1. (a) This relationship can take a number of forms, one of which is: \[ \frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{R}{C_p,m}}. \]

(b) \( \left( \frac{R}{C_p,m} \right) = \frac{2}{5} \rightarrow T_2 = 90.6 \text{ K}. \) [91 K O.K.]

(c) \( q = 0; \) \( w = \Delta U = C_v \Delta T = n C_v,m \Delta T = -3.32 \text{ kJ}; \) \( \Delta H = C_p \Delta T = \Delta U \times \frac{5}{3} = -5.53 \text{ kJ}; \) \( \Delta S = 0. \)

2. (a) \( \Delta H = C_p(l) \Delta T(l) - \Delta H_{fus} + C_p(s) \Delta T(s) = 101 \text{ cal} - 797 \text{ cal} - 50 \text{ cal} = -746 \text{ cal}. \)

\( \Delta U = \Delta H - \Delta (PV) = \Delta H - P \Delta V = \Delta H - 0.022 \text{ cal} \approx \Delta H. \)

\( \Delta S = (10.1 - 5.0) \text{ cal/K ln}(273.15/263.15) - 797 \text{ cal/273.15 K} = -2.73 \text{ cal/K}. \)

3. (a) \( \Delta H = 0 (= \Delta U). \) Thus the supercooled water must warm to the freezing point (0°C) and some must freeze, such that \( \Delta H (l \rightarrow 0^\circ) + \Delta H (l \rightarrow s) = 0. \)

(b) From the preceding problem, the heat required to warm the supercooled water to 0°C is 101 cal. Thus this heat must come from the freezing process, meaning that the fraction \( \frac{101}{797} \) of the water will freeze, since 797 cal must be removed from the 10.0 g of liquid water at 0°C to freeze it all. The final state will be 1.27 g ice in equilibrium with 8.73 g water at 0°C.

(c) \( \Delta S = 10.1 \text{ cal/K ln}(273.15/263.15) - 101 \text{ cal/273.15 K} = 0.007 \text{ cal/K}. \)

(d) This process is irreversible, so \( \Delta S_{univ} > 0 (\approx \Delta S_{syst}). \)

4. (a) \( T = 26^\circ\text{C} = 299.2 \text{ K}. \)

(b) \( \Delta U \approx \Delta H = 0; \) \( \Delta S = 0.70 \text{ cal/K}. \)

(c) No.

(d) \( \Delta S_{univ} \approx \Delta S_{syst}. \)

5. (a) \( n_{\text{He}} = 4.32 \text{ mol}; \) \( n_{\text{Ar}} = 0.688 \text{ mol}; \) \( x_{\text{He}} = 0.863; \) \( x_{\text{Ar}} = 0.137. \)

(b) \( V_{\text{He}} = 84.4 \text{ L}; \) \( V_{\text{Ar}} = 19.1 \text{ L}; \) \( V_f = 132 \text{ L}. \)

(c) \( \Delta U = \Delta H = 0; \) Since there is no temperature change, \( \Delta S = n_{\text{He}} R \ln(V_f/V_{\text{He}}) + n_{\text{Ar}} R \ln(V_f/V_{\text{Ar}}) = 27.2 \text{ J/K}. \)

6. (a) \( dU = dq + dw \rightarrow \Delta U = C_v \Delta T = w = -P_{ex} \Delta V \rightarrow C_v (T_2 - T_1) = -P_{ex} (V_2 - V_1) \rightarrow T_2 = 235 \text{ K}. \)

(b) \( q = 0; \) \( w = \Delta U = C_v \Delta T = -12.6 \text{ kJ}; \) \( \Delta H = C_p \Delta T = \Delta U \times \frac{7}{5} = -17.6 \text{ kJ}. \)

\( \Delta S = 42.5 \text{ J/K (from Eq. 3.29)}. \)

(c) Since this process is irreversible, \( \Delta S_{univ} > 0. \) It may be as large as \( \Delta S, \) but could be somewhat less.

7. (a) \( \Delta U = \int C_v \, dT = w = -P_{ex} \Delta V \rightarrow T_2 = 242.1 \text{ K}. \)

(b) \( q = 0; \) \( w = \Delta U = -13.12 \text{ kJ}; \) \( \Delta H = -17.58 \text{ kJ}. \)

\( \Delta S = 43.51 \text{ J/K (from Eq. 3.29)}. \)