

**Exc. 1** (a) We assume that the ice melts reversibly under the conditions described, therefore

$$\Delta S_{\text{ice}} = \frac{q_{\text{rev}}}{T} [2.1] = \frac{33 \text{ kJ}}{273 \text{ K}} = +0.12 \text{ kJ K}^{-1}.$$

$$(b) \quad \Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} [\text{Section 2.2(d)}] = \frac{-33 \text{ kJ}}{273 \text{ K}} = \boxed{-0.12 \text{ kJ K}^{-1}}$$

*Note:* Because this process is reversible, the total entropy change is zero.

**Exc. 2**  $\Delta S = C_p \ln \frac{T_f}{T_i} = n C_{p,m} \ln \frac{T_f}{T_i} [2.2]$

$$= \frac{100 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.5 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left( \frac{310 \text{ K}}{293 \text{ K}} \right) = \boxed{23.6 \text{ J K}^{-1}}$$

**Exc. 3** We use eqn 2.7b.

$$S_m(T) - S_m(0) = \frac{1}{3} C_p(T) [2.7b] = \frac{1}{3} \times 1.2 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1} = 4.0 \times 10^{-4} \text{ J K}^{-1} \text{ mol}^{-1}$$

As  $S_m(0)$  for the pure crystalline substance KCl is expected to be zero,

$$S_m(T) = \boxed{4.0 \times 10^{-4} \text{ J K}^{-1} \text{ mol}^{-1}}.$$

**Exc. 4**  $\Delta S = \int_{T_i}^{T_f} \frac{C}{T} dT [2.3] = \int_{T_i}^{T_f} \left( \frac{a + bT + \frac{c}{T^2}}{T} \right) dT$

$$= a \int_{T_i}^{T_f} \frac{1}{T} dT + b \int_{T_i}^{T_f} dT + c \int_{T_i}^{T_f} \frac{1}{T^3} dT = a \ln(T) \Big|_{T_i}^{T_f} + bT \Big|_{T_i}^{T_f} - \frac{c}{2T^2} \Big|_{T_i}^{T_f}$$

$$\Delta S = a \ln \left( \frac{T_f}{T_i} \right) + b(T_f - T_i) - \frac{c}{2} \left( \frac{1}{T_f^2} - \frac{1}{T_i^2} \right)$$

**Exc. 5** (a)  $\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H^\circ}{T_b} [2.5] = \frac{35.27 \times 10^3 \text{ J mol}^{-1}}{337.25 \text{ K}} = \boxed{+104.6 \text{ J K}^{-1} \text{ mol}^{-1}}$

(b) Because the vaporization process can be accomplished reversibly,  $\Delta S_{\text{total}} = 0$ ; hence

$$\Delta S_{\text{sur}} = \boxed{-104.6 \text{ J K}^{-1} \text{ mol}^{-1}}.$$

**Exc.6**

$$\Delta_{\text{fus}} C_p^\circ = C_{p,m}^\circ(\text{l}) - C_{p,m}^\circ(\text{s}) \text{ [similar to eqn 1.25]} = (28 - 19) \text{ J K}^{-1} \text{ mol}^{-1} = 9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta_{\text{fus}} S^\circ(T') &= \Delta_{\text{fus}} S^\circ(T) + \int_T^{T'} \frac{\Delta_{\text{fus}} C_p^\circ}{T} dT \quad \text{[phase transition analog of eqn 2.3]} \\ &= \Delta_{\text{fus}} S^\circ(T) + \Delta_{\text{fus}} C_p^\circ \int_T^{T'} \frac{1}{T} dT = \Delta_{\text{fus}} S^\circ(T) + \Delta_{\text{fus}} C_p^\circ \ln(T) \Big|_T^{T'} \\ &= \Delta_{\text{fus}} S^\circ(T) + \Delta_{\text{fus}} C_p^\circ \ln\left(\frac{T'}{T}\right) \end{aligned}$$

At  $T = T_{\text{fus}}$  the transition is reversible and  $\Delta_{\text{fus}} S^\circ(T_{\text{fus}}) = \frac{\Delta_{\text{fus}} H^\circ(T_{\text{fus}})}{T_{\text{fus}}}$  [2.4].

$$\Delta_{\text{fus}} S^\circ(T') = \frac{\Delta_{\text{fus}} H^\circ(T_{\text{fus}})}{T_{\text{fus}}} + \Delta_{\text{fus}} C_p^\circ \ln\left(\frac{T'}{T_{\text{fus}}}\right)$$

$$\begin{aligned} \Delta_{\text{fus}} S^\circ(298 \text{ K}) &= \frac{32 \text{ kJ mol}^{-1}}{419 \text{ K}} + (9 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{298 \text{ K}}{419 \text{ K}}\right) \\ &= \boxed{73 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

**Exc.7**

Because the temperature is so low we can assume  $C_p(T) = aT^3$  [2.7a]. Hence we can write

$$S(T) = S(0) + \int_0^T \frac{C_p(T) dT}{T} = S(0) + \int_0^T \frac{aT^3 dT}{T} = S(0) + a \int_0^T T^2 dT = \frac{1}{3} aT^3$$

If we are dealing with a substance that has no residual entropy at  $T = 0$  then  $S(0) = 0$  and  $S(T)$  becomes  $S(T) = \frac{1}{3} C_p(T)$ .

**Exc.8**

In each case  $S_m = R \ln s$ , where  $s$  is the number of orientations of about equal energy that the molecule can adopt. Therefore,

$$(a) \quad S_m = R \ln 3 = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln 3 = \boxed{9.13 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$(b) \quad S_m = R \ln 5 = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln 5 = \boxed{13.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$(c) \quad S_m = R \ln 6 = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln 6 = \boxed{14.9 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**Exc.9**

$$(a) \quad \Delta G = \Delta H - T\Delta S \text{ [2.13]}$$

$$= -125 \text{ kJ mol}^{-1} - 310 \text{ K} \times (-126 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-85.9 \text{ kJ mol}^{-1}}$$

(b) Yes,  $\Delta G$  is negative.

$$(c) \quad \Delta G = -T\Delta S_{\text{total}} \text{ [2.14]}$$

$$\Delta S_{\text{total}} = -\frac{\Delta G}{T} = -\left(\frac{-85.9 \text{ kJ mol}^{-1}}{310 \text{ K}}\right) = \boxed{+0.277 \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

**Exc.10**

$\Delta G = w_{\text{max,non-exp}} = -2808 \text{ kJ mol}^{-1}$ , so the maximum work that can be done is  $2808 \text{ kJ mol}^{-1}$ . We will assume that we will be able to extract the maximum work from the reaction.

$$\begin{aligned} w &= mgh = 65 \text{ kg} \times 9.81 \text{ m s}^{-2} \times 10 \text{ m} \\ &= 6.4 \times 10^3 \text{ J} = 6.4 \text{ kJ} \end{aligned}$$

$$\text{amount}(n) = \frac{6.4 \text{ kJ}}{2808 \text{ kJ mol}^{-1}} = 2.3 \times 10^{-3} \text{ mol}$$

$$\text{mass of glucose} = 2.3 \times 10^{-3} \text{ mol} \times 180 \text{ g mol}^{-1} = \boxed{0.41 \text{ g}}$$