 298 K and 1.0 atm, the sample of carbon dioxide is a gas. (a) After heating to 320 K at constant pressure, the system is still gaseous. (b) Isothermal compression at 320 K to 100 atm pressure brings the sample into the supercritical region. The sample is now not much different in appearance from ordinary carbon dioxide, but some of its properties are (see Box 6.1). (c) After cooling the sample to 210 K at constant pressure, the carbon dioxide sample solidifies. (d) Upon reducing the pressure to 1.0 atm at 210 K, the sample vapourizes (sublimes); and finally (e) upon heating to 298 K at 1.0 atm, the system has resumed its initial conditions in the gaseous state. Note the lack of a sharp gas to liquid transition in steps (b) and (c). This process illustrates the continuity of the gaseous and liquid states.
- E6.3(b)** First-order phase transitions show discontinuities in the first derivative of the Gibbs energy with respect to temperature. They are recognized by finite discontinuities in plots of H , U , S , and V against temperature and by an infinite discontinuity in C_p . Second-order phase transitions show discontinuities in the second derivatives of the Gibbs energy with respect to temperature, but the first derivatives are continuous. The second-order transitions are recognized by kinks in plots of H , U , S , and V against temperature, but most easily by a finite discontinuity in a plot of C_p against temperature. A λ -transition shows characteristics of both first and second-order transitions and, hence, is difficult to classify by the Ehrenfest scheme. It resembles a first-order transition in a plot of C_p against T , but appears to be a higher-order transition with respect to other properties. See the book by H. E. Stanley listed under Further reading for more details.

Numerical exercises

- E6.4(b)** Assume vapour is a perfect gas and $\Delta_{\text{vap}}H$ is independent of temperature

$$\begin{aligned}\ln \frac{p^*}{p} &= + \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \\ \frac{1}{T} &= \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H} \ln \frac{p^*}{p} \\ &= \frac{1}{293.2 \text{ K}} + \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{32.7 \times 10^3 \text{ J mol}^{-1}} \times \ln \left(\frac{58.0}{66.0} \right) \\ &= 3.378 \times 10^{-3} \text{ K}^{-1} \\ T &= \frac{1}{3.378 \times 10^{-3} \text{ K}^{-1}} = 296 \text{ K} = \boxed{23^\circ\text{C}}\end{aligned}$$

E6.5(b)

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\Delta_{\text{fus}} S = \Delta V_m \left(\frac{dp}{dT} \right) \approx \Delta V_m \frac{\Delta p}{\Delta T}$$

assuming $\Delta_{\text{fus}} S$ and ΔV_m independent of temperature.

$$\Delta_{\text{fus}} S = (152.6 \text{ cm}^3 \text{ mol}^{-1} - 142.0 \text{ cm}^3 \text{ mol}^{-1}) \times \frac{(1.2 \times 10^6 \text{ Pa}) - (1.01 \times 10^5 \text{ Pa})}{429.26 \text{ K} - 427.15 \text{ K}}$$

$$= (10.6 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times (5.21 \times 10^5 \text{ Pa K}^{-1})$$

$$= 5.52 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = \boxed{5.5 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta_{\text{fus}} H = T_f \Delta S = (427.15 \text{ K}) \times (5.52 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{2.4 \text{ kJ mol}^{-1}}$$

E6.6(b)

$$\text{Use } \int d \ln p = \int \frac{\Delta_{\text{vap}} H}{RT^2} dT$$

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}} H}{RT}$$

Terms with $\frac{1}{T}$ dependence must be equal, so

$$-\frac{3036.8 \text{ K}}{T/\text{K}} = -\frac{\Delta_{\text{vap}} H}{RT}$$

$$\Delta_{\text{vap}} H = (3036.8 \text{ K})R = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (3036.8 \text{ K})$$

$$= \boxed{25.25 \text{ kJ mol}^{-1}}$$

E6.7(b)

$$\text{(a) } \log p = \text{constant} - \frac{\Delta_{\text{vap}} H}{RT(2.303)}$$

Thus

$$\Delta_{\text{vap}} H = (1625 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (2.303)$$

$$= \boxed{31.11 \text{ kJ mol}^{-1}}$$

(b) Normal boiling point corresponds to $p = 1.000 \text{ atm} = 760 \text{ Torr}$

$$\log(760) = 8.750 - \frac{1625}{T/\text{K}}$$

$$\frac{1625}{T/\text{K}} = 8.750 - \log(760)$$

$$T/\text{K} = \frac{1625}{8.750 - \log(760)} = 276.8\bar{7}$$

$$T_b = \boxed{276.9 \text{ K}}$$

E6.8(b)

$$\Delta T = \frac{\Delta_{\text{fus}} V}{\Delta_{\text{fus}} S} \times \Delta p = \frac{T_f \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \times \Delta p = \frac{T_f \Delta p M}{\Delta_{\text{fus}} H} \times \Delta \left(\frac{1}{\rho} \right)$$

$$[T_f = -3.65 + 273.15 = 269.50 \text{ K}]$$

$$\Delta T = \frac{(269.50 \text{ K}) \times (99.9 \text{ MPa}) M}{8.68 \text{ kJ mol}^{-1}} \times \left(\frac{1}{0.789 \text{ g cm}^{-3}} - \frac{1}{0.801 \text{ g cm}^{-3}} \right)$$

$$= (3.10\overline{17} \times 10^6 \text{ K Pa J}^{-1} \text{ mol}) \times (M) \times (+.018\overline{99} \text{ cm}^3/\text{g}) \times \left(\frac{\text{m}^3}{10^6 \text{ cm}^3} \right)$$

$$= (+5.\overline{889} \times 10^{-2} \text{ K Pa m}^3 \text{ J}^{-1} \text{ g}^{-1} \text{ mol}) M = (+5.\overline{889} \times 10^{-2} \text{ K g}^{-1} \text{ mol}) M$$

$$\Delta T = (46.07 \text{ g mol}^{-1}) \times (+5.\overline{889} \times 10^{-2} \text{ K g}^{-1} \text{ mol})$$

$$= +2.\overline{71} \text{ K}$$

$$T_f = 269.50 \text{ K} + 2.\overline{71} \text{ K} = \boxed{272 \text{ K}}$$

E6.9(b)

$$\frac{dm}{dt} = \frac{dn}{dt} \times M_{\text{H}_2\text{O}} \quad \text{where } n = \frac{q}{\Delta_{\text{vap}} H}$$

$$\frac{dn}{dt} = \frac{dq/dt}{\Delta_{\text{vap}} H} = \frac{(0.87 \times 10^3 \text{ W m}^{-2}) \times (10^4 \text{ m}^2)}{44.0 \times 10^3 \text{ J mol}^{-1}}$$

$$= 197.\overline{7} \text{ J s}^{-1} \text{ J}^{-1} \text{ mol}$$

$$= 200 \text{ mol s}^{-1}$$

$$\frac{dm}{dt} = (197.\overline{7} \text{ mol s}^{-1}) \times (18.02 \text{ g mol}^{-1})$$

$$= \boxed{3.6 \text{ kg s}^{-1}}$$

E6.10(b) The vapour pressure of ice at -5°C is 3.9×10^{-3} atm, or 3 Torr. Therefore, the frost will sublime. A partial pressure of 3 Torr or more will ensure that the frost remains.

E6.11(b) (a) According to Trouton's rule (Section 4.3, eqn 4.16)

$$\Delta_{\text{vap}} H = (85 \text{ J K}^{-1} \text{ mol}^{-1}) \times T_b = (85 \text{ J K}^{-1} \text{ mol}^{-1}) \times (342.2 \text{ K}) = \boxed{29.\overline{1} \text{ kJ mol}^{-1}}$$

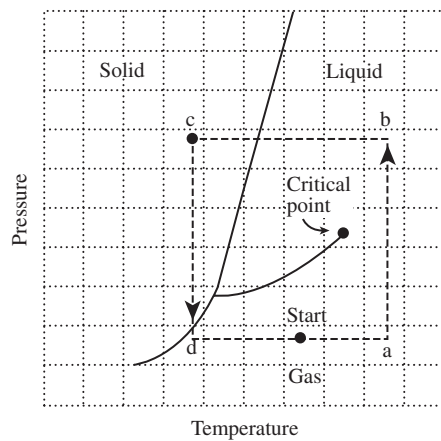


Figure 6.1

(b) Use the Clausius–Clapeyron equation [Exercise 6.11(a)]

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At $T_2 = 342.2 \text{ K}$, $p_2 = 1.000 \text{ atm}$; thus at 25°C

$$\ln p_1 = -\left(\frac{29.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{298.2 \text{ K}} - \frac{1}{342.2 \text{ K}}\right) = -1.509$$

$$p_1 = \boxed{0.22 \text{ atm}} = 168 \text{ Torr}$$

At 60°C ,

$$\ln p_1 = -\left(\frac{29.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{333.2 \text{ K}} - \frac{1}{342.2 \text{ K}}\right) = -0.276$$

$$p_1 = \boxed{0.76 \text{ atm}} = 576 \text{ Torr}$$

E6.12(b) $\Delta T = T_f(10 \text{ MPa}) - T_f(0.1 \text{ MPa}) = \frac{T_f \Delta p M}{\Delta_{\text{fus}}H} \Delta\left(\frac{1}{\rho}\right)$

$$\Delta_{\text{fus}}H = 6.01 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta T &= \left\{ \frac{(273.15 \text{ K}) \times (9.9 \times 10^6 \text{ Pa}) \times (18 \times 10^{-3} \text{ kg mol}^{-1})}{6.01 \times 10^3 \text{ J mol}^{-1}} \right\} \\ &\quad \times \left\{ \frac{1}{9.98 \times 10^2 \text{ kg m}^{-3}} - \frac{1}{9.15 \times 10^2 \text{ kg m}^{-3}} \right\} \\ &= -0.74 \text{ K} \end{aligned}$$

$$T_f(10 \text{ MPa}) = 273.15 \text{ K} - 0.74 \text{ K} = \boxed{272.41 \text{ K}}$$

E6.13(b) $\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV)$

$$\Delta_{\text{vap}}H = 43.5 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{vap}}(pV) = p\Delta_{\text{vap}}V = p(V_{\text{gas}} - V_{\text{liq}}) = pV_{\text{gas}} = RT \text{ [per mole, perfect gas]}$$

$$\Delta_{\text{vap}}(pV) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (352 \text{ K}) = 2927 \text{ J mol}^{-1}$$

$$\begin{aligned} \text{Fraction} &= \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H} = \frac{2.927 \text{ kJ mol}^{-1}}{43.5 \text{ kJ mol}^{-1}} \\ &= \boxed{6.73 \times 10^{-2}} = 6.73 \text{ per cent} \end{aligned}$$

E6.14(b) $V_m = \frac{M}{\rho} = \frac{18.02 \text{ g mol}^{-1}}{999.4 \times 10^3 \text{ g m}^{-3}} = 1.803 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$

$$\begin{aligned} \frac{2\gamma V_m}{rRT} &= \frac{2(7.275 \times 10^{-2} \text{ N m}^{-1}) \times (1.803 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})}{(20.0 \times 10^{-9} \text{ m}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (308.2 \text{ K})} \\ &= 5.119 \times 10^{-2} \end{aligned}$$

$$p = (5.623 \text{ kPa})e^{0.05119} = \boxed{5.92 \text{ kPa}}$$

$$\begin{aligned}
 \text{E6.15(b)} \quad \gamma &= \frac{1}{2} \rho g h r = \frac{1}{2} (0.9956 \text{ g cm}^{-3}) \times (9.807 \text{ m s}^{-2}) \times (9.11 \times 10^{-2} \text{ m}) \\
 &\quad \times (0.16 \times 10^{-3} \text{ m}) \times \left(\frac{1000 \text{ kg m}^{-3}}{\text{g cm}^{-3}} \right) \\
 &= \boxed{7.12 \times 10^{-2} \text{ N m}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{E6.16(b)} \quad p_{\text{in}} - p_{\text{out}} &= \frac{2\gamma}{r} = \frac{2(22.39 \times 10^{-3} \text{ N m}^{-1})}{(220 \times 10^{-9} \text{ m})} \\
 &= 2.04 \times 10^5 \text{ N m}^{-2} = \boxed{2.04 \times 10^5 \text{ Pa}}
 \end{aligned}$$

Solutions to problems

Solutions to numerical problems

$$\begin{aligned}
 \text{P6.3 (a)} \quad \frac{dp}{dT} &= \frac{\Delta_{\text{vap}} S}{\Delta_{\text{vap}} V} = \frac{\Delta_{\text{vap}} H}{T_b \Delta_{\text{vap}} V} \quad [6.6, \text{Clapeyron equation}] \\
 &= \frac{14.4 \times 10^3 \text{ J mol}^{-1}}{(180 \text{ K}) \times (14.5 \times 10^{-3} - 1.15 \times 10^{-4}) \text{ m}^3 \text{ mol}^{-1}} = \boxed{+5.56 \text{ kPa K}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \frac{dp}{dT} &= \frac{\Delta_{\text{vap}} H}{RT^2} \times p \left[11, \text{with } d \ln p = \frac{dp}{p} \right] \\
 &= \frac{(14.4 \times 10^3 \text{ J mol}^{-1}) \times (1.013 \times 10^5 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (180 \text{ K})^2} = +5.42 \text{ kPa K}^{-1}
 \end{aligned}$$

The percentage error is $\boxed{2.5 \text{ per cent}}$

$$\begin{aligned}
 \text{P6.5 (a)} \quad \left(\frac{\partial \mu(\text{l})}{\partial p} \right)_T - \left(\frac{\partial \mu(\text{s})}{\partial p} \right)_T &= V_{\text{m}}(\text{l}) - V_{\text{m}}(\text{s}) [6.13] = M \Delta \left(\frac{1}{\rho} \right) \\
 &= (18.02 \text{ g mol}^{-1}) \times \left(\frac{1}{1.000 \text{ g cm}^{-3}} - \frac{1}{0.917 \text{ g cm}^{-3}} \right) \\
 &= \boxed{-1.63 \text{ cm}^3 \text{ mol}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \left(\frac{\partial \mu(\text{g})}{\partial p} \right)_T - \left(\frac{\partial \mu(\text{l})}{\partial p} \right)_T &= V_{\text{m}}(\text{g}) - V_{\text{m}}(\text{l}) \\
 &= (18.02 \text{ g mol}^{-1}) \times \left(\frac{1}{0.598 \text{ g L}^{-1}} - \frac{1}{0.958 \times 10^3 \text{ g L}^{-1}} \right) \\
 &= \boxed{+30.1 \text{ L mol}^{-1}}
 \end{aligned}$$

At 1.0 atm and 100°C , $\mu(\text{l}) = \mu(\text{g})$; therefore, at 1.2 atm and 100°C $\mu(\text{g}) - \mu(\text{l}) \approx \Delta V_{\text{vap}} \Delta p =$
(as in Problem 6.4)

$$(30.1 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}) \times (0.2) \times (1.013 \times 10^5 \text{ Pa}) \approx \boxed{+0.6 \text{ kJ mol}^{-1}}$$

Since $\mu(\text{g}) > \mu(\text{l})$, the gas tends to condense into a liquid.

$$\text{P6.7} \quad \text{The amount (moles) of water evaporated is } n_{\text{g}} = \frac{p_{\text{H}_2\text{O}} V}{RT}$$

The heat leaving the water is $q = n \Delta_{\text{vap}} H$

$$\text{The temperature change of the water is } \Delta T = \frac{-q}{nC_{p,m}}, \quad n = \text{amount of liquid water}$$

$$\begin{aligned} \text{Therefore, } \Delta T &= \frac{-p_{\text{H}_2\text{O}} V \Delta_{\text{vap}} H}{RT n C_{p,m}} \\ &= \frac{-(23.8 \text{ Torr}) \times (50.0 \text{ L}) \times (44.0 \times 10^3 \text{ J mol}^{-1})}{(62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times (75.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{250 \text{ g}}{18.02 \text{ g mol}^{-1}}\right)} \\ &= -2.7 \text{ K} \end{aligned}$$

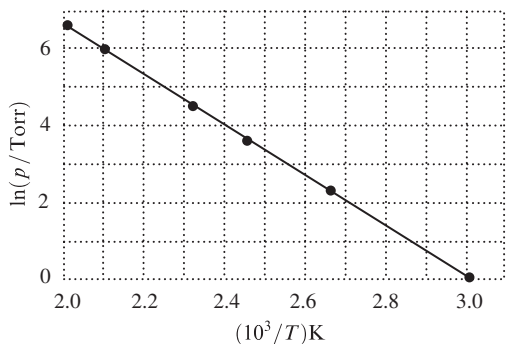
The final temperature will be about 22°C

P6.9

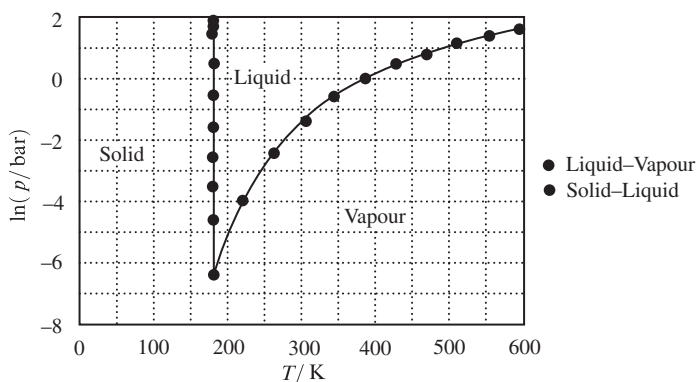
- (a) Follow the procedure in Problem 6.8, but note that $T_b = 227.5^\circ\text{C}$ is obvious from the data.
 (b) Draw up the following table

$\theta/^\circ\text{C}$	57.4	100.4	133.0	157.3	203.5	227.5
T/K	330.6	373.6	406.2	430.5	476.7	500.7
$1000 \text{ K}/T$	3.02	2.68	2.46	2.32	2.10	2.00
$\ln p/\text{Torr}$	0.00	2.30	3.69	4.61	5.99	6.63

The points are plotted in Fig. 6.2. The slope is $-6.4 \times 10^3 \text{ K}$, so $\frac{-\Delta_{\text{vap}} H}{R} = -6.4 \times 10^3 \text{ K}$,
 implying that $\Delta_{\text{vap}} H = +53 \text{ kJ mol}^{-1}$

**Figure 6.2****P6.11**

- (a) The phase diagram is shown in Fig. 6.3.

**Figure 6.3**

- (b) The standard melting point is the temperature at which solid and liquid are in equilibrium at 1 bar. That temperature can be found by solving the equation of the solid–liquid coexistence curve for the temperature

$$1 = p_3/\text{bar} + 1000(5.60 + 11.727x)x,$$

$$\text{So } 11\,727x^2 + 5600x + (4.362 \times 10^{-7} - 1) = 0$$

The quadratic formula yields

$$x = \frac{-5600 \pm \{(5600)^2 - 4(11\,727) \times (-1)\}^{1/2}}{2(11\,727)} = \frac{-1 \pm \left\{1 + \frac{4(11\,727)}{5600^2}\right\}^{1/2}}{2\left(\frac{11727}{5600}\right)}$$

The square root is rewritten to make it clear that the square root is of the form $\{1 + a\}^{1/2}$, with $a \ll 1$; thus the numerator is approximately $-1 + (1 + \frac{1}{2}a) = \frac{1}{2}a$, and the whole expression reduces to

$$x \approx 1/5600 = 1.79 \times 10^{-4}$$

Thus, the melting point is

$$T = (1 + x)T_3 = (1.000179) \times (178.15 \text{ K}) = \boxed{178.18 \text{ K}}$$

- (c) The standard boiling point is the temperature at which the liquid and vapour are in equilibrium at 1 bar. That temperature can be found by solving the equation of the liquid–vapour coexistence curve for the temperature. This equation is too complicated to solve analytically, but not difficult to solve numerically with a spreadsheet. The calculated answer is $\boxed{T = 383.6 \text{ K}}$
- (d) The slope of the liquid–vapour coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T \Delta_{\text{vap}}V} \quad \text{so} \quad \Delta_{\text{vap}}H^\ominus = T \Delta_{\text{vap}}V \frac{dp}{dT}$$

The slope can be obtained by differentiating the equation for the coexistence curve.

$$\begin{aligned} \frac{dp}{dT} &= p \frac{d \ln p}{dT} = p \frac{d \ln p}{dy} \frac{dy}{dT} \\ \frac{dp}{dT} &= \left(\frac{10.418}{y^2} - 15.996 + 2(14.015)y - 3(5.0120)y^2 - (1.70) \times (4.7224) \times (1 - y)^{0.70} \right) \\ &\quad \times \left(\frac{p}{T_c} \right) \end{aligned}$$

At the boiling point, $y = 0.6458$, so

$$\frac{dp}{dT} = 2.851 \times 10^{-2} \text{ bar K}^{-1} = 2.851 \text{ kPa K}^{-1}$$

$$\text{and } \Delta_{\text{vap}}H^\ominus = (383.6 \text{ K}) \times \left(\frac{(30.3 - 0.12) \text{ L mol}^{-1}}{1000 \text{ L m}^{-3}} \right) \times (2.851 \text{ kPa K}^{-1}) = \boxed{33.0 \text{ kJ mol}^{-1}}$$

P6.12 The slope of the solid–vapour coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{sub}}H^\ominus}{T \Delta_{\text{sub}}V} \quad \text{so} \quad \Delta_{\text{sub}}H^\ominus = T \Delta_{\text{sub}}V \frac{dp}{dT}$$

The slope can be obtained by differentiating the coexistence curve graphically (Fig. 6.4).

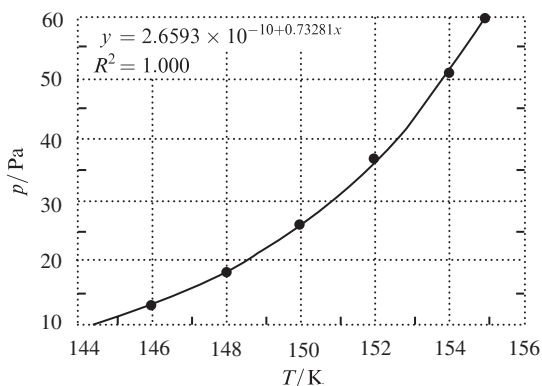


Figure 6.4

$$\frac{dp}{dT} = 4.41 \text{ Pa K}^{-1}$$

according to the exponential best fit of the data. The change in volume is the volume of the vapour

$$V_m = \frac{RT}{p} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (150 \text{ K})}{26.1 \text{ Pa}} = 47.8 \text{ m}^3$$

So

$$\Delta_{\text{sub}} H^\ominus = (150 \text{ K}) \times (47.8 \text{ m}^3) \times (4.41 \text{ Pa K}^{-1}) = 3.16 \times 10^4 \text{ J mol}^{-1} = \boxed{31.6 \text{ kJ mol}^{-1}}$$

Solutions to theoretical problems

P6.14

$$\left(\frac{\partial \Delta G}{\partial p} \right)_T = \left(\frac{\partial G_\beta}{\partial p} \right)_T - \left(\frac{\partial G_\alpha}{\partial p} \right)_T = V_\beta - V_\alpha$$

Therefore, if $V_\beta = V_\alpha$, ΔG is independent of pressure. In general, $V_\beta \neq V_\alpha$, so that ΔG is nonzero, though small, since $V_\beta - V_\alpha$ is small.

P6.16

$$\text{Amount of gas bubbled through liquid} = \frac{pV}{RT}$$

(p = initial pressure of gas and emerging gaseous mixture)

$$\text{Amount of vapour carried away} = \frac{m}{M}$$

$$\text{Mole fraction of vapour in gaseous mixture} = \frac{\frac{m}{M}}{\frac{m}{M} + \frac{pV}{RT}}$$

$$\text{Partial pressure of vapour} = p = \frac{\frac{m}{M}}{\frac{m}{M} + \frac{pV}{RT}} \times p = \frac{p \left(\frac{mRT}{pVM} \right)}{\left(\frac{mRT}{pVM} \right) + 1} = \frac{mPA}{mA + 1}, \quad A = \frac{RT}{pVM}$$

For geraniol, $M = 154.2 \text{ g mol}^{-1}$, $T = 383 \text{ K}$, $V = 5.00 \text{ L}$, $p = 1.00 \text{ atm}$, and $m = 0.32 \text{ g}$, so

$$A = \frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (383 \text{ K})}{(1.00 \text{ atm}) \times (5.00 \text{ L}) \times (154.2 \times 10^{-3} \text{ kg mol}^{-1})} = 40.76 \text{ kg}^{-1}$$

Therefore

$$p = \frac{(0.32 \times 10^{-3} \text{ kg}) \times (760 \text{ Torr}) \times (40.76 \text{ kg}^{-1})}{(0.32 \times 10^{-3} \text{ kg}) \times (40.76 \text{ kg}^{-1}) + 1} = \boxed{9.8 \text{ Torr}}$$

P6.17

$$p = p_0 e^{-Mgh/RT} \quad [\text{Box 1.1}]$$

$$p = p^* e^{-\chi} \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad [6.12]$$

Let $T^* = T_b$ the normal boiling point; then $p^* = 1 \text{ atm}$. Let $T = T_h$, the boiling point at the altitude h . Take $p_0 = 1 \text{ atm}$. Boiling occurs when the vapour (p) is equal to the ambient pressure, that is, when $p(T) = p(h)$, and when this is so, $T = T_h$. Therefore, since $p_0 = p^*$, $p(T) = p(h)$ implies that

$$e^{-Mgh/RT} = \exp \left\{ -\frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_h} - \frac{1}{T_b} \right) \right\}$$

It follows that
$$\frac{1}{T_h} = \frac{1}{T_b} + \frac{Mgh}{T \Delta_{\text{vap}}H}$$

where T is the ambient temperature and M the molar mass of the air. For water at 3000 m, using $M = 29 \text{ g mol}^{-1}$

$$\begin{aligned} \frac{1}{T_h} &= \frac{1}{373 \text{ K}} + \frac{(29 \times 10^{-3} \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (3.000 \times 10^3 \text{ m})}{(293 \text{ K}) \times (40.7 \times 10^3 \text{ J mol}^{-1})} \\ &= \frac{1}{373 \text{ K}} + \frac{1}{1.397 \times 10^4 \text{ K}} \end{aligned}$$

Hence, $T_h = \boxed{363 \text{ K}}$ (90°C)

P6.20

$$S_m = S_m(T, p)$$

$$dS_m = \left(\frac{\partial S_m}{\partial T} \right)_p dT + \left(\frac{\partial S_m}{\partial p} \right)_T dp$$

$$\left(\frac{\partial S_m}{\partial T} \right)_p = \frac{C_{p,m}}{T} \quad [\text{Problem 5.7}] \quad \left(\frac{\partial S_m}{\partial p} \right)_T = - \left(\frac{\partial V_m}{\partial T} \right)_p \quad [\text{Maxwell relation}]$$

$$dq_{\text{rev}} = T dS_m = C_{p,m} dT - T \left(\frac{\partial V_m}{\partial T} \right)_p dp$$

$$C_S = \left(\frac{\partial q}{\partial T} \right)_s = C_{p,m} - T V_m \alpha \left(\frac{\partial p}{\partial T} \right)_s = C_{p,m} - \alpha V_m \times \frac{\Delta H_m}{\Delta V_m} \quad [6.7]$$

P6.22

$$\text{C}(\text{graphite}) \rightleftharpoons \text{C}(\text{diamond}) \quad \Delta_r G^\ominus = 2.8678 \text{ kJ mol}^{-1} \text{ at } \mathfrak{T}.$$

We want the pressure at which $\Delta_r G = 0$; above that pressure the reaction will be spontaneous. Equation 5.10 determines the rate of change of $\Delta_r G$ with p at constant T .

$$(1) \quad \left(\frac{\partial \Delta_r G}{\partial p} \right)_T = \Delta_r V = (V_D - V_G)M$$

where M is the molar mass of carbon; V_D and V_G are the specific volumes of diamond and graphite, respectively.

$\Delta_r G(\mathfrak{T}, p)$ may be expanded in a Taylor series around the pressure $p^\ominus = 100 \text{ kPa}$ at \mathfrak{T} .

$$(2) \quad \begin{aligned} \Delta_r G(\mathfrak{T}, p) &= \Delta_r G^\ominus(\mathfrak{T}, p^\ominus) + \left(\frac{\partial \Delta_r G^\ominus(\mathfrak{T}, p^\ominus)}{\partial p} \right)_T (p - p^\ominus) \\ &\quad + \frac{1}{2} \left(\frac{\partial^2 \Delta_r G^\ominus(\mathfrak{T}, p^\ominus)}{\partial p^2} \right)_T (p - p^\ominus)^2 + \theta (p - p^\ominus)^3 \end{aligned}$$

We will neglect the third and higher-order terms; the derivative of the first-order term can be calculated with eqn 1. An expression for the derivative of the second-order term can be derived with eqn 1.

$$(3) \quad \left(\frac{\partial^2 \Delta_r G}{\partial p^2} \right)_T = \left\{ \left(\frac{\partial V_D}{\partial p} \right)_T - \left(\frac{\partial V_G}{\partial p} \right)_T \right\} M = \{V_G \kappa_T(G) - V_D \kappa_T(D)\} M \quad [3.13]$$

Calculating the derivatives of eqns 1 and 2 at \mathfrak{T} and p^\ominus

$$(4) \quad \left(\frac{\partial \Delta_r G(\mathfrak{T}, p^\ominus)}{\partial p} \right)_T = (0.284 - 0.444) \times \left(\frac{\text{cm}^3}{\text{g}} \right) \times \left(\frac{12.01 \text{ g}}{\text{mol}} \right) = -1.92 \text{ cm}^3 \text{ mol}^{-1}$$

$$(5) \quad \left(\frac{\partial^2 \Delta_r G(\mathfrak{T}, p^\ominus)}{\partial p^2} \right)_T = \{0.444(3.04 \times 10^{-8}) - 0.284(0.187 \times 10^{-8})\} \\ \times \left(\frac{\text{cm}^3 \text{ kPa}^{-1}}{\text{g}} \right) \times \left(\frac{12.01 \text{ g}}{\text{mol}} \right) \\ = 1.56 \times 10^{-7} \text{ cm}^3 (\text{kPa})^{-1} \text{ mol}^{-1}$$

It is convenient to convert the value of $\Delta_r G^\ominus$ to the units $\text{cm}^3 \text{ kPa mol}^{-1}$

$$\Delta_r G^\ominus = 2.8678 \text{ kJ mol}^{-1} \left(\frac{8.315 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{10^3 \text{ cm}^3}{\text{L}} \right) \times \left(\frac{10^5 \text{ Pa}}{\text{bar}} \right)$$

$$(6) \quad \Delta_r G^\ominus = 2.8678 \times 10^6 \text{ cm}^3 \text{ kPa mol}^{-1}$$

Setting $\chi = p - p^\ominus$, eqns 2 and 3–6 give

$$2.8678 \times 10^6 \text{ cm}^3 \text{ kPa mol}^{-1} - (1.92 \text{ cm}^3 \text{ mol}^{-1})\chi + (7.80 \times 10^{-8} \text{ cm}^3 \text{ kPa}^{-1} \text{ mol}^{-1})\chi^2 = 0$$

when $\Delta_r G(\mathfrak{T}, p) = 0$. One real root of this equation is

$$\chi = 1.60 \times 10^6 \text{ kPa} = p - p^\ominus \text{ or}$$

$$p = 1.60 \times 10^6 \text{ kPa} + 10^2 \text{ kPa}$$

$$= 1.60 \times 10^6 \text{ kPa} = \boxed{1.60 \times 10^4 \text{ bar}}$$

Above this pressure the reaction is spontaneous. The other real root is much higher: $2.3 \times 10^7 \text{ kPa}$.

Question. What interpretation might you give to the other real root?