Chemistry 230
Problem Set # 6 -- Answers

1. See soln manual. Note that $\ln(1-p) \approx -p$ when $p << 1$.

   (a) $0.1 \geq (11/12)^n \rightarrow n = 27$ (b) $N^{-1/2} = 0.01 \rightarrow N = 10^4$.

2. (a) $\Delta H = 374.5$ (374.48) cal; $\Delta S = 1.479_3$ cal/K.
   (b) $\Delta H = 2003$ (2002.8) cal; $\Delta S = 6.248$ (6.2479) cal/K.
   (c) $\Delta H = 3839$ (3839.2) cal; $\Delta S = 6.992_1$ cal/K.
   (d) $\Delta H = 18.66$ (18.657) kcal; $\Delta S = 50.75$ (50.749) cal/K; $\Delta U = \Delta H - \Delta(PV) = 16.95_1$ kcal.

3. (a) Since both phase changes are equilibrium processes at fixed T and P, $\Delta G = 0$ for both. $\Delta A = \Delta G - \Delta(PV) \approx 0$ for fusion, but $= -823$ cal for vaporization.

   (b) Since $\Delta U \approx \Delta H$, $\Delta A \approx \Delta G = \Delta H - T\Delta S = 28.1_3$ cal (for 10.00 g); 56.26 cal (for 20.00 g).

4. (a) $(\partial U/\partial V)_T = bP^2$ (b) $C_{P,\mathrm{m}} - C_{V,\mathrm{m}} = (1+bP)^2 R$ (c) $\mu_{JT} = 0$.

5. (a) $q = w = \Delta U = \Delta T = \Delta H = 0$; $\Delta V = 45.0$ L (gas); $\Delta P = -2.22$ atm; $\Delta S = 9.57$ J/K;
   $\Delta A = \Delta G = \Delta H - T\Delta S = -2.88$ kJ.

6. $q = w = \Delta U = 0$ (Joule expansion). We need $\mu_J \equiv (\partial T/\partial V)_U = -(\partial U/\partial V)_T/C_V = -bP^2/C_V$. This gives

$$C_V\, dT = -bP^2\, dV = -b\left(\frac{RT}{V_\mathrm{m} - bRT}\right)^2 dV \approx -b\, dV\, (RT/V_\mathrm{m})^2 ,$$

   where the last step can be taken because $bRT << V_\mathrm{m}$ at all times in this problem. Separating variables,

$$\frac{dT}{T^2} = -\frac{b\; n^2\; R^2}{C_V}\frac{dV}{V^2} .$$

   Integrating the right-hand side between $V_1 = 5.00$ L and $V_2 = 50.0$ L and the LHS between $T_1 = 301$ K and T_2 yields $T_2 = 300.56$ K. (Since the T change is so small, the LHS integral is, to a very good approximation, also $= \Delta T/T_1^2$.)

   Other results follow: $\Delta V = 45.0$ L (gas); $\Delta T = -0.45$ K; $\Delta P = -2.23$ atm; $\Delta H = -4.66$ J.

7. Find P such that $\Delta G_\mathrm{rx} = 0$. Use $(\partial G/\partial P)_T = V \rightarrow (\partial \Delta G/\partial P)_T = \Delta V \rightarrow d(\Delta G)_T = \Delta V\, dP \rightarrow$

$$\Delta G_2 - \Delta G_1 = \int_{P_1}^{P_2} \Delta V\, dP \rightarrow 0 - (-801 \text{ J/mol}) = \Delta V_\mathrm{m}(P_2 - P_1)$$

   $P_2 = 2.88\times10^3$ atm.