

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

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

For water at 3000 m, taking the average molar mass of air to be  $M = 29 \text{ g mol}^{-1}$ ,

$$\begin{aligned} \frac{1}{T_h} &= \frac{1}{373 \text{ K}} + \frac{(29 \times 10^{-3} \text{ kg mol}^{-1}) \times 9.81 \text{ m s}^{-2} \times (3000 \text{ m})}{(293 \text{ K}) \times (40.7 \times 10^3 \text{ J mol}^{-1})} \\ &= \frac{1}{373 \text{ K}} + \frac{1}{1.397 \times 10^4 \text{ K}} = \frac{2.73 \times 10^{-3}}{\text{K}} \end{aligned}$$

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

**P4.19** The Clapeyron equation is inadequate because both  $V$  and  $S$  are continuous through a second-order transition. Thus,  $\Delta V$  and  $\Delta S$  vanish, resulting in an indeterminate form  $0/0$ . Just as with l'Hospital's rule in calculus, examining derivatives helps resolve the indeterminate form.

(1)  $V = V(T, p)$

so  $dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$

$$\left(\frac{\partial V}{\partial T}\right)_p = \alpha V \text{ [2.42]}, \quad \left(\frac{\partial V}{\partial p}\right)_T = -\kappa_T V \text{ [2.43]}$$

hence,  $dV = \alpha V dT - \kappa_T V dp$ .

This equation applies to both phases 1 and 2, and since  $V$  is continuous through a second-order transition

$$\alpha_1 dT - \kappa_{T,1} dp = \alpha_2 dT - \kappa_{T,2} dp$$

Solving for  $\frac{dp}{dT}$  yields  $\boxed{\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}}}$ .

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

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

To evaluate the derivative  $\partial S_m / \partial T$ , consider  $dS$  at constant  $p$ :

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

Also,  $\left(\frac{\partial S_m}{\partial p}\right)_T = -\left(\frac{\partial V_m}{\partial T}\right)_p$  [Maxwell relation; Table 3.5]  $= -\alpha V_m$

Thus,  $dS_m = \frac{C_{p,m}}{T} dT - \alpha V_m dp$

This relationship applies to both phases. For second-order transitions both  $S_m$  and  $V_m$  are continuous through the transition, so that

$$\frac{C_{p,m1}}{T} dT - \alpha_1 V_m dp = \frac{C_{p,m2}}{T} dT - \alpha_2 V_m dp$$

Solving for  $\frac{dp}{dT}$  yields  $\boxed{\frac{dp}{dT} = \frac{C_{p,m2} - C_{p,m1}}{TV_m(\alpha_2 - \alpha_1)}}$

### Solutions to applications

P4.21

(a)  $\Delta G_m = (n-4)\Delta_{hb}H_m - (n-2)T_m\Delta_{hb}S_m$  (1)

Enthalpy and entropy terms give a Gibbs energy change of  $\Delta G = \Delta H - T\Delta S$  for a constant temperature process. The enthalpy term is justified by  $n-4$  independent hydrogen bonds for which each requires  $\Delta_{hb}H_m$  of heat to break during melting dissociation. The entropy term is justified by  $n-2$  highly ordered, but independent, structures for which each experiences an entropy increase of  $\Delta_{hb}H_m$  during the melting process.

(b)  $\Delta_{tr}S = \frac{\Delta_{tr}H}{T_{tr}}$  [3.20] yields  $T_{tr} = \frac{\Delta_{tr}H}{\Delta_{tr}S}$ , which here becomes

$$T_m = \frac{(n-4)\Delta_{hb}H_m}{(n-2)\Delta_{hb}S_m}$$

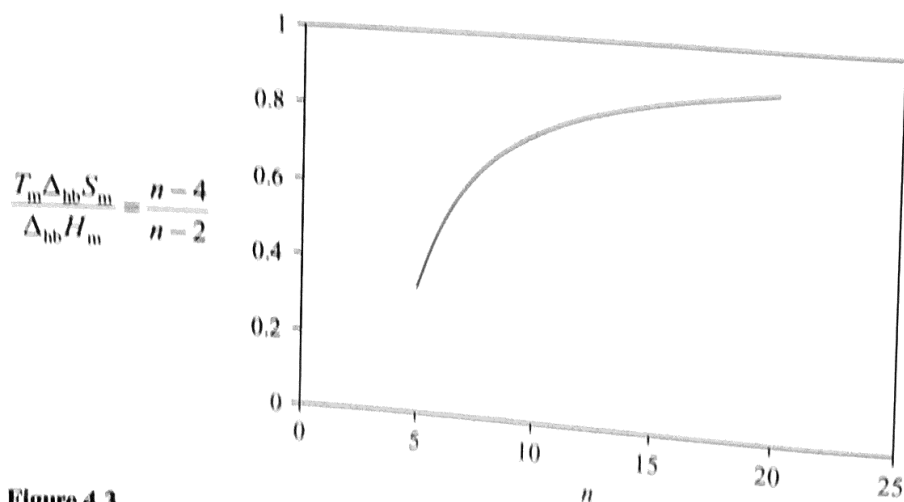


Figure 4.3

(c) See Figure 4.3.

$$\begin{aligned} \text{Consider } \frac{1}{T_m} \frac{dT_m}{dn} &= \frac{\Delta_{hb}H_m}{T_m \Delta_{hb}S_m} \frac{d(T_m \Delta_{hb}S_m / \Delta_{hb}H_m)}{dn} = \left( \frac{n-2}{n-4} \right) \frac{d}{dn} \left( \frac{n-4}{n-2} \right) \\ &= \left( \frac{n-2}{n-4} \right) \left( \frac{2}{(n-2)^2} \right) = \frac{2}{(n-4)(n-2)} \end{aligned}$$