

Chem 401—Physical Chemistry
Chapter 4 Homework Solutions

E4.10(b)

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

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

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

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

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

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 (a) $\left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{s})}{\partial T}\right)_p = -S_{\text{m}}(\text{l}) + S_{\text{m}}(\text{s})$ [Section 4.7, eqn 13]

$$= -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_{\text{f}}}; \quad \Delta_{\text{fus}}H = 6.01 \text{ kJ mol}^{-1} \text{ [Table 2.3]}$$

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

(b) $\left(\frac{\partial\mu(\text{g})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p = -S_{\text{m}}(\text{g}) + S_{\text{m}}(\text{l}) = -\Delta_{\text{vap}}S$

$$= \frac{-\Delta_{\text{vap}}H}{T_{\text{b}}} = \frac{-40.6 \text{ kJ mol}^{-1}}{373.15 \text{ K}} = \boxed{-109.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(c) $\Delta\mu \approx \left(\frac{\partial\mu}{\partial T}\right)_p \Delta T = -S_{\text{m}}\Delta T$ [4.1]

$$\Delta\mu(\text{l}) - \Delta\mu(\text{s}) = \mu(\text{l}, -5^\circ\text{C}) - \mu(\text{l}, 0^\circ\text{C}) - \mu(\text{s}, -5^\circ\text{C}) + \mu(\text{s}, 0^\circ\text{C})$$

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

$$\approx -\{S_{\text{m}}(\text{l}) - S_{\text{m}}(\text{s})\}\Delta T \approx -\Delta_{\text{fus}}S\Delta T$$

$$= -(5 \text{ K}) \times (-22.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{+110 \text{ J mol}^{-1}}$$

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

P4.6 $\frac{dp}{dT} = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V}$ [4.6] $= \frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}$

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

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

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

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 $\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2}$ [4.11], 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/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 K , so

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

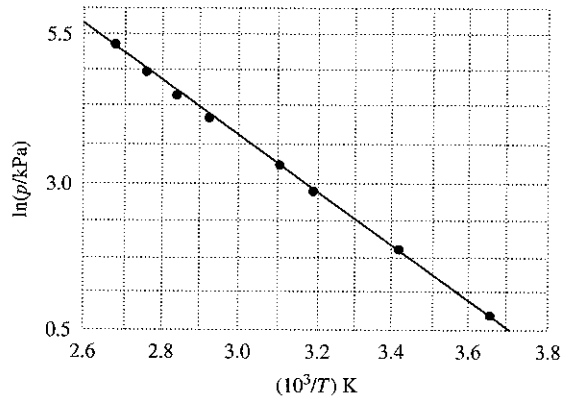


Figure 4.1

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°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.

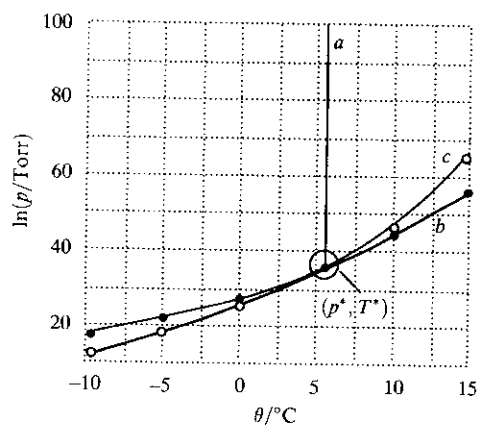


Figure 4.2

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

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

So

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

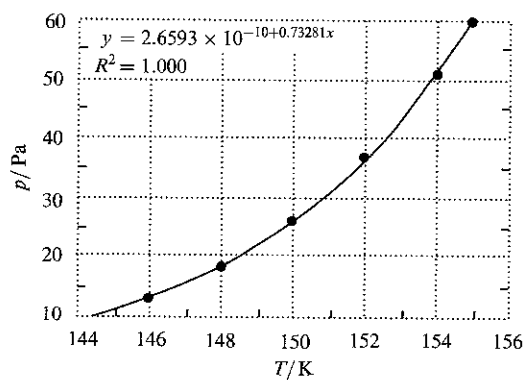


Figure 4.3

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°C).