Chemistry 230
Problem Set # 5 -- Answers

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

   (b) $(R/C_{P,m}) = {}^2/_5 \rightarrow T_2 = 90.6$ K. [91 K O.K.]
   (c) $q = 0$; $w = \Delta U = C_V\,\Delta T = n\,C_{V,m}\,\Delta T = -3.32$ kJ; $\Delta H = C_P\,\Delta T = \Delta U \times {}^5/_3 = -5.53$ kJ; $\Delta S = 0$.

2. (a) $\Delta H = C_P(l)\,\Delta T(l) - \Delta H_{fus} + C_P(s)\,\Delta T(s) = 101$ cal – 797 cal – 50 cal = –746 cal.
   $\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V = \Delta H - 0.022\text{ cal} \approx \Delta H$.

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

3. (a) $\Delta H = 0$ ($\approx \Delta U$). Thus the supercooled water must warm to the freezing point (0˚C) and some must freeze, such that $\Delta H\,(l, -10^\circ \rightarrow 0^\circ) + \Delta H\,(l \rightarrow s) = 0.0$.
   (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 (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) $\Delta S = 10.1$ cal/K ln(273.15/263.15) – 101 cal/273.15 K = 0.007 cal/K.
   (d) This process is irreversible, so $\Delta S_{univ} > 0$ ($\approx \Delta S_{syst}$).

4. (a) $T = 26$˚C = 299.2 K.
   (b) $\Delta U \approx \Delta H = 0$; $\Delta S = 0.70$ cal/K.
   (c) No.
   (d) $\Delta S_{univ} \approx \Delta S_{syst}$.

5. (a) $n_{He} = 4.32$ mol; $n_{Ar} = 0.688$ mol; $x_{He} = 0.863$; $x_{Ar} = 0.137$.
   (b) $V_{He} = 84.4$ L; $V_{Ar} = 19.1$ L; $V_f = 132$ L.
   (c) $\Delta U = \Delta H = 0$; Since there is no temperature change, $\Delta S = n_{He}R\,\ln(V_f/V_{He}) + n_{Ar}R\,\ln(V_f/V_{Ar}) =$ 27.2 J/K.

6. (a) $dU = dq + dw \rightarrow \Delta U = C_V\,\Delta T = w = -P_{ex}\,\Delta V \rightarrow C_V\,(T_2 - T_1) = -P_{ex}\,(V_2 - V_1) \rightarrow T_2 = 235$ K.
   (b) $q = 0$; $w = \Delta U = C_V\,\Delta T = -12.6$ kJ; $\Delta H = C_P\,\Delta T = \Delta U \times {}^7/_5 = -17.6$ kJ.
   $\Delta S = 42.5$ J/K (from Eq. 3.29).

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

7. (a) $\Delta U = \int C_V\,dT = w = -P_{ex}\,\Delta V \rightarrow T_2 = 242._1$ K.
   (b) $q = 0$; $w = \Delta U = -13.1_2$ kJ; $\Delta H = -17.5_8$ kJ.
   $\Delta S = 43.5_1$ J/K (from Eq. 3.29).