

Chapter 4 Homework Solutions

4.1 (a) $q = 33 \text{ kJ}$ $T = 0 \text{ }^\circ\text{C}$

$$\Delta S_{\text{sys}} = \frac{q}{T} = \frac{33 \times 10^3 \text{ J}}{273 \text{ K}} = +121 \text{ J/K}$$

(b) $\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{q}{T} = -\frac{33 \times 10^3 \text{ J}}{273 \text{ K}} = -121 \text{ J/K}$

Note: Because the ice is melting reversibly at its normal freezing point,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

4.2 $C_{P,m} = 24.35 \text{ J/mol}\cdot\text{K}$ $\text{mass} = 1.25 \text{ kg}$ $n = 1.25 \times 10^3 \text{ g} / 27. \text{ g/mol} = 46.3 \text{ mol}$
 $\Delta T = -13 \text{ }^\circ\text{C} - 27 \text{ }^\circ\text{C} = -40 \text{ }^\circ\text{C} = -40 \text{ K}$

$$q = nC_{P,m}\Delta T = 46.3 \text{ mol}(24.35 \text{ J/mol}\cdot\text{K})(-40 \text{ K}) = -45,100 \text{ J} = -45.1 \text{ kJ}$$

$$\Delta S = nC_{P,m} \ln\left(\frac{T_2}{T_1}\right) = 46.3 \text{ mol}(24.35 \text{ J/mol}\cdot\text{K}) \ln\left(\frac{260 \text{ K}}{300 \text{ K}}\right) = -161 \text{ J/K}$$

4.3 $V_1 = 15 \text{ L}$ $V_2 = ??$ $T = -23 \text{ }^\circ\text{C} = 250 \text{ K}$ $P = 1 \text{ atm} = 101.3 \text{ kPa}$

$$n = \frac{PV}{RT} = \frac{(101.3 \text{ kPa})(15 \text{ L})}{(8.31 \text{ kPa}\cdot\text{L/mol}\cdot\text{K})(250 \text{ K})} = 0.73 \text{ mol}$$

$$\Delta S = -10 \text{ J/K} = nR \ln\left(\frac{V_2}{V_1}\right) = (0.73 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K}) \ln\left(\frac{V_2}{15 \text{ L}}\right) = (6.07 \text{ J/K}) \ln\left(\frac{V_2}{15 \text{ L}}\right)$$

$$\ln\left(\frac{V_2}{15 \text{ L}}\right) = \frac{-10 \text{ J/K}}{6.07 \text{ J/K}} = -1.65 \rightarrow \frac{V_2}{15 \text{ L}} = e^{-1.65} = 0.192$$

$$V_2 = 0.192(15 \text{ L}) = 2.88 \text{ L} \approx 2.9 \text{ L}$$

4.4 $n = 25 \text{ g} / 16 \text{ g/mol} = 1.56 \text{ mol}$ $T = -23 \text{ }^\circ\text{C} = 250 \text{ K}$ $P_1 = 185 \text{ kPa}$ $P_2 = 2.5 \text{ kPa}$

For isothermal process, $P_2V_2 = P_1V_1 \rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$

(a) Reversible Isothermal Expansion

$$\begin{aligned} \Delta S &= nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right) = (1.56 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K}) \ln\left(\frac{185 \text{ kPa}}{2.5 \text{ kPa}}\right) \\ &= 55.8 \text{ J/K} \approx 56 \text{ J/K} \end{aligned}$$

(b) Because expansion (b) is **irreversible**, ΔS cannot be calculated directly. However, because S is a state function, ΔS is the same as for the reversible expansion in (a): $\Delta S = 56 \text{ J/K}$

- 4.5** Break process up into two steps: (1) Compression from 2 L to 0.5 L, (2) Heat at constant volume from 300 K to 400 K.

$$n = 80 \text{ g} / 40 \text{ g/mol mol} = 2 \text{ mol} \quad C_{V,m} = 12.5 \text{ J/mol}\cdot\text{K}$$

$$(1) \Delta S_1 = nR \ln \left(\frac{V_2}{V_1} \right) = (2 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K}) \ln \left(\frac{0.5 \text{ L}}{2.0 \text{ L}} \right) = -23.0 \text{ J/K}$$

$$(2) \Delta S_2 = nC_{V,m} \ln \left(\frac{T_2}{T_1} \right) = (2 \text{ mol})(12.5 \text{ J/mol}\cdot\text{K}) \ln \left(\frac{400 \text{ K}}{300 \text{ K}} \right) = +7.2 \text{ J/K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = -23.0 + 7.2 = -15.8 \text{ J/K}$$

- 4.6** $T = 62 \text{ }^\circ\text{C} = 335. \text{ K}$

$$(a) \Delta_{\text{vap}} S = \frac{q}{T} = \frac{\Delta_{\text{vap}} H}{T} = \frac{29.4 \times 10^3 \text{ J/mol}}{335. \text{ K}} = 87.8 \text{ J/mol}\cdot\text{K}$$

$$(b) \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-q}{T} = \frac{-\Delta_{\text{vap}} H}{T} = \frac{-29.4 \times 10^3 \text{ J/mol}}{335. \text{ K}} = -87.8 \text{ J/mol}\cdot\text{K}$$

Because the chloroform is vaporizing reversibly at its normal boiling point, $\Delta S_{\text{unv}} = 0$

- 4.7** Molar entropies given in table in question

$$(a) \Delta_r S^0 = 2 S_m^0(\text{CH}_3\text{COOH}, l) - 2 S_m^0(\text{CH}_3\text{CHO}, g) - S_m^0(\text{O}_2, g) \\ = [(2 \times 159.8) - (2 \times 250.3) - 205.1] \\ = -386.1 \text{ J/K}$$

$$(b) \Delta_r S^0 = 2 S_m^0(\text{AgBr}, s) + S_m^0(\text{Cl}_2, g) - 2 S_m^0(\text{AgCl}, s) - S_m^0(\text{Br}_2, l) \\ = [(2 \times 107.1) + 223.1 - (2 \times 96.2) - 152.2] \\ = 92.6 \text{ J/K}$$

- 4.8** (a) **Reversible Isothermal Expansion**

$$n = 0.35 \text{ mol} \quad T = 289 \text{ K} \quad V_1 = 1.2 \text{ L} \quad V_2 = 7.4 \text{ L} \quad P_{\text{ex}} = P = 1 \text{ bar} = 100 \text{ kPa}$$

$$\Delta U = nC_{V,m}\Delta T = 0 \quad \Delta H = nC_{P,m}\Delta T = 0$$

$$w = -nRT \ln(V_2/V_1) = -0.35 \text{ mol}(8.31 \text{ J/mol}\cdot\text{K}) \ln(7.4/1.2) = -1530 \text{ J}$$

$$q = \Delta U - w = -w = +1530 \text{ J}$$

$$\Delta S = q/T = 1530 \text{ J}/289 \text{ K} = 5.29 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S = 0 - (289 \text{ K})(5.29 \text{ J/K}) = -1530 \text{ J}$$

- (b) **Irreversible Isothermal Expansion against constant pressure**

$$n = 0.35 \text{ mol} \quad T = 16 \text{ }^\circ\text{C} = 289 \text{ K} \quad V_1 = 1.2 \text{ L} \quad V_2 = 7.4 \text{ L}$$

$$\Delta U = nC_{V,m}\Delta T = 0 \quad \Delta H = nC_{P,m}\Delta T = 0$$

$$w = -P(V_2 - V_1) = -100 \text{ kPa}(7.4 \text{ L} - 1.2 \text{ L}) = -620 \text{ J}$$

$$\Delta U = nC_{V,m}\Delta T = 0 \quad \Delta H = nC_{P,m}\Delta T = 0 \quad q = \Delta U - w = -2 = +620 \text{ J}$$

$\Delta S \neq \frac{q}{T}$!!! Cannot use q for irreversible path. Instead use answer to part (a), which is reversible. $\Delta S = 5.29 \text{ J/K}$

$$\Delta G = \Delta H - T\Delta S = 0 - (289 \text{ K})(5.29 \text{ J/K}) = -1530 \text{ J}$$

- 4.9** Use two step process: (1) $\text{H}_2\text{O(l)}[25 \text{ }^\circ\text{C}] \rightarrow \text{H}_2\text{O(l)}[100 \text{ }^\circ\text{C}]$
 (2) $\text{H}_2\text{O(l)}[100 \text{ }^\circ\text{C}] \rightarrow \text{H}_2\text{O(g)}[100 \text{ }^\circ\text{C}]$

Step 1: $\Delta H_1 = nC_{P,m}\Delta T = 1 \text{ mol}(75.3 \text{ J/mol}\cdot\text{K})(75 \text{ K}) = 5650 \text{ J}$

$$\Delta U_1 \approx \Delta H_1 = 5650 \text{ J} \quad [\text{since } \Delta(PV) \approx 0]$$

$$\Delta S_1 = nC_{P,m} \ln(T_2/T_1) = 1 \text{ mol}(75.3 \text{ J/mol}\cdot\text{K}) \ln(373 \text{ K}/298 \text{ K}) = 16.9 \text{ J/K}$$

Step 2: $\Delta H_2 = n \times \Delta_{\text{vap}}H^\circ = 1 \text{ mol} \times 40.7 \times 10^3 \text{ J/mol} = 40,700 \text{ J}$

$$\Delta U_2 = \Delta H_2 - (PV_g - PV_l) \approx \Delta H_2 - PV_g = \Delta H_2 - nRT$$

$$= 40,700 \text{ J} - (1 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(373 \text{ K}) = 37,600 \text{ J}$$

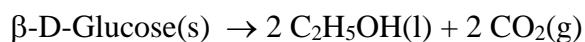
$$\Delta S_2 = \Delta H_2/T = 40,700 \text{ J}/373 \text{ K} = 109.1 \text{ J/K}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 5650 \text{ J} + 40,700 \text{ J} = 46,350 \text{ J} = 46.4 \text{ kJ}$$

$$\Delta U = \Delta U_1 + \Delta U_2 = 5650 \text{ J} + 37,600 \text{ J} = 43,250 \text{ J} = 43.3 \text{ kJ}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 16.9 \text{ J/K} + 109.1 \text{ J/K} = 126.0 \text{ J/K}$$

4.10 Compound	$\Delta_f H^\circ$	S°	$\Delta_f G^\circ$
β -D-Glucose(s)	-1268.0 kJ/mol	212.0 J/mol-K	-910.0 kJ/mol
$\text{C}_2\text{H}_5\text{OH(l)}$	-277.7	160.7	-174.8
$\text{CO}_2\text{(g)}$	-393.5	213.7	-394.4



(a) $\Delta H = 2 \Delta_f H^\circ(\text{C}_2\text{H}_5\text{OH}) + 2 \Delta_f H^\circ(\text{CO}_2) - 1 \Delta_f H^\circ(\text{Glucose})$
 $= 2(-277.7) + 2(-393.5) - (-1268.0) = -74.4 \text{ kJ}$

$$\Delta S = 2 S^\circ(\text{C}_2\text{H}_5\text{OH}) + 2 S^\circ(\text{CO}_2) - 1 S^\circ(\text{Glucose})$$

$$= 2(160.7) + 2(213.7) - 212.0 = 536.8 \text{ J/K} = 0.5368 \text{ kJ/K}$$

$$\Delta G = \Delta H - T\Delta S = -74.4 \text{ kJ} - 298 \text{ K}(0.5368 \text{ J/K}) = -234.4 \text{ kJ}$$

$$\begin{aligned} \text{(b) } \Delta G &= 2 \Delta_f G^\circ(\text{C}_2\text{H}_5\text{OH}) + 2 \Delta_f G^\circ(\text{CO}_2) - 1 \Delta_f G^\circ(\text{Glucose}) \\ &= 2(-174.8) + 2(-394.4) - (-910.0) = -228.4 \text{ kJ} \end{aligned}$$

Note: The difference probably arises from a small error in the table in the appendix.

$$\mathbf{4.11} \quad \text{Native} \rightarrow \text{Random Coil} \quad \Delta H = 512 \text{ kJ/mol} \quad \Delta S = 1600 \text{ kJ/mol-K} = 1.60 \text{ kJ/mol-K}$$

At equilibrium, $\Delta G = 0 = \Delta H - T\Delta S$.

$$\text{Therefore: } T = \frac{\Delta H}{\Delta S} = \frac{512 \text{ kJ/mol}}{1.60 \text{ kJ/mol} \cdot \text{K}} = 320 \text{ K} = 47^\circ \text{C}$$

$$\mathbf{S4.12} \quad \Delta H = n \times \Delta_{\text{fus}} H^\circ = 2 \text{ mol} \times 9.87 \text{ kJ/mol} = 19.74 \text{ kJ}$$

$$\Delta S = n \times \Delta_{\text{fus}} S^\circ = 2 \text{ mol} \times 35.4 \text{ J/mol-K} = 70.8 \text{ J/K} = 0.0708 \text{ kJ/K}$$

$$\text{(a) } T = -25^\circ \text{C} = 248 \text{ K} \quad \Delta G = \Delta H - T\Delta S = 19.74 - (248)(0.0708) = +2.18 \text{ kJ}$$

not spontaneous below melting temperature: spontaneous in opposite direction (freezing)

$$\text{(b) } T = 6^\circ \text{C} = 279 \text{ K} \quad \Delta G = \Delta H - T\Delta S = 19.74 - (279)(0.0708) = 0 \text{ kJ}$$

in equilibrium at the melting point

$$\text{(c) } T = +25^\circ \text{C} = 298 \text{ K} \quad \Delta G = \Delta H - T\Delta S = 19.74 - (298)(0.0708) = -1.36 \text{ kJ}$$

spontaneously melts above melting temperature