

**Chem 401—Physical Chemistry**  
**Chapter 4 Homework Solutions**

**E4.10(b)**

$$\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV)$$

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

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

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

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H} = \frac{2.927 \text{ kJ mol}^{-1}}{43.5 \text{ kJ mol}^{-1}}$$

$$= \boxed{6.73 \times 10^{-2}} = 6.73 \text{ percent}$$

**Solutions to problems**

**Solutions to numerical problems**

**P4.1** At the triple point,  $T_3$ , the vapor pressures of liquid and solid are equal; hence

$$10.5916 - \frac{1871.2 \text{ K}}{T_3} = 8.3186 - \frac{1425.7 \text{ K}}{T_3}; \quad T_3 = \boxed{196.0 \text{ K}}$$

$$\log(p_3/\text{Torr}) = \frac{-1871.2 \text{ K}}{196.0 \text{ K}} + 10.5916 = 1.0447; \quad p_3 = \boxed{11.1 \text{ Torr}}$$

**P4.3** (a)  $\frac{dp}{dT} = \frac{\Delta_{\text{vap}}S}{\Delta_{\text{vap}}V} = \frac{\Delta_{\text{vap}}H}{T_b \Delta_{\text{vap}}V}$  [4.6, Clapeyron equation]

$$= \frac{14.4 \times 10^3 \text{ J mol}^{-1}}{(180 \text{ K}) \times (14.5 \times 10^{-3} - 1.15 \times 10^{-4}) \text{ m}^3 \text{ mol}^{-1}} = \boxed{+5.56 \text{ kPa K}^{-1}}$$

(b)  $\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{RT^2} \times p$  [4.11, with  $d \ln p = \frac{dp}{p}$ ]

$$= \frac{(14.4 \times 10^3 \text{ J mol}^{-1}) \times (1.013 \times 10^5 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (180 \text{ K})^2} = +5.42 \text{ kPa K}^{-1}$$

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

**P4.5** (a)  $\left(\frac{\partial \mu(l)}{\partial p}\right)_T - \left(\frac{\partial \mu(s)}{\partial p}\right)_T = V_m(l) - V_m(s)$  [4.13]  $= M \Delta \left(\frac{1}{\rho}\right)$

$$= (18.02 \text{ g mol}^{-1}) \times \left(\frac{1}{1.000 \text{ g cm}^{-3}} - \frac{1}{0.917 \text{ g cm}^{-3}}\right)$$

$$= \boxed{-1.63 \text{ cm}^3 \text{ mol}^{-1}}$$

(b)  $\left(\frac{\partial \mu(g)}{\partial p}\right)_T - \left(\frac{\partial \mu(l)}{\partial p}\right)_T = V_m(g) - V_m(l)$

$$= (18.02 \text{ g mol}^{-1}) \times \left(\frac{1}{0.598 \text{ g dm}^{-3}} - \frac{1}{0.958 \times 10^3 \text{ g dm}^{-3}}\right)$$

$$= \boxed{+30.1 \text{ dm}^3 \text{ mol}^{-1}}$$

## Solutions to numerical problems

**P4.2** Use the definite integral form of the Clausius–Clapeyron equation [Solution to Exercise 4.8(b)].

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right); \quad T_1 = \text{normal boiling point}; \quad p_1 = 1.000 \text{ atm}$$

$$\ln(p_2/\text{atm}) = \left(\frac{20.25 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{244.0 \text{ K}} - \frac{1}{313.2 \text{ K}}\right) = 2.206$$

$$p_2 = \boxed{9.07 \text{ atm}} \approx 9 \text{ atm}$$

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

**P4.4**

$$\begin{aligned} \text{(a)} \quad \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{s})}{\partial T}\right)_p &= -S_{\text{m}}(\text{l}) + S_{\text{m}}(\text{s}) \text{ [Section 4.7, eqn 13]} \\ &= -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_{\text{f}}}; \quad \Delta_{\text{fus}}H = 6.01 \text{ kJ mol}^{-1} \text{ [Table 2.3]} \\ &= \frac{-6.01 \text{ kJ mol}^{-1}}{273.15 \text{ K}} = \boxed{-22.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \left(\frac{\partial\mu(\text{g})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p &= -S_{\text{m}}(\text{g}) + S_{\text{m}}(\text{l}) = -\Delta_{\text{vap}}S \\ &= \frac{-\Delta_{\text{vap}}H}{T_{\text{b}}} = \frac{-40.6 \text{ kJ mol}^{-1}}{373.15 \text{ K}} = \boxed{-109.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta\mu &\approx \left(\frac{\partial\mu}{\partial T}\right)_p \Delta T = -S_{\text{m}}\Delta T \text{ [4.1]} \\ \Delta\mu(\text{l}) - \Delta\mu(\text{s}) &= \mu(\text{l}, -5^\circ\text{C}) - \mu(\text{l}, 0^\circ\text{C}) - \mu(\text{s}, -5^\circ\text{C}) + \mu(\text{s}, 0^\circ\text{C}) \\ &= \mu(\text{l}, -5^\circ\text{C}) - \mu(\text{s}, -5^\circ\text{C}) \text{ [}\mu(\text{l}, 0^\circ\text{C}) = \mu(\text{s}, 0^\circ\text{C})\text{]} \\ &\approx -\{S_{\text{m}}(\text{l}) - S_{\text{m}}(\text{s})\}\Delta T \approx -\Delta_{\text{fus}}S\Delta T \\ &= -(5 \text{ K}) \times (-22.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{+110 \text{ J mol}^{-1}} \end{aligned}$$

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

**P4.6**

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V} \text{ [4.6]} = \frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}$$

$$\Delta T = \int_{T_{\text{m},1}}^{T_{\text{m},2}} dT = \int_{p_{\text{top}}}^{p_{\text{bot}}} \frac{T_{\text{m}}\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} dp$$

$$\Delta T \approx \frac{T_{\text{m}}\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p \text{ [}T_{\text{m}}, \Delta_{\text{fus}}H, \text{ and } \Delta_{\text{fus}}V \text{ assumed constant]}$$

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

Therefore

$$\begin{aligned}\Delta T &= \frac{T_m \rho g h \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \\ &= \frac{(234.3 \text{ K}) \times (13.6 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (10 \text{ m}) \times (0.517 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{2.292 \times 10^3 \text{ J mol}^{-1}} \\ &= 0.070 \text{ K}\end{aligned}$$

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

**P4.8**

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2} \quad [4.11], \text{ yields upon indefinite integration}$$

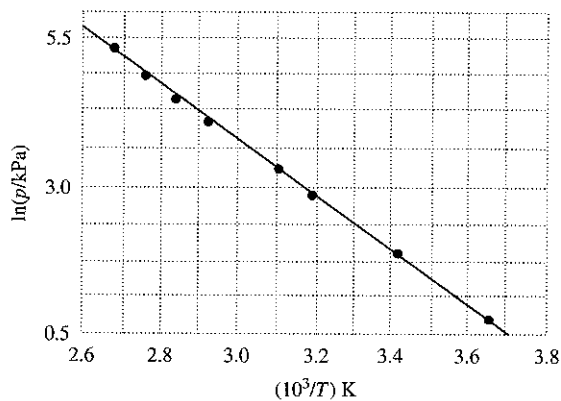
$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}} H}{RT}$$

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

The points are plotted in Figure 4.1. The slope is  $-4569 \text{ K}$ , so

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



**Figure 4.1**

The normal boiling point occurs at  $p = 760 \text{ Torr}$ , or at  $\ln(p/\text{Torr}) = 6.633$ , which from the figure corresponds to  $1000 \text{ K}/T \approx 2.80$ . Therefore,  $T_b = \boxed{357 \text{ K } (84^\circ\text{C})}$ . The accepted value is  $83^\circ\text{C}$ .

**P4.10** The equations describing the coexistence curves for the three states are

(a) Solid–liquid boundary

$$p = p^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln \frac{T}{T^*} \quad [4.8]$$

(b) Liquid–vapor boundary

$$p = p^* e^{-\chi}, \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \times \left( \frac{1}{T} - \frac{1}{T^*} \right) \quad [4.12]$$

(c) Solid–vapor boundary

$$p = p^* e^{-\chi}, \quad \chi = \frac{\Delta_{\text{sub}}H}{R} \times \left( \frac{1}{T} - \frac{1}{T^*} \right) \quad [\text{similar to 4.12}]$$

We need  $\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H = 41.4 \text{ kJ mol}^{-1}$

$$\Delta_{\text{fus}}V = M \times \left( \frac{1}{\rho(\text{l})} - \frac{1}{\rho(\text{s})} \right) = \left( \frac{78.11 \text{ g mol}^{-1}}{\text{g cm}^{-3}} \right) \times \left( \frac{1}{0.879} - \frac{1}{0.891} \right) = +1.197 \text{ cm}^3 \text{ mol}^{-1}$$

After insertion of these numerical values into the above equations, we obtain

$$\begin{aligned} \text{(a)} \quad p &= p^* + \left( \frac{10.6 \times 10^3 \text{ J mol}^{-1}}{1.197 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} \right) \ln \frac{T}{T^*} \\ &= p^* + 8.855 \times 10^9 \text{ Pa} \times \ln \frac{T}{T^*} = p^* + (6.64 \times 10^7 \text{ Torr}) \ln \frac{T}{T^*} \quad (1 \text{ Torr} = 133.322 \text{ Pa}) \end{aligned}$$

This line is plotted as *a* in Figure 4.2, starting at  $(p^*, T^*) = (36 \text{ Torr}, 5.50 \text{ }^\circ\text{C} (278.65 \text{ K}))$ .

$$\begin{aligned} \text{(b)} \quad \chi &= \left( \frac{30.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left( \frac{1}{T} - \frac{1}{T^*} \right) = (3705 \text{ K}) \times \left( \frac{1}{T} - \frac{1}{T^*} \right) \\ p &= p^* e^{-3705 \text{ K} \times (1/T - 1/T^*)} \end{aligned}$$

This equation is plotted as line *b* in Figure 4.2, starting from  $(p^*, T^*) = (36 \text{ Torr}, 5.50 \text{ }^\circ\text{C} (278.65 \text{ K}))$ .

$$\begin{aligned} \text{(c)} \quad \chi &= \left( \frac{41.4 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left( \frac{1}{T} - \frac{1}{T^*} \right) = (4980 \text{ K}) \times \left( \frac{1}{T} - \frac{1}{T^*} \right) \\ p &= p^* e^{-4980 \text{ K} \times (1/T - 1/T^*)} \end{aligned}$$

These points are plotted as line *c* in Figure 4.2, starting at  $(36 \text{ Torr}, 5.50 \text{ }^\circ\text{C})$ .

The lighter lines in Figure 4.2 represent extensions of lines *b* and *c* into regions where the liquid and solid states respectively are not stable.

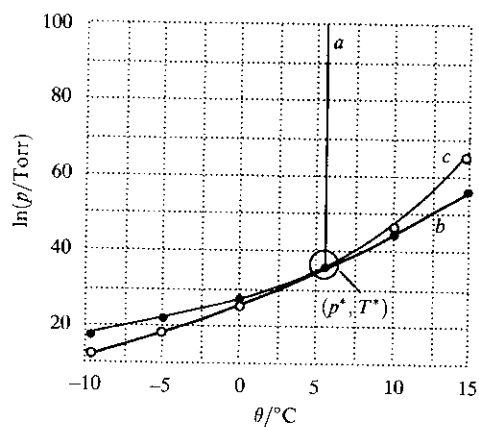


Figure 4.2

**P4.12** The slope of the solid–vapor coexistence curve is given by

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

The slope can be obtained by differentiating the coexistence curve graphically (Figure 4.3)

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

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

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

So

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

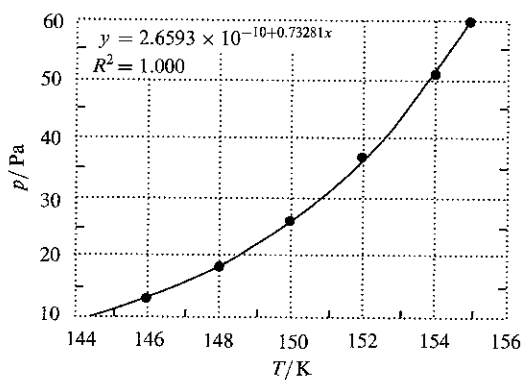


Figure 4.3

### Solutions to theoretical problems

**P4.14**  $dH = C_p dT + V dp$  implying that  $d\Delta H = \Delta C_p dT + \Delta V dp$

However, along a phase boundary  $dp$  and  $dT$  are related by

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \text{ [Clapeyron equation, e.g. 4.6, 4.7, or 4.10]}$$

Therefore,

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

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,

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

**P4.16**

$$p = p_0 e^{-Mgh/RT} \text{ [Impact I1.1]}$$

$$p = p^* e^{-\chi} \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \times \left( \frac{1}{T} - \frac{1}{T^*} \right) \text{ [4.12]}$$

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 vapor ( $p$ ) 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,  $T_h = \boxed{363 \text{ K}}$  ( $90^\circ\text{C}$ ).