

## 4 Physical transformations of pure substances

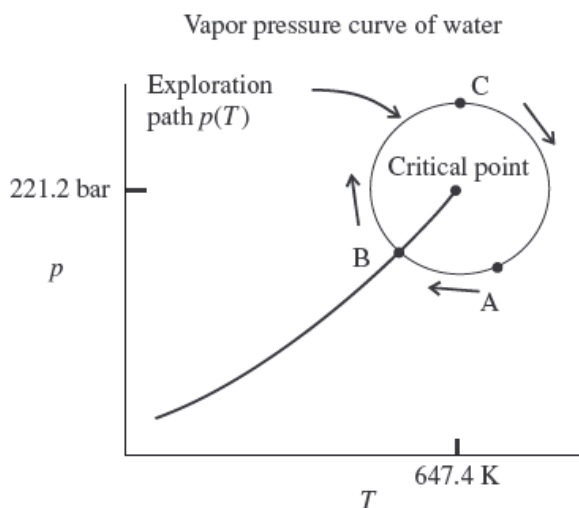
### 4A Phase diagrams of pure substances

#### Answers to discussion questions

- 4A.2** Mathematically we can trace the change in chemical potential when pressure is changed to the  $pV$  term within the Gibbs energy (part of the definition of enthalpy); the product changes when the pressure changes. Physically, an incompressible system does not store energy like a spring (or like a highly compressible gas); however, it can transmit energy as it does in a hydraulic cylinder. Furthermore, an incompressible system under pressure is under stress at a molecular level. Its bonds or intermolecular repulsive forces resist external forces without contraction. Finally, one can observe changes in phases in equilibrium with incompressible liquids (the pressure of their vapours, for example) when pressure is applied to the liquid; see Topic 4B.1(c).

**4A.4**

**Figure 4A.1**



Refer to Figure 4A.1. Starting at point A and continuing clockwise on path  $p(T)$  toward point B, we see a gaseous phase only within the container with water at pressures and temperatures  $p(T)$ . Upon reaching point B on the vapour pressure curve, liquid appears on the bottom of the container and a phase boundary or meniscus is evident between the liquid and less dense gas above it. The liquid and gaseous phases are at equilibrium at this point. Proceeding clockwise away from the vapour pressure curve the meniscus disappears and the system becomes wholly liquid. Continuing along  $p(T)$  to point C at the critical temperature no abrupt changes are observed in the isotropic fluid. Before point C is reached, it is possible to return to the vapour pressure curve and a liquid-gas equilibrium by reducing the pressure isothermally. Continuing clockwise from point C along path  $p(T)$  back to point A, no phase boundary is observed even though we now consider the water to have returned to the gaseous state. Additionally, if the pressure is isothermally reduced at any point after point C, it is impossible to return to a liquid-gas equilibrium.

When the path  $p(T)$  is chosen to be very close to the critical point, the water appears opaque. At near critical conditions, densities and refractive indices of both the liquid and gas phases are nearly identical. Furthermore, molecular fluctuations cause spatial variations of densities and refractive indices on a scale large enough to strongly scatter visible light. This is called critical opalescence.

#### Solutions to Exercises

- 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.2(b)** For pure substances (one-component systems), the chemical potential is the molar Gibbs energy:

$$dG = (\mu_2 - \mu_1)dn$$

$$\text{so } \Delta G = (\mu_2 - \mu_1)n = (-8.3 \text{ kJ mol}^{-1})(0.15 \times 10^{-3} \text{ mol}) = +1.2 \times 10^{-3} \text{ kJ} = \boxed{1.2 \text{ J}}.$$

**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 Phase diagrams of pure substances

### Answers to discussion questions

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**4B.2** See Topic 4B.1(b). The mathematical reason can be seen in eqn 4B.2,

$$\left( \frac{\partial \mu}{\partial p} \right)_T = V_m$$

Because  $V_m > 0$  for all pure substances, the slope of the change in chemical potential with respect to change in pressure is positive: chemical potential increases with increasing pressure. See also the answer to Discussion question 4A.2, which addresses why the chemical potential changes even in incompressible substances.

**4B.4** See Topic 4B.3 for classification of phase transitions. 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  $\lambda$ -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.

At the molecular level first-order transitions are associated with discontinuous changes in the interaction energies between the atoms or molecules constituting the system and in the volume they occupy. One kind of second-order transition may involve only a continuous change in the arrangement of the atoms from one crystal structure (symmetry) to another while preserving their orderly arrangement. In one kind of  $\lambda$ -transition, called an order-disorder transition, randomness is introduced into the atomic arrangement. See Figures 4B.9 through 4B.12 of the text.

### Solutions to Exercises

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**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:

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

where  $\Delta p$  is defined as  $p_{\text{norm}} - p_{\text{std}}$ . Rearrange to isolate  $\Delta T$ :

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

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

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):

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

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

**4B.2(b)** Equation 4B.1 shows how the chemical potential changes with temperature

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

$$\begin{aligned} \text{so } \Delta \mu &= -\int S_m dT = -S_m \Delta T = -53 \text{ J K}^{-1} \text{ mol}^{-1} \times (1000 - 100) \text{ K} \\ &= \boxed{4.8 \times 10^4 \text{ J mol}^{-1}} = \boxed{48 \text{ kJ mol}^{-1}} \end{aligned}$$

**4B.3(b)** Equation 4B.2 shows how the chemical potential changes with pressure

$$d\mu = \left( \frac{\partial \mu}{\partial p} \right)_T dp = V_m dp = \frac{M}{\rho} dp$$

$$\begin{aligned} \text{so } \Delta \mu &= \int \frac{M}{\rho} dp = \frac{M}{\rho} \Delta p = \frac{78.11 \text{ g mol}^{-1}}{0.879 \text{ g cm}^{-3}} \times (10 \times 10^6 - 100 \times 10^3) \text{ Pa} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \\ &= \boxed{8.8 \times 10^2 \text{ J mol}^{-1}} = \boxed{0.088 \text{ kJ mol}^{-1}} \end{aligned}$$

Note: we assumed that the sample is incompressible.

**4B.4(b)** The effect on vapour pressure of a change in applied external pressure on a liquid is given by eqn 4B.3:

$$p = p^* e^{V_m(1)\Delta P/RT}.$$

For liquid naphthalene, the molar volume is

$$V_m = \frac{M}{\rho} = \frac{118.16 \text{ g mol}^{-1}}{0.962 \text{ g cm}^{-3}} = 122.8 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{so } \frac{V_m(1)\Delta P}{RT} = \frac{122.8 \text{ cm}^3 \text{ mol}^{-1} \times (15 \times 10^6 - 1.0 \times 10^5) \text{ Pa}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 368 \text{ K}} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = 0.598$$

$$\text{and } p = p^* e^{V_m(1)\Delta P/RT} = (2.0 \text{ kPa}) e^{0.598} = \boxed{3.6 \text{ kPa}}.$$

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

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

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

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

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]

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

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

**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.8(b)** (i) The indefinitely integrated form of eqn 4B.10 is used as in Exercise 4B.7(b).

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}}H}{RT}, \quad \text{or } \log p = \text{constant} - \frac{\Delta_{\text{vap}}H}{2.303 RT}$$

$$\text{Thus } \Delta_{\text{vap}}H = 1625 \text{ K} \times R \times 2.303 = 1625 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.303$$

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

(ii) The normal boiling point corresponds to  $p = 1.000 \text{ atm} = 760 \text{ Torr}$ ,

$$\text{so } \log 760 = 8.750 - \frac{1625 \text{ K}}{T}$$

$$\text{and } T = \frac{1625 \text{ K}}{8.750 - \log 760} = \boxed{276.9 \text{ K}}$$

**4B.9(b)**

$$\begin{aligned}\Delta T &\approx \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}S} \times \Delta p \quad [4B.5a \text{ and Exercise 4B.5(a)}] \\ &\approx \frac{T_f \Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p = \frac{T_f M \Delta p}{\Delta_{\text{fus}}H} \times \Delta \left(\frac{1}{\rho}\right) \quad [V_m = M / \rho]\end{aligned}$$

Normal freezing point is  $T_f = (273.15 - 3.65) \text{ K} = 269.50 \text{ K}$  at a pressure of 1 atm, which is about 0.1 MPa. Thus, to the nearest MPa,  $\Delta p = 100 \text{ MPa} = 1.00 \times 10^8 \text{ Pa}$

$$\Delta T \approx \frac{269.50 \text{ K} \times 46.1 \text{ g mol}^{-1} \times (1.00 \times 10^8 \text{ Pa})}{8.68 \times 10^3 \text{ J mol}^{-1}} \times \left( \frac{1}{0.789 \text{ g cm}^{-3}} - \frac{1}{0.801 \text{ g cm}^{-3}} \right)$$

$$\approx 2.7 \text{ K}$$

Therefore, at 100 MPa,  $T_f = (269.50 + 2.7) \text{ K} = \boxed{272.2 \text{ K}}$  or  $\boxed{-1.0^\circ\text{C}}$ .

**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.11(b)** The equilibrium vapour pressure of ice at  $-5^\circ\text{C}$  is 0.40 kPa. Therefore, the frost would sublime. A partial pressure of  $\boxed{0.40 \text{ kPa}}$  or more would ensure that the frost remains.

**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  $25^\circ\text{C}$

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

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

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

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

$$\text{4B.13(b)} \quad \Delta T = T_f(10 \text{ MPa}) - T_f(0.1 \text{ MPa}) = \frac{T_f \Delta p M}{\Delta_{\text{fus}}H} \Delta\left(\frac{1}{\rho}\right) \quad [\text{Exercise 4B.9(b)}]$$

$$\Delta T = \left( \frac{(273.15 \text{ K}) \times 9.9 \times 10^6 \text{ Pa} \times 18.0 \text{ g mol}^{-1}}{6.01 \times 10^3 \text{ J mol}^{-1}} \right) \times \left( \frac{1}{0.998 \text{ g cm}^{-3}} - \frac{1}{0.915 \text{ g cm}^{-3}} \right) = -0.74 \text{ K}$$

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

$$\text{4B.14(b)} \quad \Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV) = 43.5 \text{ kJ mol}^{-1}$$

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

$$\Delta_{\text{vap}}(pV) \approx (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (352 \text{ K}) = 2.93 \times 10^3 \text{ J mol}^{-1}$$

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H} = \frac{2.93 \text{ kJ mol}^{-1}}{43.5 \text{ kJ mol}^{-1}} = \boxed{0.0673} = 6.73 \text{ per cent}$$

## Solutions to problems

**4B.2** Use the definite integral form of the Clausius–Clapeyron equation [Exercise 4B.12(b)].

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

At  $T_1 = (273.15 - 29.2) \text{ K} = 244.0 \text{ K}$  (normal boiling point),  $p_1 = 1.000 \text{ atm}$ ; thus at  $40^\circ\text{C}$

$$\ln\left(\frac{p_2}{1.000 \text{ atm}}\right) = \left(\frac{20.25 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{244.0 \text{ K}} - \frac{1}{313.2 \text{ K}}\right) = 2.205$$

and  $p_2 = 1.000 \text{ atm} \times e^{2.205} = \boxed{9.07 \text{ atm}}$

**Comment.** Three significant figures are not really warranted in this answer because of the approximations employed.

**4B.4 (a)** 
$$\left(\frac{\partial\mu(l)}{\partial T}\right)_p - \left(\frac{\partial\mu(s)}{\partial T}\right)_p = -S_m(l) + S_m(s) = -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_f} \quad [4B.12]$$

$$= \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273.15 \text{ K}} = \boxed{-22.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**(b)** 
$$\left(\frac{\partial\mu(g)}{\partial T}\right)_p - \left(\frac{\partial\mu(l)}{\partial T}\right)_p = -S_m(g) + S_m(l) = -\Delta_{\text{vap}}S = \frac{-\Delta_{\text{vap}}H}{T_b}$$

$$= \frac{-40.6 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K}} = \boxed{-108.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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

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

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

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

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

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

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

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

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  $\Delta p = p_{\text{bot}} - p_{\text{top}} = \rho gh$ ;

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

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

$$= 0.071 \text{ K}$$

Therefore, the freezing point changes to  $\boxed{234.4 \text{ K}}$

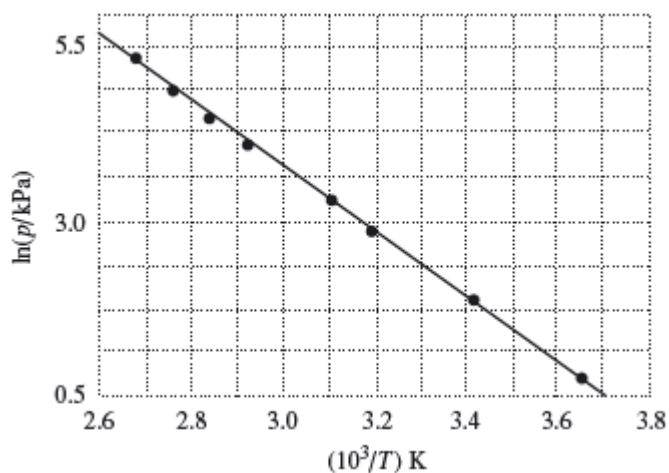
**4B.8** Integrating the Clausius-Clapeyron equation [4B.10] yields an expression for  $\ln p$ :

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

Therefore, plot  $\ln p$  against  $1/T$  and identify  $-\Delta_{\text{vap}}H/R$  as the slope of the plot. Construct the following table

$\theta/^\circ\text{C}$	0	20	40	50	70	80	90	100
$T/\text{K}$	273	293	313	323	343	353	363	373
$1000 \text{ K} / T$	3.66	3.41	3.19	3.10	2.92	2.83	2.75	2.68
$\ln(p / \text{kPa})$	0.652	1.85	2.87	3.32	4.13	4.49	4.83	5.14

Figure 4B.1



The points are plotted in Figure 4B.1. The slope is  $-4569 \text{ K}$ , so

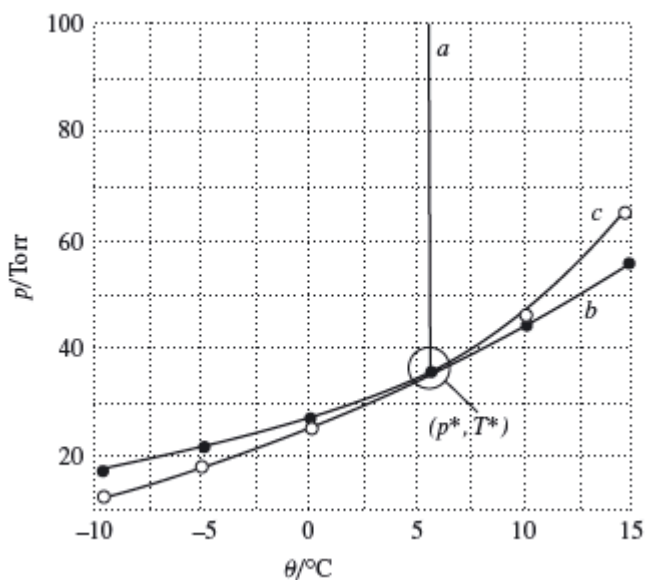
$$\frac{-\Delta_{\text{vap}} H}{R} = -4569 \text{ K}, \text{ or } \Delta_{\text{vap}} H = \boxed{+38.0 \text{ kJ mol}^{-1}}$$

The normal boiling point occurs at  $p = 1 \text{ atm} = 101.3 \text{ kPa}$ , or at  $\ln(p/\text{kPa}) = 4.618$ , which from the figure corresponds to  $1000 \text{ K}/T = 2.80$ . Therefore,  $T_b = \boxed{357 \text{ K} (84^\circ\text{C})}$ . The accepted value is  $83^\circ\text{C}$ .

**4B.10** The slope of the solid–vapour coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{sub}} H}{T \Delta_{\text{sub}} V} \text{ [analogous to 4B.9] so } \Delta_{\text{sub}} H = T \Delta_{\text{sub}} V \frac{dp}{dT}$$

Figure 4B.2



The slope can be obtained by differentiating an equation fit to the coexistence curve (Figure 4B.2). Fit the data to an exponential function or take natural logarithms of the pressures and make a linear fit to the transformed data. The fit equation is

$$p/\text{Pa} = 2.659 \times 10^{-10} e^{0.16877/\text{K}}$$

so  $\frac{dp}{dT} = (2.659 \times 10^{-10} \text{ Pa}) \times (0.1687 \text{ K}^{-1}) \times e^{0.1687T/K} = 4.41 \text{ Pa K}^{-1}$  at 150 K.

The change in volume is essentially the volume of the vapour

$$V_m = \frac{RT}{p} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (150 \text{ K})}{(2.659 \times 10^{-10} \text{ Pa}) \times e^{0.1687 \times 150}} = 47.7 \text{ m}^3$$

So  $\Delta_{\text{sub}} H^\ominus = (150 \text{ K}) \times (47.7 \text{ m}^3) \times 4.41 \text{ Pa K}^{-1} = 3.16 \times 10^4 \text{ J mol}^{-1} = \boxed{31.6 \text{ kJ mol}^{-1}}$

**4B.12**

$dH = C_p dT + V dp$  implies  $d\Delta H = \Delta C_p dT + \Delta V dp$ ,

where  $\Delta$  signifies a difference between phases. Along a phase boundary  $dp$  and  $dT$  are related by

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \quad [4B.6 \text{ or } 4B.9]$$

Therefore,

$$d\Delta H = \left( \Delta C_p + \Delta V \times \frac{\Delta H}{T \Delta V} \right) dT = \left( \Delta C_p + \frac{\Delta H}{T} \right) dT \quad \text{and} \quad \frac{d\Delta H}{dT} = \Delta C_p + \frac{\Delta H}{T}$$

Then, since

$$\frac{d}{dT} \left( \frac{\Delta H}{T} \right) = \frac{1}{T} \frac{d\Delta H}{dT} - \frac{\Delta H}{T^2} = \frac{1}{T} \left( \frac{d\Delta H}{dT} - \frac{\Delta H}{T} \right)$$

substituting the first result gives

$$\frac{d}{dT} \left( \frac{\Delta H}{T} \right) = \frac{\Delta C_p}{T}$$

Therefore,

$$d \left( \frac{\Delta H}{T} \right) = \frac{\Delta C_p dT}{T} = \boxed{\Delta C_p d \ln T}$$

**4B.14** Equation 4B.3 gives the vapour pressure of a liquid under an additional applied pressure  $\Delta P$ :

$$p = p^* e^{V_m(1)\Delta P/RT}$$

The applied pressure is the hydrostatic pressure of the liquid overlying the depth  $d$ :

$$\Delta P = \rho g d$$

The molar volume of the liquid is

$$V_m(l) = M / \rho$$

Substituting into eqn. 4B.3 yields

$$\boxed{p = p^* e^{Mgd/RT}}$$

For a 10-m column of water at 25°C,

$$\frac{Mgd}{RT} = \frac{(18.02 \times 10^{-3} \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (10 \text{ m})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 7.1 \times 10^{-4}$$

so  $\frac{p}{p^*} = e^{7.1 \times 10^{-4}} \approx 1 + 7.1 \times 10^{-4}$

That is, the fractional increase in vapor pressure is  $\boxed{7.1 \times 10^{-4}}$  or  $\boxed{0.071 \text{ per cent}}$ .

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

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

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.

4B.18

$$S = S(T,p)$$

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

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad [\text{Problem 4B.16}] \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad [\text{Table 3D.1}] = -\alpha V_m$$

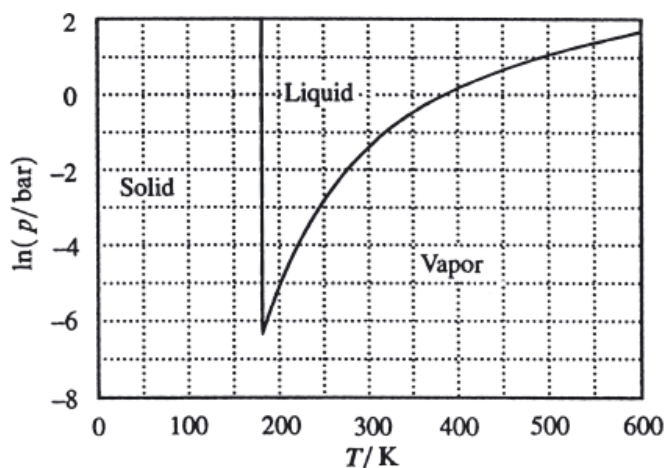
$$dq_{\text{rev}} = T dS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$C_s = \left(\frac{\partial q}{\partial T}\right)_s = C_p - TV\alpha\left(\frac{\partial p}{\partial T}\right)_s = \boxed{C_p - \alpha V \times \frac{\Delta_{\text{trs}} H}{\Delta_{\text{trs}} V}} \quad [4B.6]$$

### Integrated activities

4.2 (a) The phase diagram is shown in Figure I4.1.

Figure I4.1



(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:

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

Put the equation into standard form:

$$11727x^2 + 5600x + (4.362 \times 10^{-7} - 1) = 0$$

The quadratic formula yields

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

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  $-1 + \left(1 + \frac{1}{2}a\right) = \frac{1}{2}a$ , 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  $y = 0.6459$ ,

so  $T = 0.6459 \times 593.95 \text{ K} = \boxed{383.6 \text{ K}}$ .

(d) The slope of the liquid–vapour coexistence curve is given by

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

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

$$\begin{aligned} \frac{dp}{dT} &= p \frac{d \ln p}{dT} = p \frac{d \ln p}{dy} \frac{dy}{dT} \\ \frac{dp}{dT} &= \left( \frac{10.413}{y^2} - 15.996 + 2(14.015)y - 3(5.0120)y^2 - (1.70) \times (4.7224) \times (1-y)^{0.70} \right) \\ &\quad \times \left( \frac{p}{T_c} \right) \end{aligned}$$

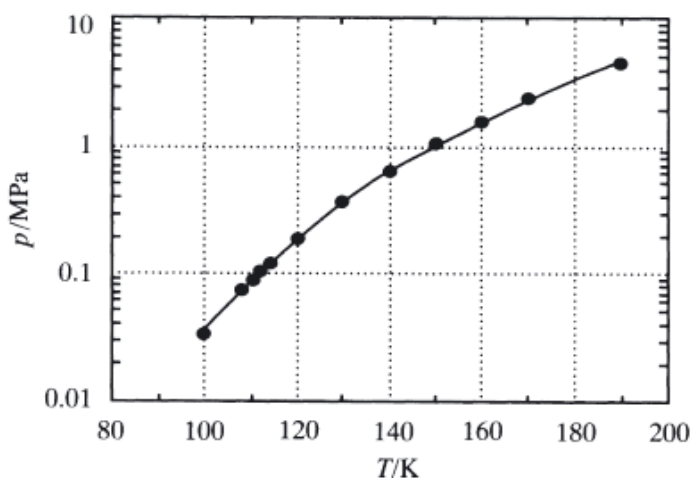
Substituting the value of  $y$  at the boiling point yields,

$$\frac{dp}{dT} = 2.848 \times 10^{-2} \text{ bar K}^{-1} = 2.848 \text{ kPa K}^{-1}$$

and  $\Delta_{\text{vap}} H = (383.6 \text{ K}) \times \left( \frac{(30.3 - 0.12) \text{ dm}^3 \text{ mol}^{-1}}{1000 \text{ dm}^3 \text{ m}^{-3}} \right) \times (2.848 \text{ kPa K}^{-1}) = \boxed{33.0 \text{ kJ mol}^{-1}}$

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  $T_b = \boxed{112 \text{ K}}$ .

(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

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

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