

Exercise

4A.1(b) The phase rule (eqn 4A.1) relates the number of phases (P), components (C), and degrees of freedom (F) of a thermodynamic system:

$$F = C - P + 2 .$$

Restricting to pure substances ($C=1$) and rearranging for phases gives

$$P = 3 - F .$$

Areas in the phase diagram have two degrees of freedom; one can vary pressure and temperature independently (within limits) and stay within the area. Thus, $F = 2$ and $P = 1$ in areas. Lines have one degree of freedom; one can vary pressure or temperature, but to stay on the line the value of the other is determined by the line. Thus, $F = 1$ and $P = 2$ on lines. Points on the phase diagram have zero degrees of freedom; one can vary neither pressure nor temperature and on a given point. Thus, $F = 0$ and $P = 3$ on points.

(a) is in an area, so there is a single phase. (b) and (c) are points, so there are three phases present. (d) is on a line, so there are two phases present.

4A.3(b) Use the phase rule (eqn 4A.1)

$$F = C - P + 2$$

to solve for the number of phases:

$$P = C - F + 2 = 4 - F + 2 = 6 - F \leq \boxed{6} .$$

The maximum number of phases in equilibrium occurs when the number of degrees of freedom is at a minimum, namely zero; that number is six.

4B.1(b) The difference between the definition of normal and standard transition temperatures is the pressure at which the transition takes place: normal refers to exactly 1 atm (101325 Pa),

while standard refers to exactly 1 bar (exactly 10^5 Pa). At the standard boiling temperature and pressure, the liquid and gas phases are in equilibrium, so their chemical potentials are equal:

$$\mu_{\text{liquid}}(T_{\text{std}}, p_{\text{std}}) = \mu_{\text{gas}}(T_{\text{std}}, p_{\text{std}})$$

The same can be said at the normal boiling temperature and pressure:

$$\mu_{\text{liquid}}(T_{\text{norm}}, p_{\text{norm}}) = \mu_{\text{gas}}(T_{\text{norm}}, p_{\text{norm}})$$

Equations 4B.1 and 4B.2 show how the chemical potential changes with temperature and pressure, so for small changes we can write

$$d\mu = \left(\frac{\partial \mu}{\partial T} \right)_p dT + \left(\frac{\partial \mu}{\partial p} \right)_T dp = -S_m dT + V_m dp$$

Assuming that the differences between standard and normal boiling point are small enough, we can equate the differences in the chemical potentials of the two phases:

$$\Delta \mu_{\text{gas}} = -S_{\text{m, gas}} \Delta T + V_{\text{m, gas}} \Delta p = -S_{\text{m, liquid}} \Delta T + V_{\text{m, liquid}} \Delta p = \Delta \mu_{\text{liquid}} ,$$

where Δp is defined as $p_{\text{norm}} - p_{\text{std}}$. Rearrange to isolate ΔT :

$$(S_{\text{m, liquid}} - S_{\text{m, gas}}) \Delta T = (V_{\text{m, liquid}} - V_{\text{m, gas}}) \Delta p ,$$

$$(-\Delta_{\text{vap}} S) \Delta T = (V_{\text{m, liquid}} - V_{\text{m, gas}}) \Delta p \approx -V_{\text{m, gas}} \Delta p$$

Use the ideal gas law to find the molar volume of the gas. Also, we need to find $\Delta_{\text{vap}} S$ or to use Trouton's rule (eqn 3A.17):

$$\begin{aligned} \Delta T &\approx \frac{V_{\text{m, gas}} \Delta p}{\Delta_{\text{vap}} S} = \frac{RT \Delta p}{p \Delta_{\text{vap}} S} = \frac{RT_b^2 \Delta p}{p \Delta_{\text{vap}} H} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(373 \text{ K})^2 (1325 \text{ Pa})}{(10^5 \text{ Pa})(40.656 \times 10^3 \text{ J})} \\ &= \boxed{0.38 \text{ K}} \end{aligned}$$

That is, the normal boiling temperature is 0.38 K higher than the standard boiling temperature.

4B.5(b) Use the Clapeyron equation (eqn 4B.5a)

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V}$$

Assume that $\Delta_{\text{fus}} S$ and $\Delta_{\text{fus}} T$ are independent of temperature:

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

$$\begin{aligned} \Delta_{\text{fus}} S &= (152.6 \text{ cm}^3 \text{ mol}^{-1} - 142.0 \text{ cm}^3 \text{ mol}^{-1}) \times \frac{(1.2 \times 10^6 \text{ Pa} - 1.01 \times 10^5 \text{ Pa})}{429.26 \text{ K} - 427.15 \text{ K}} \\ &= (10.6 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times (5.21 \times 10^5 \text{ Pa K}^{-1}) \\ &= 5.52 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = \boxed{+5.5 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

At the melting temperature

$$\Delta_{\text{fus}} H = T_f \Delta_{\text{fus}} S = (427.15 \text{ K}) \times (5.52 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{+2.4 \text{ kJ mol}^{-1}}$$

4B.6(b) On the assumption that the vapour is a perfect gas and that $\Delta_{\text{vap}} H$ is independent of temperature, we may write [4B.11]

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

$$\begin{aligned} \frac{1}{T} &= \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}} H} \ln \frac{p^*}{p} \\ &= \frac{1}{293.2 \text{ K}} + \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{32.7 \times 10^3 \text{ J mol}^{-1}} \times \ln \left(\frac{58.0}{66.0} \right) = 3.378 \times 10^{-3} \text{ K}^{-1} \end{aligned}$$

$$\text{Hence } T = \frac{1}{3.378 \times 10^{-3} \text{ K}^{-1}} = 296 \text{ K} = \boxed{23^\circ \text{C}}$$

4B.7(b) Integrating the Clausius-Clapeyron equation (4B.10) yields an expression for $\ln p$:

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

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

$$\text{Therefore, } \Delta_{\text{vap}} H = 3036.8 \text{ K} \times R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times (3036.8 \text{ K}) = \boxed{+25.25 \text{ kJ mol}^{-1}}$$

4B.10(b) The rate of loss of mass of water may be expressed as

$$\frac{dm}{dt} = \frac{d}{dt}(nM) \quad \text{where} \quad n = \frac{q}{\Delta_{\text{vap}}H}$$

$$\text{Thus} \quad \frac{dn}{dt} = \frac{dq/dt}{\Delta_{\text{vap}}H} = \frac{(0.87 \times 10^3 \text{ W m}^{-2}) \times (10^4 \text{ m}^2)}{44.0 \times 10^3 \text{ J mol}^{-1}} = 200 \text{ mol s}^{-1}$$

$$\text{and} \quad \frac{dm}{dt} = (200 \text{ mol s}^{-1}) \times (18.02 \text{ g mol}^{-1}) = \boxed{3.6 \text{ kg s}^{-1}}$$

4B.12(b) (i) According to Trouton's rule (eqn 3A.17)

$$\Delta_{\text{vap}}H \approx 85 \text{ J K}^{-1} \text{ mol}^{-1} \times T_b = 85 \text{ J K}^{-1} \text{ mol}^{-1} \times 342.2 \text{ K} = \boxed{29.1 \text{ kJ mol}^{-1}}$$

(ii) Use the integrated form of the Clausius–Clapeyron equation (eqn 4B.11) rearranged to

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

At $T_1 = 342.2 \text{ K}$, $p_1 = 1.000 \text{ atm}$ [normal boiling point]; thus at 25°C

$$\ln\left(\frac{p_2}{1.000 \text{ atm}}\right) = \left(\frac{2.91 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{342.2 \text{ K}} - \frac{1}{298.2 \text{ K}}\right) = -1.51$$

and $p_2 = e^{-1.51} \text{ atm} = \boxed{0.22 \text{ atm}}$.

$$\text{At } 60^\circ\text{C}, \ln\left(\frac{p_2}{1.000 \text{ atm}}\right) = \left(\frac{2.91 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{342.2 \text{ K}} - \frac{1}{333.2 \text{ K}}\right) = -0.276$$

and $p_2 = e^{-0.276} \text{ atm} = \boxed{0.76 \text{ atm}}$.

Problem

$$\begin{aligned} \mathbf{4B.4} \quad (\mathbf{a}) \quad \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{s})}{\partial T}\right)_p &= -S_m(\text{l}) + S_m(\text{s}) = -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_f} \quad [4B.12] \\ &= \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273.15 \text{ K}} = \boxed{-22.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} (\mathbf{b}) \quad \left(\frac{\partial\mu(\text{g})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p &= -S_m(\text{g}) + S_m(\text{l}) = -\Delta_{\text{vap}}S = \frac{-\Delta_{\text{vap}}H}{T_b} \\ &= \frac{-40.6 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K}} = \boxed{-108.8 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$(\mathbf{c}) \quad \mu(\text{l}, -5^\circ\text{C}) - \mu(\text{s}, -5^\circ\text{C}) = \mu(\text{l}, -5^\circ\text{C}) - \mu(\text{l}, 0^\circ\text{C}) - \{\mu(\text{s}, -5^\circ\text{C}) - \mu(\text{s}, 0^\circ\text{C})\}$$

because $\mu(\text{l}, 0^\circ\text{C}) = \mu(\text{s}, 0^\circ\text{C})$

$$\text{Thus} \quad \mu(\text{l}, -5^\circ\text{C}) - \mu(\text{s}, -5^\circ\text{C}) = \Delta\mu(\text{l}) - \Delta\mu(\text{s})$$

where $\Delta\mu$ is the difference in chemical potential of a given phase at -5°C compared to that at normal freezing temperature.

$$\Delta\mu \approx \left(\frac{\partial\mu}{\partial T}\right)_p \Delta T = -S_m \Delta T \quad [4B.1]$$

$$\text{so} \quad \{\mu(\text{l}, -5^\circ\text{C}) - \mu(\text{l}, 0^\circ\text{C})\} - \{\mu(\text{s}, -5^\circ\text{C}) - \mu(\text{s}, 0^\circ\text{C})\} = -\Delta_{\text{fus}}S \Delta T$$

$$\mu(\text{l}, -5^\circ\text{C}) - \mu(\text{s}, -5^\circ\text{C}) = -(+22.0 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-5 \text{ K}) = \boxed{+110 \text{ J mol}^{-1}}$$

Since $\mu(\text{l}, -5^\circ\text{C}) > \mu(\text{s}, -5^\circ\text{C})$, there is a thermodynamic tendency to freeze.

$$4B.6 \quad \frac{dp}{dT} = \frac{\Delta_{\text{fus}} S}{\Delta_{\text{fus}} V} [4B.5a] = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V} [4B.6]$$

Thus $dT = \frac{T \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} dp$.

Integrate both sides:

$$\Delta T = \int_{T_{\text{top}}}^{T_{\text{bot}}} dT = \int_{p_{\text{top}}}^{p_{\text{bot}}} \frac{T_m \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} dp = \frac{T_m \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \Delta p \quad [\text{assuming the integrand is constant}]$$

Now $\Delta p = p_{\text{bot}} - p_{\text{top}} = \rho g h$:

so
$$\Delta T = \frac{T_m \rho g h \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H}$$

$$= \frac{(234.3 \text{ K}) \times (13.6 \text{ g cm}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (10.0 \text{ m}) \times (0.517 \text{ cm}^3 \text{ mol}^{-1})}{2.292 \times 10^3 \text{ J mol}^{-1}} \times \frac{1 \text{ kg}}{10^3 \text{ g}}$$

$$= 0.071 \text{ K}$$

Therefore, the freezing point changes to 234.4 K

4B.16 In each phase the slopes of curves of chemical potential plotted against temperature are

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -S_m [4.1]$$

The curvatures of the graphs are given by

$$\left(\frac{\partial^2 \mu}{\partial T^2} \right)_p = - \left(\frac{\partial S_m}{\partial T} \right)_p$$

To evaluate this derivative, consider dS at constant p :

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{dH}{T} = \frac{C_p dT}{T} \quad \text{so} \quad \left(\frac{\partial^2 \mu}{\partial T^2} \right)_p = - \left(\frac{\partial S_m}{\partial T} \right)_p = - \frac{C_{p,m}}{T}$$

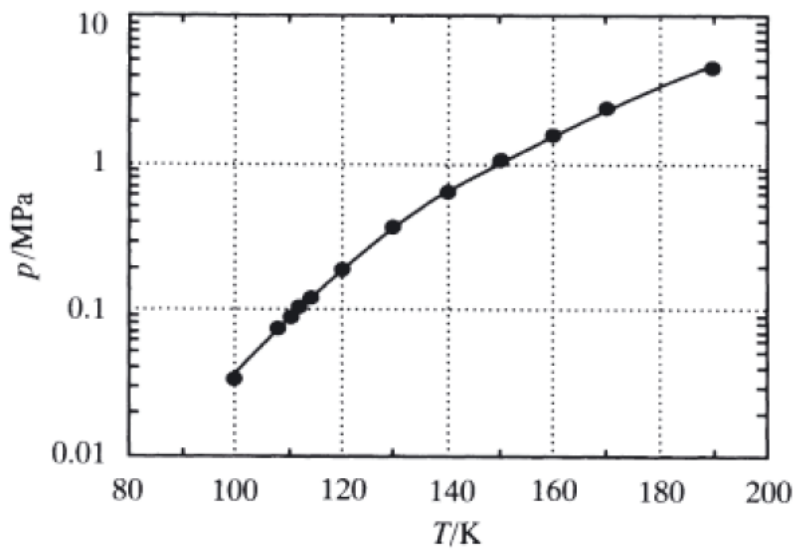
Since $C_{p,m}$ is necessarily positive, the curvatures in all states of matter are necessarily negative. $C_{p,m}$ is often largest for the liquid state, though not always. In any event, it is the

ratio $C_{p,m}/T$ that determines the magnitude of the curvature, so no general answer can be given for the state with the greatest curvature. It depends upon the substance.

Integrated activities

4.4 (a) The phase boundary is plotted in Figure I4.2.

Figure I4.2



(b) The standard boiling point is the temperature at which the liquid is in equilibrium with the standard pressure of 1 bar (0.1 MPa). Interpolation of the plotted points gives $T_b = 112 \text{ K}$.

(c) The slope of the liquid–vapor coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \quad [4B.9] \quad \text{so} \quad \Delta_{\text{vap}}H = (T\Delta_{\text{vap}}V) \frac{dp}{dT}$$

The slope can be obtained graphically or by fitting the points nearest the boiling point. Then

$$\frac{dp}{dT} = 8.14 \times 10^{-3} \text{ MPa K}^{-1}$$

$$\text{so} \quad \Delta_{\text{vap}}H = (112 \text{ K}) \times \left(\frac{(8.89 - 0.0380) \text{ dm}^3 \text{ mol}^{-1}}{1000 \text{ dm}^3 \text{ m}^{-3}} \right) \times (8.14 \text{ kPa K}^{-1}) = 8.07 \text{ kJ mol}^{-1}$$