

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

3 The Second and Third Laws

3A Entropy

Answers to discussion questions

3A.2 Everyday experience indicates that the direction of spontaneous change in an isolated system is accompanied by the dispersal of the total energy of the system. For example, for a gas expanding freely and spontaneously into a vacuum, the process is accompanied by a dispersal of energy and matter. It is easy to calculate the increase in the thermodynamic entropy that accompanies this process. For a

perfect gas this entropy change is given by the formula $\Delta S = nR \ln \frac{V_f}{V_i}$ [eqn. 3A.14], which is clearly

positive if V_f is greater than V_i . The molecular interpretation of this thermodynamic result is based on the identification of entropy with molecular disorder. An increase in disorder results from the chaotic dispersal of matter and energy and the only changes that can take place within an isolated system (the universe) are those in which this kind of dispersal occurs. This interpretation of entropy in terms of dispersal and disorder allows for a direct connection of the thermodynamic entropy to the statistical entropy through the Boltzmann formula $S = k \ln W$, where W is the number of microstates, the number of ways in which the molecules of the system can be arranged while keeping the total energy constant. The concept of the number of microstates makes quantitative the more ill-defined qualitative concepts of “disorder” and “the dispersal of matter and energy” used above to give a physical feel for the concept of entropy. A more “disorderly” distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy.

3A.4 The explanation of Trouton’s rule is that $\frac{\Delta_{\text{vap}} H^\ominus}{T_b}$ is the standard entropy of vaporization, and we expect a comparable change in volume (with an accompanying comparable change in the number of accessible microstates) whenever an unstructured liquid forms a vapor. Hence, all unstructured liquids can be expected to have similar entropies of vaporization. Liquids that show significant deviations from Trouton’s rule do so on account of strong molecular interactions that restrict molecular motion. As a result there is a greater dispersal of matter and energy when such liquids vaporize. Water is an example of a liquid with strong intermolecular interactions (hydrogen bonding) which tend to organize the molecules in the liquid, hence we expect its entropy of vaporization to be greater than $85 \text{ J K}^{-1} \text{ mol}^{-1}$.

Solutions to exercises

3A.1(b) All spontaneous processes are irreversible processes, which implies through eqn. 3A.12, the Clausius inequality, that $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$, for all spontaneous processes. In this case, $\Delta S_{\text{tot}} = 10 \text{ J K}^{-1} > 0$, so the process may be spontaneous.

3A.2(b) Efficiency, η , is $\frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h} = \frac{0.71 \text{ kJ}}{2.71 \text{ kJ}} = 0.262$. For an ideal

Heat engine we have $\eta_{\text{rev}} = 1 - \frac{T_c}{T_h}$ [3A.10] $= 0.262 = 1 - \frac{T_c}{273.16 \text{ K}}$. Solving for T_c , we

obtain $T_c = 201.6 \text{ K}$ as the temperature of the organic liquid.

3A.3(b) Assume that the block is so large that its temperature does not change significantly as a result of the heat transfer. Then

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} \quad [3A.2] = \frac{1}{T} \int_i^f dq_{\text{rev}} \quad [\text{constant } T] = \frac{q_{\text{rev}}}{T}$$

$$(a) \Delta S = \frac{250 \times 10^3 \text{ J}}{293.15 \text{ K}} = \boxed{853 \text{ J K}^{-1}} \quad (b) \Delta S = \frac{250 \times 10^3 \text{ J}}{373.15 \text{ K}} = \boxed{670 \text{ J K}^{-1}}$$

3A.4(b) $\text{CO}_2(\text{g})$ will have the higher standard molar entropy, primarily because ΔS_{fus} and ΔS_{vap} are greater for $\text{CO}_2(\text{g})$.

3A.5(b) We use

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) \quad [3A.14]$$

$$= \left(\frac{4.00 \text{ g}}{28.0 \text{ g/mol}} \right) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left(\frac{750}{500} \right) = \boxed{0.482 \text{ J K}^{-1}}$$

3A.6(b) Trouton's rule in the form $\Delta_{\text{vap}} H^\ominus = T_b \times 85 \text{ J K}^{-1} \text{ mol}^{-1}$ can be used to obtain approximate enthalpies of vaporization. For cyclohexane

$$\Delta_{\text{vap}} H^\ominus = (273.2 + 80.7) \text{ K} \times 85 \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{30.1 \text{ kJ/mol}^{-1}}$$

3A.7(b) At 250 K, the entropy is equal to its entropy at 298 K plus ΔS where

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{V,m} dT}{T} = C_{V,m} \ln \frac{T_f}{T_i}$$

so $S = 154.84 \text{ J K}^{-1} \text{ mol}^{-1} + [(20.786 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}] \times \ln \frac{250 \text{ K}}{298 \text{ K}}$

$$S = \boxed{152.65 \text{ J K}^{-1} \text{ mol}^{-1}}$$

3A.8(b) No matter how the change occurred, ΔS has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2)

$$\Delta S = \Delta S_1 + \Delta S_2$$

For the first step

$$\Delta S_1 = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{p,m} dT}{T} = C_{p,m} \ln \frac{T_f}{T_i}$$

$$\Delta S_1 = (2.00 \text{ mol}) \times \left(\frac{7}{2} \right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{(135 + 273) \text{ K}}{(25 + 273) \text{ K}} = 18.3 \text{ J K}^{-1}$$

and for the second

$$\Delta S_2 = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

$$\text{where } q_{\text{rev}} = -w = \int p dV = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{p_i}{p_f}$$

$$\text{so } \Delta S_2 = nR \ln \frac{p_i}{p_f} = (2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{1.50 \text{ atm}}{7.00 \text{ atm}} = -25.6 \text{ J K}^{-1}$$

$$\Delta S = (18.3 - 25.6) \text{ J K}^{-1} = \boxed{-7.3 \text{ J K}^{-1}}$$

The heat lost in step 2 was more than the heat gained in step 1, resulting in a net loss of entropy. Or the ordering represented by confining the sample to a smaller volume in step 2 overcame the disordering represented by the temperature rise in step 1. A negative entropy change is allowed for a system as long as an increase in entropy elsewhere results in $\Delta S_{\text{total}} > 0$.

3A.9(b) Since the masses are equal and the heat capacity is assumed constant, the final temperature will be the average of the two initial temperatures,

$$T_f = \frac{1}{2}(100^\circ\text{C} + 25^\circ\text{C}) = 62.5^\circ\text{C}$$

The heat capacity of each block is $C = mC_s$ where C_s is the specific heat capacity. So,

$$\Delta H(\text{individual}) = mC_s\Delta T = 10.0 \times 10^3 \text{ g} \times 0.449 \text{ J K}^{-1} \text{ g}^{-1} \times (\pm 37.5 \text{ K}) = \pm 168 \text{ kJ}$$

These two enthalpy changes add up to zero: $\Delta H_{\text{tot}} = 0$

$$\Delta S = mC_s \ln\left(\frac{T_f}{T_i}\right); \quad 100^\circ\text{C} = 373.2 \text{ K}; \quad 25^\circ\text{C} = 298.2 \text{ K}; \quad 62.5^\circ\text{C} = 335.7 \text{ K}$$

$$\Delta S_1 = (10.0 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{335.7}{298.2}\right) = 532 \text{ J K}^{-1}$$

$$\Delta S_2 = (10.0 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{335.7}{373.2}\right) = -475 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 = 57 \text{ J K}^{-1}$$

3A.10(b) (i)

$$\Delta S(\text{gas}) = nR \ln\left(\frac{V_f}{V_i}\right) [3A.14] = \left(\frac{21 \text{ g}}{39.95 \text{ g mol}^{-1}}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{4.60 \text{ dm}^3}{1.20 \text{ dm}^3}$$

$$= 5.873 \text{ J K}^{-1} = 5.9 \text{ J K}^{-1}$$

$$\Delta S(\text{surroundings}) = -\Delta S(\text{gas}) = -5.9 \text{ J K}^{-1} \text{ [reversible]}$$

$$\Delta S(\text{total}) = 0$$

(ii) $\Delta S(\text{gas}) = +5.9 \text{ J K}^{-1}$ [S is a state function]

$$\Delta S(\text{surroundings}) = 0 \text{ [no change in surroundings]}$$

$$\Delta S(\text{total}) = +5.9 \text{ J K}^{-1}$$

(iii) $q_{\text{rev}} = 0$ so $\Delta S(\text{gas}) = 0$

$$\Delta S(\text{surroundings}) = 0 \text{ [No heat is transferred to the surroundings]}$$

$$\Delta S(\text{total}) = 0$$

3A.11(b) (i)

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_b} = \frac{35.27 \times 10^3 \text{ J mol}^{-1}}{(64.1 + 273.15) \text{ K}} = +104.58 \text{ J K}^{-1} = 104.6 \text{ J K}^{-1}$$

(ii) If vaporization occurs reversibly, as is generally assumed

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0 \quad \text{so} \quad \Delta S_{\text{sur}} = -104.6 \text{ J K}^{-1}$$

Comment. This calculation has been based on the assumption that the heat capacities remain constant over the range of temperatures involved and that the enthalpy of vaporization at 298.15 K given in Table 3A.2 can be applied to the vaporization at 373.15 K. Neither one of these assumptions are strictly valid. Therefore, the calculated value is only approximate.

$$3A.12(b) \quad \Delta S = nC_p(\text{H}_2\text{O},s)\ln\frac{T_f}{T_i} + n\frac{\Delta_{\text{fus}}H}{T_{\text{fus}}} + nC_p(\text{H}_2\text{O},l)\ln\frac{T_f}{T_i} + n\frac{\Delta_{\text{vap}}H}{T_{\text{vap}}} + nC_p(\text{H}_2\text{O},g)\ln\frac{T_f}{T_i}$$

$$n = \frac{15.0 \text{ g}}{18.02 \text{ g mol}^{-1}} = 0.832 \text{ mol}$$

$$\begin{aligned} \Delta S &= 0.832 \text{ mol} \times 38.02 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{273.15}{261.15} + 0.832 \text{ mol} \times \frac{6.008 \text{ kJ/mol}^{-1}}{273.15 \text{ K}} \\ &+ 0.832 \text{ mol} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{373.15}{273.15} \\ &+ 0.832 \text{ mol} \times \frac{40.657 \text{ kJ/mol}^{-1}}{373.15 \text{ K}} + 0.832 \text{ mol} \times 33.58 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{378.15}{373.15} \end{aligned}$$

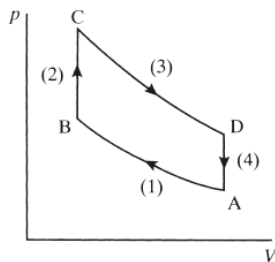
$$\boxed{\Delta S = 130.3 \text{ J K}^{-1}}$$

Comment. This calculation was based on the assumption that heat capacities were constant over the range of temperatures involved. This assumption is not strictly valid. Therefore the calculated value is only approximate.

Problems

3A.2 The Otto cycle is represented in Fig. 3.1. Assume one mole of air.

Figure 3A.1



$$\eta = \frac{|w|_{\text{cycle}}}{|q_2|} \quad [3A.8]$$

$$w_{\text{cycle}} = w_1 + w_3 = \Delta U_1 + \Delta U_3 \quad [q_1 = q_3 = 0] = C_V(T_B - T_A) + C_V(T_D - T_C)$$

$$q_2 = \Delta U_2 = C_V(T_C - T_B)$$

$$\eta = \frac{|T_B - T_A + T_D - T_C|}{|T_C - T_B|} = 1 - \left(\frac{T_D - T_A}{T_C - T_B} \right)$$

We know that

$$\frac{T_A}{T_B} = \left(\frac{V_B}{V_A} \right)^{1/c} \quad \text{and} \quad \frac{T_D}{T_C} = \left(\frac{V_C}{V_D} \right)^{1/c} \quad [2E.2a]$$

Since $V_B = V_C$ and $V_A = V_D$, $\frac{T_A}{T_B} = \frac{T_D}{T_C}$, or $T_D = \frac{T_A T_C}{T_B}$

Then $\eta = 1 - \frac{\frac{T_A T_C}{T_B} - T_A}{T_C - T_B} = 1 - \frac{T_A}{T_B}$ or $\eta = 1 - \left(\frac{V_B}{V_A}\right)^{1/c}$

Given that $C_{p,m} = 7/2R$, we have $C_{v,m} = 5/2R$ [2D.11] and $c = \frac{2}{5}$

For $\frac{V_A}{V_B} = 10$, $\eta = 1 - \left(\frac{1}{10}\right)^{2/5} = \boxed{0.47}$

$\Delta S_1 = \Delta S_3 = \Delta S_{\text{sur},1} = \Delta S_{\text{sur},3} = \boxed{0}$ [adiabatic reversible steps]

$\Delta S_2 = C_{v,m} \ln\left(\frac{T_C}{T_B}\right)$

At constant volume $\left(\frac{T_C}{T_B}\right) = \left(\frac{P_C}{P_B}\right) = 5.0$

$\Delta S_2 = \left(\frac{5}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (\ln 5.0) = \boxed{+33 \text{ J K}^{-1}}$

$\Delta S_{\text{sur},2} = -\Delta S_2 = \boxed{-33 \text{ J K}^{-1}}$

$\Delta S_4 = -\Delta S_2 \left[\frac{T_C}{T_D} = \frac{T_B}{T_A}\right] = \boxed{-33 \text{ J K}^{-1}}$

$\Delta S_{\text{sur},4} = -\Delta S_4 = \boxed{+33 \text{ J K}^{-1}}$

3A.4 (a) As suggested, relate the work to the temperature-dependent coefficient of performance :

$$|dw| = \frac{|dq_c|}{c} = \frac{|C_p dT|}{\left(\frac{T}{T_h - T}\right)} = C_p \left| \frac{T_h dT}{T} - dT \right|$$

Integrating yields

$$|w| = C_p \left| T_h \int_{T_i}^{T_f} \frac{dT}{T} + \int_{T_i}^{T_f} dT \right| = C_p \left| T_h \ln \frac{T_f}{T_i} - (T_f - T_i) \right| = C_p \left(T_h \ln \frac{T_f}{T_i} - T_i + T_f \right)$$

(b) The heat capacity is $C_p = (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (250 \text{ g}) = 1046 \text{ J K}^{-1}$, so the work associated with cooling the water from 293 K to the freezing temperature is

$$|w|_{\text{cooling}} = 1046 \text{ J K}^{-1} \times \left(293 \text{ K} \times \ln \frac{293 \text{ K}}{273 \text{ K}} - 293 \text{ K} + 273 \text{ K} \right) = 748 \text{ J}$$

The refrigerator must also remove the heat of fusion at the freezing temperature. For this isothermal process, the coefficient of performance does not change, so

$$\begin{aligned} |w|_{\text{freeze}} &= \frac{|q_c|}{c} = \frac{\Delta_{\text{fus}} H}{\left(\frac{T_c}{T_h - T_c}\right)} = \Delta_{\text{fus}} H \left(\frac{T_h - T_c}{T_c}\right) \\ &= 6.008 \times 10^3 \text{ J mol}^{-1} \times \frac{250 \text{ g}}{18.0 \text{ g mol}^{-1}} \times \left(\frac{293 - 273}{273}\right) = 6113 \text{ J} \end{aligned}$$

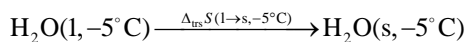
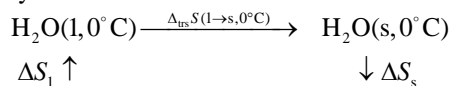
The total work is

$$|w|_{\text{total}} = |w|_{\text{cooling}} + |w|_{\text{freeze}} = (748 + 6113) \text{ J} = \boxed{6.86 \times 10^3 \text{ J} = 6.86 \text{ kJ}}$$

At the rate of $100 \text{ W} = 100 \text{ J s}^{-1}$, the refrigerator would freeze the water in

$$t = \frac{6.86 \times 10^3 \text{ J}}{100 \text{ J s}^{-1}} = \boxed{68.6 \text{ s}}$$

3A.6 (a) Because entropy is a state function $\Delta_{\text{us}}S(1 \rightarrow s, -5^\circ\text{C})$ may be determined indirectly from the following cycle



Thus $\Delta_{\text{us}}S(1 \rightarrow s, -5^\circ\text{C}) = \Delta S_1 + \Delta_{\text{us}}S(1 \rightarrow s, 0^\circ\text{C}) + \Delta S_s$,

where $\Delta S_1 = C_{p,m}(l) \ln \frac{T_f}{T}$ [3A.20; $\theta_f = 0^\circ\text{C}$, $\theta = -5^\circ\text{C}$]

and $\Delta S_s = C_{p,m}(s) \ln \frac{T}{T_f}$

$$\Delta S_1 + \Delta S_s = -\Delta C_p \ln \frac{T}{T_f} \quad \text{with } \Delta C_p = C_{p,m}(l) - C_{p,m}(s) = +37.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{\text{us}}S(1 \rightarrow s, T_f) = \frac{-\Delta_{\text{fus}}H}{T_f} \quad [3A.17]$$

Thus, $\Delta_{\text{us}}S(1 \rightarrow s, T) = \frac{-\Delta_{\text{fus}}H}{T_f} - \Delta C_p \ln \frac{T}{T_f}$

$$\begin{aligned} \Delta_{\text{us}}S(1 \rightarrow s, -5^\circ\text{C}) &= \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}} - (37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{268}{273} \\ &= \boxed{-21.3 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\Delta S_{\text{sur}} = \frac{\Delta_{\text{fus}}H(T)}{T}$$

$$\Delta_{\text{fus}}H(T) = -\Delta H_1 + \Delta_{\text{fus}}H(T_f) - \Delta H_s$$

$$\Delta H_1 + \Delta H_s = C_{p,m}(l)(T_f - T) + C_{p,m}(s)(T - T_f) = \Delta C_p(T_f - T)$$

$$\Delta_{\text{fus}}H(T) = \Delta_{\text{fus}}H(T_f) - \Delta C_p(T_f - T)$$

Thus, $\Delta S_{\text{sur}} = \frac{\Delta_{\text{fus}}H(T)}{T} = \frac{\Delta_{\text{fus}}H(T_f)}{T} + \Delta C_p \frac{(T - T_f)}{T}$

$$\begin{aligned} \Delta S_{\text{sur}} &= \frac{6.01 \text{ kJ mol}^{-1}}{268 \text{ K}} + (37.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{268 - 273}{268} \right) \\ &= \boxed{+21.7 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sur}} + \Delta S = (21.7 - 21.3) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+0.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Because $\Delta S_{\text{total}} > 0$, the transition $1 \rightarrow s$ is spontaneous at -5°C .

(b) A similar cycle and analysis can be set up for the transition liquid \rightarrow vapour at 95°C . However, since the transformation here is to the high temperature state (vapour) from the low temperature state (liquid), which is the opposite of part (a), we can expect that the analogous equations will occur with a change of sign.

$$\begin{aligned} \Delta_{\text{us}}S(1 \rightarrow g, T) &= \Delta_{\text{us}}S(1 \rightarrow g, T_b) + \Delta C_p \ln \frac{T}{T_b} \\ &= \frac{\Delta_{\text{vap}}H}{T_b} + \Delta C_p \ln \frac{T}{T_b}, \quad \Delta C_p = -41.9 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{us}}S(1 \rightarrow g, T) &= \frac{40.7 \text{ kJ mol}^{-1}}{373 \text{ K}} - (41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{368}{373} \right) \\ &= \boxed{+109.7 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned}\Delta S_{\text{sur}} &= \frac{-\Delta_{\text{vap}} H(T)}{T} = -\frac{\Delta_{\text{vap}} H(T_b)}{T} - \frac{\Delta C_p (T - T_b)}{T} \\ &= \left(\frac{-40.7 \text{ kJ mol}^{-1}}{368 \text{ K}} \right) - (-41.9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{368 - 373}{368} \right) \\ &= \boxed{-111.2 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

$$\Delta S_{\text{total}} = (109.7 - 111.2) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-1.5 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Since $\Delta S_{\text{total}} < 0$, the reverse transition, $g \rightarrow l$, is spontaneous at 95°C .

3A.8 (a) $q(\text{total}) = q(\text{H}_2\text{O}) + q(\text{Cu}) = 0$, hence $-q(\text{H}_2\text{O}) = q(\text{Cu})$

$$q(\text{H}_2\text{O}) = n(-\Delta_{\text{vap}} H) + nC_{p,m}(\text{H}_2\text{O}, l) \times (\theta - 100^\circ\text{C})$$

where θ is the final temperature of the water and copper.

$$q(\text{Cu}) = mC_s(\theta - 0) = mC_s\theta, \quad C_s = 0.385 \text{ J K}^{-1} \text{ g}^{-1} [C_s = C_{p,m}/M]$$

Setting $-q(\text{H}_2\text{O}) = q(\text{Cu})$ allows us to solve for θ .

$$n(\Delta_{\text{vap}} H) - nC_{p,m}(\text{H}_2\text{O}, l) \times (\theta - 100^\circ\text{C}) = mC_s\theta$$

Solving for θ yields:

$$\begin{aligned}\theta &= \frac{n\{\Delta_{\text{vap}} H + C_{p,m}(\text{H}_2\text{O}, l) \times 100^\circ\text{C}\}}{mC_s + nC_{p,m}(\text{H}_2\text{O}, l)} \\ &= \frac{(1.00 \text{ mol}) \times (40.656 \times 10^3 \text{ J mol}^{-1} + 75.3 \text{ J}^\circ\text{C}^{-1} \text{ mol}^{-1} \times 100^\circ\text{C})}{2.00 \times 10^3 \text{ g} \times 0.385 \text{ J}^\circ\text{C}^{-1} \text{ g}^{-1} + 1.00 \text{ mol} \times 75.3 \text{ J}^\circ\text{C}^{-1} \text{ mol}^{-1}} \\ &= 57.0^\circ\text{C} = 330.2 \text{ K}\end{aligned}$$

$$q(\text{Cu}) = (2.00 \times 10^3 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times (57.0 \text{ K}) = 4.39 \times 10^4 \text{ J} = \boxed{43.9 \text{ kJ}}$$

$$q(\text{H}_2\text{O}) = \boxed{-43.9 \text{ kJ}}$$

$$\Delta S(\text{total}) = \Delta S(\text{H}_2\text{O}) + \Delta S(\text{Cu})$$

$$\begin{aligned}\Delta S(\text{H}_2\text{O}) &= \frac{-n\Delta_{\text{vap}} H}{T_b} [3A.17] + nC_{p,m} \ln\left(\frac{T_f}{T_i}\right) [3A.20] \\ &= -\frac{(1.00 \text{ mol}) \times (40.656 \times 10^3 \text{ J mol}^{-1})}{373.2 \text{ K}}\end{aligned}$$

$$+ (1.00 \text{ mol}) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{330.2 \text{ K}}{373.2 \text{ K}}\right)$$

$$= -108.9 \text{ J K}^{-1} - 9.22 \text{ J K}^{-1} = \boxed{-118.1 \text{ J K}^{-1}}$$

$$\begin{aligned}\Delta S(\text{Cu}) &= mC_s \ln\left(\frac{T_f}{T_i}\right) = (2.00 \times 10^3 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{330.2 \text{ K}}{273.2 \text{ K}}\right) \\ &= \boxed{145.9 \text{ J K}^{-1}}\end{aligned}$$

$$\Delta S(\text{total}) = -118.1 \text{ J K}^{-1} + 145.9 \text{ J K}^{-1} = \boxed{28 \text{ J K}^{-1}}$$

This process is spontaneous since $\Delta S(\text{surroundings})$ (surroundings) is zero and, hence,

$$\Delta S(\text{universe}) = \Delta S(\text{total}) > 0$$

(b) The volume of the container may be calculated from the perfect gas law.

$$V = \frac{nRT}{p} = \frac{(1.00 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (373.2 \text{ K})}{1.00 \text{ atm}} = 30.6 \text{ dm}^3$$

At 57°C the vapor pressure of water is 130 Torr (*Handbook of Chemistry and Physics*, 81st edition). The amount of water vapor present at equilibrium is then

$$n = \frac{pV}{RT} = \frac{(130 \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right) \times (30.6 \text{ dm}^3)}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (330.2 \text{ K})} = 0.193 \text{ mol}$$

This is a substantial fraction of the original amount of water and cannot be ignored. Consequently the calculation needs to be redone taking into account the fact that only a part, n_1 , of the vapor condenses into a liquid while the remainder $(1.00 \text{ mol} - n_1)$ remains gaseous. The heat flow involving water, then, becomes

$$q(\text{H}_2\text{O}) = -n_1 \Delta_{\text{vap}} H + n_1 C_{p,m}(\text{H}_2\text{O}, l) \Delta T(\text{H}_2\text{O}) \\ + (1.00 \text{ mol} - n_1) C_{p,m}(\text{H}_2\text{O}, g) \Delta T(\text{H}_2\text{O})$$

Because n_1 depends on the equilibrium temperature through

$n_1 = 1.00 \text{ mol} - \frac{pV}{RT}$, where p is the vapor pressure of water, we will have two unknowns (p and T) in

the equation $-q(\text{H}_2\text{O}) = q(\text{Cu})$. There are two ways out of this dilemma: (1) p may be expressed as a function of T by use of the Clapeyron equation, or (2) by use of successive approximations. Redoing the calculation yields:

$$\theta = \frac{n_1 \Delta_{\text{vap}} H + n_1 C_{p,m}(\text{H}_2\text{O}, l) \times 100^\circ\text{C} + (1.00 - n_1) C_{p,m}(\text{H}_2\text{O}, g) \times 100^\circ\text{C}}{mC_s + nC_{p,m}(\text{H}_2\text{O}, l) + (1.00 - n_1) C_{p,m}(\text{H}_2\text{O}, g)}$$

With

$$n_1 = (1.00 \text{ mol}) - (0.193 \text{ mol}) = 0.807 \text{ mol}$$

(noting that $C_{p,m}(\text{H}_2\text{O}, g) = 33.6 \text{ J mol}^{-1} \text{ K}^{-1}$ [Table 2C.2]) $\theta = 47.2^\circ\text{C}$. At this temperature, the vapor pressure of water is 80.41 Torr, corresponding to

$$n_1 = (1.00 \text{ mol}) - (0.123 \text{ mol}) = 0.877 \text{ mol}$$

This leads to $\theta = 50.8^\circ\text{C}$. The successive approximations eventually converge to yield a value of $\theta = \boxed{49.9^\circ\text{C} = 323.1 \text{ K}}$ for the final temperature. (At this temperature, the vapor pressure is 0.123 bar.)

Using this value of the final temperature, the heat transferred and the various entropies are calculated as in part (a).

$$q(\text{Cu}) = (2.00 \times 10^3 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times (49.9 \text{ K}) = \boxed{38.4 \text{ kJ}} = -q(\text{H}_2\text{O})$$

$$\Delta S(\text{H}_2\text{O}) = \frac{-n \Delta_{\text{vap}} H}{T_b} + n C_{p,m} \ln \left(\frac{T_f}{T_i} \right) = \boxed{-119.8 \text{ J K}^{-1}}$$

$$\Delta S(\text{Cu}) = m C_s \ln \frac{T_f}{T_i} = \boxed{129.2 \text{ J K}^{-1}}$$

$$\Delta S(\text{total}) = -119.8 \text{ J K}^{-1} + 129.2 \text{ J K}^{-1} = \boxed{9 \text{ J K}^{-1}}$$

3A.10 ΔS depends on only the initial and final states, so we can use $\Delta S = n C_{p,m} \ln \frac{T_f}{T_i}$ [3A.20]

Since $q = n C_{p,m} (T_f - T_i)$, $T_f = T_i + \frac{q}{n C_{p,m}} = T_i + \frac{I^2 R t}{n C_{p,m}}$ [$q = ItV = I^2 R t$]

That is, $\Delta S = n C_{p,m} \ln \left(1 + \frac{I^2 R t}{n C_{p,m} T_i} \right)$

Since $n = \frac{500 \text{ g}}{63.5 \text{ g mol}^{-1}} = 7.87 \text{ mol}$

$$\Delta S = (7.87 \text{ mol}) \times (24.4 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(1 + \frac{(1.00 \text{ A})^2 \times (1000 \Omega) \times (15.0 \text{ s})}{(7.87) \times (24.4 \text{ J K}^{-1}) \times (293 \text{ K})} \right) \\ = (192 \text{ J K}^{-1}) \times (\ln 1.27) = \boxed{+45.4 \text{ J K}^{-1}}$$

$$[1 \text{ J} = 1 \text{ AVs} = 1 \text{ A}^2 \Omega \text{ s}]$$

For the second experiment, no change in state occurs for the copper, hence, $\Delta S(\text{copper}) = 0$. However, for the water, considered as a large heat sink

$$\Delta S(\text{water}) = \frac{q}{T} = \frac{I^2 R t}{T} = \frac{(1.00 \text{ A})^2 \times (1000 \Omega) \times (15.0 \text{ s})}{293 \text{ K}} = \boxed{+51.2 \text{ J K}^{-1}}$$

3A.12 Let us write Newton's law of cooling as follows:

$$\frac{dT}{dt} = -A(T - T_s)$$

Where A is a constant characteristic of the system and T_s is the temperature of the surroundings. The negative sign appears because we assume $T > T_s$. Separating variables

$$\frac{dT}{T - T_s} = -A dt, \text{ and integrating, we obtain}$$

$$\ln(T - T_s) = -At + K, \text{ where } K \text{ is a constant of integration.}$$

Let T_i be the initial temperature of the system when $t = 0$, then

$$K = \ln(T_i - T_s)$$

Introducing this expression for K gives

$$\ln\left(\frac{T - T_s}{T_i - T_s}\right) = -At \text{ or } T = T_s + (T_i - T_s)e^{-At}$$

$$\frac{dS}{dt} = \frac{d}{dt}\left(C \ln \frac{T}{T_i}\right) = \frac{d}{dt}(C \ln T)$$

From the above expression for T , we obtain $\ln T = \ln T_s - At \ln(T_i - T_s)$. Substituting $\ln t$ we

obtain $\boxed{\frac{dS}{dt} = -CA \ln(T_i - T_s)}$, where now T_i can be interpreted as any temperature T during the course of the cooling process.

3B The measurement of entropy

Solutions to exercises

3B.1(b) Use $S_m = R \ln s$, where s is the number of orientations of about equal energy that the molecule can adopt.

Draw up the following table:

$n:$	0	1	2			3			4			5	6
			o	m	p	a	b	c	o	m	p		
s	1	6	6	6	3	6	6	2	6	6	3	6	1
S_m/R	0	1.8	1.8	1.8	1.1	1.8	1.8	0.7	1.8	1.8	1.1	1.8	0

where a is the 1,2,3 isomer, b the 1,2,4 isomer, and c the 1,3,5 isomer.

3B.2(b)

(i)
$$\Delta_r S^\ominus = S_m^\ominus(\text{Zn}^{2+}, \text{aq}) + S_m^\ominus(\text{Cu}, \text{s}) - S_m^\ominus(\text{Zn}, \text{s}) - S_m^\ominus(\text{Cu}^{2+}, \text{aq})$$

$$= [-112.1 + 33.15 - 41.63 + 99.6] \text{J K}^{-1} \text{mol}^{-1} = \boxed{-21.0 \text{J K}^{-1} \text{mol}^{-1}}$$

(ii)
$$\Delta_r S^\ominus = 12S_m^\ominus(\text{CO}_2, \text{g}) + 11S_m^\ominus(\text{H}_2\text{O}, \text{l}) - S_m^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12S_m^\ominus(\text{O}_2, \text{g})$$

$$= [(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14)] \text{J K}^{-1} \text{mol}^{-1}$$

$$= \boxed{+512.0 \text{J K}^{-1} \text{mol}^{-1}}$$

Solutions to problems

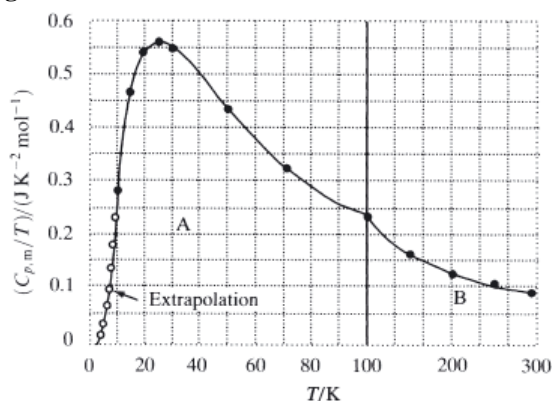
3B.2
$$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}}{T} dT \quad [3A.19]$$

From the data, draw up the following table

T / K	10	15	20	25	30	50
$\frac{C_{p,m}}{T} / (\text{J K}^{-2} \text{mol}^{-1})$	0.28	0.47	0.540	0.564	0.550	0.428
T / K	70	100	150	200	250	298
$\frac{C_{p,m}}{T} / (\text{J K}^{-2} \text{mol}^{-1})$	0.333	0.245	0.169	0.129	0.105	0.089

Plot $C_{p,m}/T$ against T (Fig. 3B.1). This has been done on two scales. The region 0 to 10 K has been constructed using $C_{p,m} = aT^3$, fitted to the point at $T = 10 \text{ K}$, at which $C_{p,m} = 2.8 \text{ J K}^{-1} \text{mol}^{-1}$, so $a = 2.8 \times 10^{-3} \text{ J K}^{-4} \text{mol}^{-1}$. The area can be determined (primitively) by counting squares. Area A = $38.28 \text{ J K}^{-1} \text{mol}^{-1}$. Area B up to $0^\circ\text{C} = 25.60 \text{ J K}^{-1} \text{mol}^{-1}$; area B up to $25^\circ\text{C} = 27.80 \text{ J K}^{-1} \text{mol}^{-1}$. Hence

Figure 3B.1



(a)
$$S_m(273 \text{ K}) = S_m(0) + \boxed{63.88 \text{J K}^{-1} \text{mol}^{-1}}$$

(b)
$$S_m(298 \text{ K}) = S_m(0) + \boxed{66.08 \text{J K}^{-1} \text{mol}^{-1}}$$

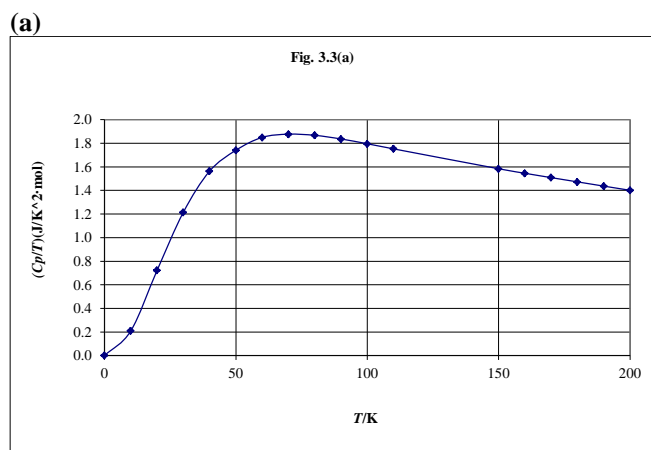
3B.4
$$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}}{T} dT \quad [3A.19]$$

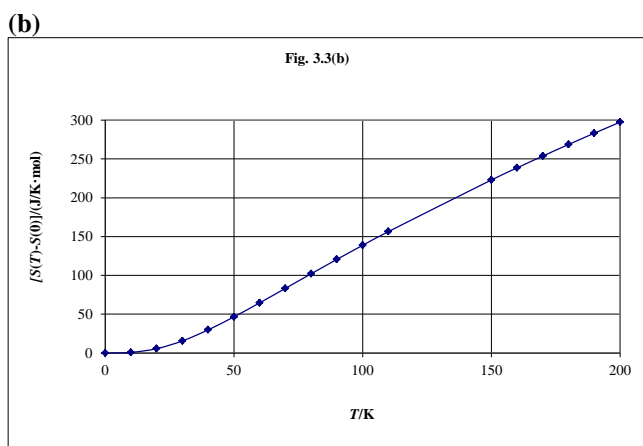
Perform a graphical integration by plotting $C_{p,m}/T$ against T and determining the area under the curve. Draw up the following table. (The last two columns come from determining areas under the curves described below.)

T/K	$\frac{C_{p,m}}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{C_{p,m}}{T}/\text{J K}^{-2} \text{mol}^{-1}$	$\frac{S_m^\ominus - S_m^\ominus(0)}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{H_m^\ominus - H_m^\ominus(0)}{\text{kJ mol}^{-1}}$
0.00	0.00	0.00	0.00	0.00
10.00	2.09	0.21	0.80	0.01
20.00	14.43	0.72	5.61	0.09
30.00	36.44	1.21	15.60	0.34
40.00	62.55	1.56	29.83	0.85
50.00	87.03	1.74	46.56	1.61
60.00	111.00	1.85	64.62	2.62
70.00	131.40	1.88	83.29	3.84
80.00	149.40	1.87	102.07	5.26
90.00	165.30	1.84	120.60	6.84
100.00	179.60	1.80	138.72	8.57
110.00	192.80	1.75	156.42	10.44
150.00	237.60	1.58	222.91	19.09
160.00	247.30	1.55	238.54	21.52
170.00	256.50	1.51	253.79	24.05
180.00	265.10	1.47	268.68	26.66
190.00	273.00	1.44	283.21	29.35
200.00	280.30	1.40	297.38	32.13

Plot $C_{p,m}$ against T (Fig. 3B.2(a)). Extrapolate to $T = 0$ using $C_{p,m} = aT^3$ fitted to the point at $T = 10$ K, which gives $a = 2.09 \text{ mJ K}^{-2} \text{ mol}^{-1}$. Determine the area under the graph up to each T and plot S_m against T (Fig. 3B.2(b)).

Figure 3B.2

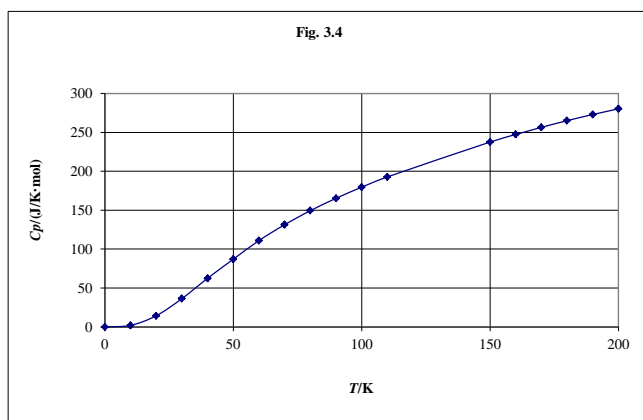




The molar enthalpy is determined in a similar manner from a plot of $C_{p,m}$ against T by determining the area under the curve (Fig. 3.4)

$$H_m^\ominus(200\text{ K}) - H_m^\ominus(0) = \int_0^{200\text{ K}} C_{p,m} dT = \boxed{32.1\text{ kJ mol}^{-1}}$$

Figure 3B.3



3B.6 The entropy at 200 K is calculated from

$$S_m^\ominus(200\text{ K}) = S_m^\ominus(100\text{ K}) + \int_{100\text{ K}}^{200\text{ K}} \frac{C_{p,m} dT}{T}$$

The integrand may be evaluated at each of the data points; the transformed data appear below. The numerical integration can be carried out by a standard procedure such as the trapezoid rule (taking the integral within any interval as the mean value of the integrand times the length of the interval). Programs for performing this integration are readily available for personal computers. Many graphing calculators will also perform this numerical integration.

T / K	100	120	140	150	160	180	200
$C_{p,m} / (\text{J K}^{-1} \text{ mol}^{-1})$	23.00	23.74	24.25	24.44	24.61	24.89	25.11
$\frac{C_{p,m}}{T} / (\text{J K}^{-2} \text{ mol}^{-1})$	0.230	0.1978	0.1732	0.1629	0.1538	0.1383	0.1256

Integration by the trapezoid rule yields

$$S_m^\ominus(200\text{ K}) = (29.79 + 16.81) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{46.60 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Taking $C_{p,m}$ constant yields

$$\begin{aligned} S_m^\ominus(200 \text{ K}) &= S_m^\ominus(100 \text{ K}) + C_{p,m} \ln(200 \text{ K} / 100 \text{ K}) \\ &= [29.79 + 24.44 \ln(200 / 100 \text{ K})] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{46.60 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

The difference is slight.

3B.8

$S = k \ln W$ [also see Exercises 3B.1(a) and (b)]

$$S = k \ln 4^N = Nk \ln 4$$

so

$$= (5 \times 10^8) \times (1.38 \times 10^{-23} \text{ J K}^{-1}) \times \ln 4 = \boxed{9.57 \times 10^{-15} \text{ J K}^{-1}}$$

Question. Is this a large residual entropy? The answer depends on what comparison is made. Multiply the answer by Avogadro's number to obtain the molar residual entropy, $5.76 \times 10^9 \text{ J K}^{-1} \text{ mol}^{-1}$, surely a large number—but then DNA is a macromolecule. The residual entropy per mole of base pairs may be a more reasonable quantity to compare to molar residual entropies of small molecules. To obtain that answer, divide the molecule's entropy by the number of base pairs before multiplying by N_A . The result is $11.5 \text{ J K}^{-1} \text{ mol}^{-1}$, a quantity more in line with examples discussed in Exercises 3B.1(a) and (b).

3C Concentrating on the system

Answers to discussion questions

3C.2 All of the thermodynamic properties of a system that we have encountered, U , H , S , A , and G can be used as the criteria for the spontaneity of a process under specific conditions. The criteria are derived directly from the fundamental relation of thermodynamics which is a combination of the first and second laws, namely

$$-dU - p_{\text{ext}} dV + dw_{\text{non-pV}} + TdS \geq 0$$

The inequality sign gives the criteria for the spontaneity of a process, the equality gives the criteria for equilibrium.

The specific conditions we are interested in and the criteria that follow from inserting these conditions into the fundamental relation are the following:

- (1) Constant U and V , no work at all
 $dS_{U,V} \geq 0$
- (2) Constant S and V , no work at all
 $dU_{S,V} \leq 0$
- (3) Constant S and p , no work at all
 $dH_{S,p} \leq 0$
- (4) Constant T
 $dA_T \leq dw$
- (5) Constant T and V , only non- pV work
 $dA_{T,V} \leq dw_{\text{non-pV}}$
- (6) Constant T and V , no work at all
 $dA_{T,V} \leq 0$
- (7) Constant T and p , $p = p_{\text{ext}}$
 $dG_{T,p} \leq dw_{\text{non-pV}}$
- (8) Constant T and p , no non- pV work
 $dG_{T,p} \leq 0$

Exercises

3C.1(b) (i) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f H^\ominus(\text{Cu}^{2+}, \text{aq})$
 $= -153.89 - 64.77 \text{ kJ mol}^{-1} = -218.66 \text{ kJ mol}^{-1}$
 $\Delta_r G^\ominus = -218.66 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (-21.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-212.40 \text{ kJ mol}^{-1}}$

(ii) $\Delta_r H^\ominus = \Delta_c H^\ominus = -5645 \text{ kJ mol}^{-1}$
 $\Delta_r G^\ominus = -5645 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (512.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-5798 \text{ kJ mol}^{-1}}$



$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus \quad [2\text{C.5}]$$

$$= -510.7 \text{ kJ mol}^{-1} - (-277.69 \text{ kJ mol}^{-1}) - (-110.53 \text{ kJ mol}^{-1})$$

$$= -122.5 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus \quad [3\text{B.2}]$$

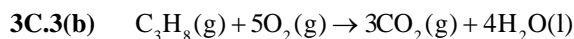
$$= 191.0 \text{ J K}^{-1} \text{ mol}^{-1} - 160.7 \text{ J K}^{-1} \text{ mol}^{-1} - 197.67 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -167.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$$

$$= -122.5 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-167.4 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{-72.6 \text{ kJ mol}^{-1}}$$



$$\Delta_r G^\ominus = 3\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 4\Delta_f G^\ominus(\text{H}_2\text{O, l}) - \Delta_f G^\ominus(\text{C}_3\text{H}_8, \text{g}) - 0$$

$$= 3(-394.36 \text{ kJ mol}^{-1}) + 4(-237.13 \text{ kJ mol}^{-1}) - 1(-23.49 \text{ kJ mol}^{-1})$$

$$= -2108.11 \text{ kJ mol}^{-1}$$

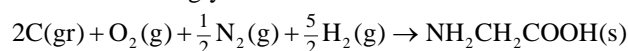
The maximum non-expansion work is $\boxed{2108.11 \text{ kJ mol}^{-1}}$ since $|w_{\text{add}}| = |\Delta G|$

3C.4(b) (a) $\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f G^\ominus(\text{Cu}^{2+}, \text{aq})$
 $= -147.06 - 65.49 \text{ kJ mol}^{-1} = \boxed{-212.55 \text{ kJ mol}^{-1}}$

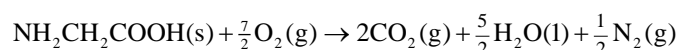
(b) $\Delta_r G^\ominus = 12\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 11\Delta_f G^\ominus(\text{H}_2\text{O, l}) - \Delta_f G^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12\Delta_f G^\ominus(\text{O}_2, \text{g})$
 $= [12 \times (-394.36) + 11 \times (-237.13) - (-1543) - 12 \times 0] \text{ kJ mol}^{-1} = \boxed{-5798 \text{ kJ mol}^{-1}}$

Comment. In each case these values of $\Delta_r G^\ominus$ agree closely with the calculated values in Exercise 3C.1(b).

3C.5(b) The formation reaction of glycine is



The combustion reaction is



$$\Delta_c H = 2\Delta_f H^\ominus(\text{CO}_2, \text{g}) + \frac{5}{2}\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\ominus(\text{NH}_2\text{CH}_2\text{COOH}(\text{s}))$$

$$\Delta_f H^\ominus(\text{NH}_2\text{CH}_2\text{COOH}(\text{s})) = 2\Delta_f H^\ominus(\text{CO}_2, \text{g}) + \frac{5}{2}\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_c H(\text{NH}_2\text{CH}_2\text{COOH}(\text{s}))$$

$$= -2 \times 393.51 \text{ kJ mol}^{-1} + \left(\frac{5}{2}\right) \times (-285.83 \text{ kJ mol}^{-1}) - (-969 \text{ kJ mol}^{-1})$$

$$= -532.6 \text{ kJ mol}^{-1}$$

$$\Delta_f S^\ominus = S_m^\ominus(\text{NH}_2\text{CH}_2\text{COOH}(\text{s})) - 2 \times S_m^\ominus(\text{C}, \text{gr}) - S_m^\ominus(\text{O}_2, \text{g}) - \frac{1}{2} \times S_m^\ominus(\text{N}_2, \text{g}) - \frac{5}{2} \times S_m^\ominus(\text{H}_2, \text{g})$$

$$= 103.5 \text{ J K}^{-1} \text{ mol}^{-1} - 2 \times 5.740 \text{ J K}^{-1} \text{ mol}^{-1} - (205.138 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$- \frac{1}{2} \times 191.61 \text{ J K}^{-1} \text{ mol}^{-1} - \frac{5}{2} \times (130.684 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= -535.63 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T \Delta_f S^\ominus$$

$$= -532.6 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (-535.63 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{-373 \text{ kJ mol}^{-1}}$$

Solutions to problems

3C.2 Begin with the partition function of an oscillator [See Chapter 15].

$$q = \frac{1}{1 - e^{-x}}, \quad x = \frac{\theta_v}{T} = hc\tilde{\nu}\beta = \hbar\omega\beta$$

The molar internal energy, molar entropy, and molar Helmholtz energy are obtained from the partition function as follows:

$$U - U(0) = -N \left(\frac{\partial q}{\partial \beta} \right)_v = -N(1 - e^{-x}) \frac{d}{d\beta} (1 - e^{-x})^{-1} = \frac{N\hbar\omega e^{-x}}{1 - e^{-x}} = \boxed{\frac{N\hbar\omega}{e^x - 1}}$$

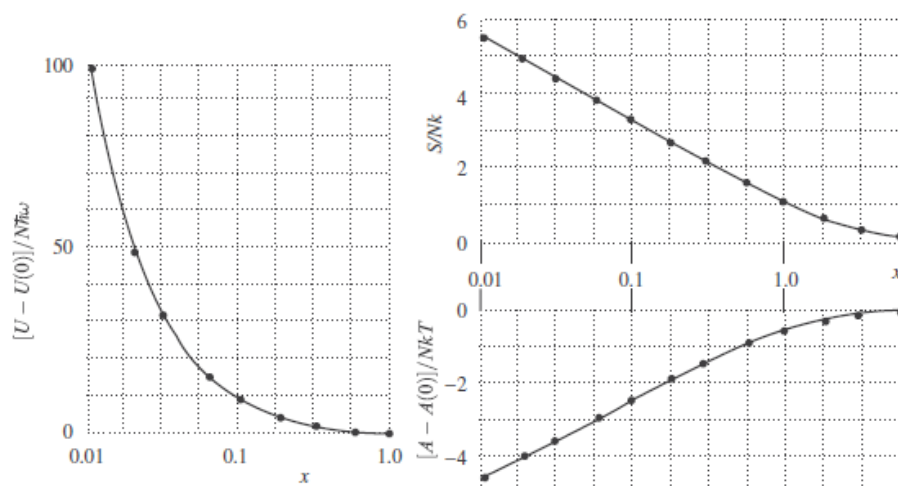
$$S = \frac{U - U(0)}{T} + nR \ln q = \frac{Nkx e^{-x}}{1 - e^{-x}} - Nk \ln(1 - e^{-x})$$

$$= \boxed{Nk \left(\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right)}$$

$$A - A(0) = G - G(0) = -nRT \ln q = \boxed{NkT \ln(1 - e^{-x})}$$

The functions are plotted in Fig. 3C.1.

Figure 3C.1



3D Combining the First and Second Laws

Answers to discussion questions

- 3D.2** The relation $(\partial G / \partial p)_T = V$, eqn 3D.8, shows that the Gibbs function of a system increases with p at constant T in proportion to the magnitude of its volume. This makes good sense when one considers the definition of G , which is $G = U + pV - TS$. Hence, G is expected to increase with p in proportion to V when T is constant.

Solutions to exercises

3D.1(b) $\Delta G = nRT \ln\left(\frac{p_f}{p_i}\right)$ [3D.14] $= nRT \ln\left(\frac{V_i}{V_f}\right)$ [Boyle's law]

$$\Delta G = (6.0 \times 10^{-3} \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln\left(\frac{52}{122}\right) = \boxed{-13 \text{ J}}$$

3D.2(b) $\left(\frac{\partial G}{\partial T}\right)_p = -S$ [3D.8]; hence $\left(\frac{\partial G_f}{\partial T}\right)_p = -S_f$, and $\left(\frac{\partial G_i}{\partial T}\right)_p = -S_i$

$$\begin{aligned} \Delta S &= S_f - S_i = -\left(\frac{\partial G_f}{\partial T}\right)_p + \left(\frac{\partial G_i}{\partial T}\right)_p = -\left(\frac{\partial(G_f - G_i)}{\partial T}\right)_p \\ &= -\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\frac{\partial}{\partial T}(-73.1 \text{ J} + 42.8 \text{ J} \times \frac{T}{\text{K}}) \\ &= \boxed{-42.8 \text{ J K}^{-1}} \end{aligned}$$

- 3D.3(b)** We will assume that the volume and molar volume of water changes little over the range of pressures given and that, therefore, equation 3D.13 which applies to incompressible substances can be used to solve this exercise. The change in Gibbs energy for this sample is then given by

$$\Delta G = nV_m \Delta p \text{ [3D.13]} = V \Delta p$$

$$\Delta G = (100 \text{ cm}^3) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times 400 \text{ kPa} = 40 \text{ Pa m}^3 = \boxed{+40 \text{ J}}$$

In order to calculate the change in Gibbs energy per mole we calculate the molar volume

$$V_m = \frac{M}{\rho(\text{density})} = \frac{18.02 \text{ g mol}^{-1}}{0.997 \text{ g cm}^{-3}} \times \frac{10^{-6} \text{ m}^3}{\text{cm}^3} = 1.81 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}, \text{ then}$$

$$\Delta G_m = V_m \Delta p \text{ [3D.13]} = 1.81 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \times 400 \text{ kPa} \times \frac{10^3 \text{ Pa}}{\text{kPa}} = \boxed{7.2 \text{ J mol}^{-1}}$$

3D.4(b)

$$\begin{aligned} \Delta G_m &= RT \ln \left(\frac{p_f}{p_i} \right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K}) \times \ln \left(\frac{100.0 \text{ kPa}}{50.0 \text{ kPa}} \right) \\ &= \boxed{+2.88 \text{ kJ mol}^{-1}} \end{aligned}$$

Solutions to problems

3D.2 The Gibbs–Helmholtz equation [3D.9] may be recast into an analogous equation involving ΔG and ΔH , since

$$\left(\frac{\partial \Delta G}{\partial T} \right)_p = \left(\frac{\partial G_f}{\partial T} \right)_p - \left(\frac{\partial G_i}{\partial T} \right)_p$$

and $\Delta H = H_f - H_i$

Thus, $\left(\frac{\partial}{\partial T} \frac{\Delta_r G^\ominus}{T} \right)_p = - \frac{\Delta_r H^\ominus}{T^2}$

$$d \left(\frac{\Delta_r G^\ominus}{T} \right) = \left(\frac{\partial}{\partial T} \frac{\Delta_r G^\ominus}{T} \right)_p dT [\text{constant pressure}] = - \frac{\Delta_r H^\ominus}{T^2} dT$$

$$\Delta \left(\frac{\Delta_r G^\ominus}{T} \right) = - \int_{T_c}^T \frac{\Delta_r H^\ominus}{T^2} dT$$

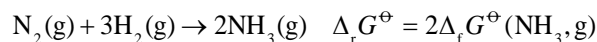
$$\approx -\Delta_r H^\ominus \int_{T_c}^T \frac{dT}{T^2} = \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T_c} \right) \quad [\Delta_r H^\ominus \text{ assumed constant}]$$

Therefore, $\frac{\Delta_r G^\ominus(T)}{T} - \frac{\Delta_r G^\ominus(T_c)}{T_c} \approx \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T_c} \right)$

and so $\Delta_r G^\ominus(T) = \frac{T}{T_c} \Delta_r G^\ominus(T_c) + \left(1 - \frac{T}{T_c} \right) \Delta_r H^\ominus(T_c)$

$$= \tau \Delta_r G^\ominus(T_c) + (1 - \tau) \Delta_r H^\ominus(T_c) \quad \text{where } \tau = \frac{T}{T_c}$$

For the reaction



(a) At 500 K, $\tau = \frac{500}{298} = 1.678$,

so $\Delta_r G^\ominus(500 \text{ K}) = \{(1.678) \times 2 \times (-16.45) + (1 - 1.678) \times 2 \times (-46.11)\} \text{ kJ mol}^{-1}$

$$\boxed{= -7 \text{ kJ mol}^{-1}}$$

(b) At 1000 K, $\tau = \frac{1000}{298} = 3.356$,
so $\Delta_r G^\ominus(1000 \text{ K}) = \{(3.356) \times 2 \times (-16.45) + (1 - 3.356) \times 2 \times (-46.11)\} \text{ kJ mol}^{-1}$
= +107 kJ mol⁻¹

3D.4 $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ [Table 3D.1]

(a) For a van der Waals gas

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Hence, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m - b}$

(b) For a Dieterici gas

$$p = \frac{RTe^{-a/RTV_m}}{V_m - b}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R \left(1 + \frac{a}{RV_m T}\right) e^{-a/RTV_m}}{V_m - b}$$

For an isothermal expansion,

$$\Delta S = \int_{V_i}^{V_f} dS = \int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V}\right)_T dV$$

so we can simply compare $\left(\frac{\partial S}{\partial V}\right)_T$ expressions for the three gases. For a perfect gas,

$$p = \frac{nRT}{V} = \frac{RT}{V_m} \quad \text{so} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m}$$

$\left(\frac{\partial S}{\partial V}\right)_T$ is certainly greater for a van der Waals gas than for a perfect gas, for the denominator is smaller for the van der Waals gas. To compare the van der Waals gas to the Dieterici gas, we assume that both have the same parameter b . (That is reasonable, for b is an excluded volume in both equations of state.) In that case,

$$\left(\frac{\partial S}{\partial V}\right)_{T,\text{Die}} = \frac{R \left(1 + \frac{a}{RV_m T}\right) e^{-a/RTV_m}}{V_m - b} = \left(\frac{\partial S}{\partial V}\right)_{T,\text{vdW}} \left(1 + \frac{a}{RV_m T}\right) e^{-a/RTV_m}$$

Now notice that the additional factor in $\left(\frac{\partial S}{\partial V}\right)_{T,\text{Die}}$ has the form $(1+x)e^{-x}$, where $x > 0$. This factor is always less than 1. Clearly $(1+x)e^{-x} < 1$ for large x , for then the exponential dominates. But $(1+x)e^{-x} < 1$ even for small x , as can be seen by using the power series expansion for the exponential: $(1+x)(1 - x + x^2/2 + \dots) = 1 - x^2/2 + \dots$. So $\left(\frac{\partial S}{\partial V}\right)_{T,\text{Die}} < \left(\frac{\partial S}{\partial V}\right)_{T,\text{vdW}}$. To summarize, for isothermal expansions:

$$\Delta S_{\text{vdW}} > \Delta S_{\text{Die}} \quad \text{and} \quad \Delta S_{\text{vdW}} > \Delta S_{\text{perfect}}$$

The comparison between a perfect gas and a Dieterici gas depends on particular values of the constants a and b and on the physical conditions.

3D.6 (a) $\alpha = \left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial T}\right)_p$; $\kappa_T = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_T$

$$\begin{aligned}
(1) \quad \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \quad [\text{Maxwell relation}] \\
\left(\frac{\partial p}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \quad [\text{Euler chain relation, } \textit{Mathematical Background 2}] \\
&= -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \quad [\text{reciprocal identity, } \textit{Mathematical Background 2}] \\
&= -\frac{\left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial p}\right)_T} = \boxed{+\frac{\alpha}{\kappa_T}} \\
\left(\frac{\partial V}{\partial S}\right)_p &= \left(\frac{\partial T}{\partial p}\right)_S \quad [\text{Maxwell relation}] \\
\left(\frac{\partial T}{\partial p}\right)_S &= -\left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T \quad [\text{Euler chain}] = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} \quad [\text{reciprocal}]
\end{aligned}$$

First treat the numerator:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad [\text{Maxwell relation}] = -\alpha V$$

As for the denominator, at constant p

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT \quad \text{and} \quad dq_{\text{rev}} = dH = \frac{C_p dT}{T} \quad [dq_p = dH]$$

$$\text{Therefore, } \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad \text{and} \quad \left(\frac{\partial V}{\partial S}\right)_p = \boxed{\frac{\alpha TV}{C_p}}$$

$$\begin{aligned}
(2) \quad \left(\frac{\partial p}{\partial S}\right)_V &= -\left(\frac{\partial T}{\partial V}\right)_S \quad [\text{Maxwell relation}] \\
-\left(\frac{\partial T}{\partial V}\right)_S &= \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T} \quad [\text{Euler chain}] = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} \quad [\text{reciprocal}] \\
&= \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial V}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} \quad [\text{Maxwell relation}] = \frac{-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} \quad [\text{Euler chain relation}] \\
&= \frac{-\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial U}{\partial T}\right)_V} \quad [\text{reciprocal identity, twice}] = \boxed{\frac{\alpha T}{\kappa_T C_V}} \left[\left(\frac{\partial U}{\partial S}\right)_V = T \right]
\end{aligned}$$

$$\begin{aligned}
(\text{b}) \quad \mu_1 &= \left(\frac{\partial T}{\partial V}\right)_U \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V \\
\mu_1 C_V &= \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T} \quad [\text{Euler chain relation}] \\
&= -\left(\frac{\partial U}{\partial V}\right)_T \quad [\text{reciprocal identity}] = p - T \left(\frac{\partial p}{\partial T}\right)_V \quad [3D.6]
\end{aligned}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T} [\text{Euler chain}] = \frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa_T}$$

Therefore, $\boxed{\mu_1 C_V = p - \frac{\alpha T}{\kappa_T}}$

3D.8 $\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$ [3D.6]

$$A = -kT \ln Q \text{ [Chapter 15]} \quad p = -\left(\frac{\partial A}{\partial V}\right)_T = kT \left[\frac{\partial \ln Q}{\partial V}\right]_T$$

$$Q = \frac{q^N}{N!} \text{ then } p = \frac{NkT}{q} \left(\frac{\partial q}{\partial V}\right)_T$$

Substitute this expression for p into eqn. 3D.6. We obtain after differentiating p with respect to T at constant V

$$\boxed{\pi_T = \frac{NkT^2}{q} \frac{\partial}{\partial T} \left(\frac{\partial q}{\partial V}\right)_T}$$

3D.10 The Gibbs–Helmholtz equation is

$$\frac{\partial}{\partial T} \left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

so for a small temperature change

$$\Delta \left(\frac{\Delta_r G^\ominus}{T}\right) = \frac{\Delta_r H^\ominus}{T^2} \Delta T \quad \text{and} \quad \frac{\Delta_r G_2^\ominus}{T_2} = \frac{\Delta_r G_1^\ominus}{T_1} - \frac{\Delta_r H^\ominus}{T^2} \Delta T$$

so $\int d \frac{\Delta_r G^\ominus}{T} = -\int \frac{\Delta_r H^\ominus dT}{T^2}$ and $\frac{\Delta_r G_{190}^\ominus}{T_{190}} = \frac{\Delta_r G_{220}^\ominus}{T_{220}} + \Delta_r H^\ominus \left(\frac{1}{T_{190}} - \frac{1}{T_{220}}\right)$

$$\Delta_r G_{190}^\ominus = \Delta_r G_{220}^\ominus \frac{T_{190}}{T_{220}} + \Delta_r H^\ominus \left(1 - \frac{T_{190}}{T_{220}}\right)$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (46.2 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}}\right) + (127 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{57.2 \text{ kJ mol}^{-1}}$$

For the dihydrate

$$\Delta_r G_{190}^\ominus = (69.4 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}}\right) + (188 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{85.6 \text{ kJ mol}^{-1}}$$

For the trihydrate

$$\Delta_r G_{190}^\ominus = (93.2 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}}\right) + (237 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{112.8 \text{ kJ mol}^{-1}}$$

Integrated activities

- 3.2** For a thorough discussion of the relationship between the thermodynamic and statistical definitions of entropy, see Section 3A. We will not repeat all of that discussion here and will merely summarize the main points.

The thermodynamic entropy is defined in terms of the quantity $dS = \frac{dq_{\text{rev}}}{T}$ where dq_{rev} is the infinitesimal quantity of energy supplied as heat to the system reversibly at a temperature T .

The statistical entropy is defined in terms of the Boltzmann formula for the entropy: $S = k \ln W$ where k is the Boltzmann constant and W is the number of microstates, the total number of ways in which the molecules of the system can be arranged to achieve the same total energy of the system. These two definitions turn out to be equivalent provided the thermodynamic entropy is taken to be zero at $T = 0$.

The concept of the number of microstates makes quantitative the ill-defined qualitative concepts of 'disorder' and 'dispersal of matter and energy' that are used widely to introduce the concept of entropy: a more 'disorderly' distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy. The more molecules that can participate in the distribution of energy, the more microstates there are for a given total energy and the greater the entropy than when the energy is confined to a smaller number of molecules.

The molecular interpretation of entropy given by the Boltzmann formula also suggests the thermodynamic definition. At high temperatures where the molecules of a system can occupy a large number of available energy levels, a small additional transfer of energy as heat will cause only a small change in the number of accessible energy levels, whereas at low temperatures the transfer of the same quantity of heat will increase the number of accessible energy levels and microstates significantly. Hence, the change in entropy upon heating will be greater when the energy is transferred to a cold body than when it is transferred to a hot body. This argument suggests that the change in entropy should be inversely proportional to the temperature at which the transfer takes place as indicated in the thermodynamic definition.