1) The density of graphite is 2.25 g/cm$^3$ and that of diamond is 3.51 g/cm$^3$.
   If $\Delta G_{298}^o = 2.9$ kJ for C(graphite) $\leftrightarrow$ C(diamond), determine the pressure at which graphite and diamond are in equilibrium at 25 °C.
   
   **Hint**: What is $\Delta G$ at equilibrium? How does free energy change with pressure?

\[ \Delta G = 0 \] at equilibrium at a high pressure.

\[ \Delta G = 0 = \Delta G_{298}^o + \Delta G(\text{from 1 atm to high pressure}) \]

Use Maxwell Relation: $\Delta V = \left( \frac{\partial G}{\partial P} \right)_T$; $\Delta G = \Delta V \Delta P$

\[ \Delta V = \frac{1}{d(\text{graphite})} - \frac{1}{d(\text{diamond})} = \frac{1}{2.25 \text{ g/cm}^3} - \frac{1}{3.51 \text{ g/cm}^3} = \frac{1}{2.25} \text{ g}^3/\text{g} \]

\[ \Delta V = 0.16 \text{ cm}^3/\text{g} = 1.91 \text{ cm}^3/\text{mol} \]

\[ \Delta G = 0 = 2.9 \text{ kJ/mol} + 1.91 \text{ cm}^3/\text{mol}(1 \text{ atm} - P \text{ atm}) \]

\[ \Delta G = 0 = 2.9 \text{ kJ/mol} + 1.91 \text{ cm}^3/\text{mol}(1 \text{ L/1000 cm}^3)(1 \text{ atm} - P \text{ atm}) \]

\[ 1 \text{ L-atm} = 101.325 \text{ J} \]

\[ \Delta G = 0 = 2.9 \text{ kJ/mol} + 1.91 \text{ cm}^3/\text{mol}(1 \text{ L/1000 cm}^3)(1 \text{ atm} - P \text{ atm})(101.325 \text{ J/1 L-atm}) \]

\[ P = \frac{(-2.9 \text{ kJ/mol} - 1.91 \text{ cm}^3/\text{mol}(1 \text{ L/1000 cm}^3)(101.325 \text{ J/1 L-atm}))}{(-1.91 \text{ cm}^3/\text{mol}(1 \text{ L/1000 cm}^3)(101.325 \text{ J/1 L-atm}))} \]

\[ P = 15,264.2 \text{ atm} \]

That's a lot of pressure.
2) Sulfur in its cyclic molecular form (S₈) has two easily accessible solid phases. The rhombic crystal is stable at T < 95.5 °C and has a density of 2.07 g/cm³. The monoclinic phase is stable at T > 95.5 °C and less than the melting point of sulfur, and has a density of 1.96 g/cm³.

Estimate the pressure in atmospheres that is necessary to make rhombic sulfur the stable phase at 100 °C if the entropy of the transition is 1.00 J/mole-K. Assume that ΔS is a constant.

Use Clapeyron Equation (dp/dT) = ΔS_{transition}/ΔV_{transition}

The Clapeyron equation can be derived from using the cyclic relation with G, T & p

(?G/?p)_T(?p/?T)_G(?T/?G)_p = -1

(?(?p/?T)_G = -(?G/?(?T)_p)(?(?p/?(?G)_T = -(?G/?(?p)_T

(?(?p/?T)_G = -(?G/?(?T)_p/(?(?G/?(?p)_T = ΔS/ΔV

using the Maxwell relations (?G/?p)_T =V & (?G/?(?T)_p = -S

Constant G due to ΔG = 0 at equilibrium

density = mass/volume; volume = mass/density

V_{rhombic} = 256 g/mole/2.07 g/cm³ = 123.672 cm³/mole
V_{monoclinic} = 256 g/mole/1.96 g/cm³ = 130.612 cm³/mole

ΔV_{transition} = V_{monoclinic} - V_{rhombic} = 130.612 cm³/mole - 123.672 cm³/mole = 6.940 cm³/mole

ΔV_{transition} = 6.94 x 10⁻⁶ m³/mole

(dp/dT) = ΔS_{transition}/ΔV_{transition}

?dp = ΔS_{transition}/ΔV_{transition}dT = ΔS_{transition}/ΔV_{transition}dT

Integrate p from 1 atmosphere pressure to p and T from 368.5 K to 373 K.

p – 1 atm = ΔS_{transition}/ΔV_{transition}(373 K – 368.5 K)

p – 1 atm = (1 J/mole-K/6.94 x 10⁻⁶ m³/mole)(373 K – 368.5 K)

p – 1 atm = 6.483 x 10⁵ J/m³ or kg-m³/sec²-m³ or kg/sec²-m or Pa

1 L-atm = 101.325 J & 1000 L = 1 m³ therefore 1 atm = 101,325 J/m³

p – 1 atm = 6.40 atm

p = 7.40 atm
3) A liquid has a vapor pressure of 40.00 kPa at 298.15 K. When 0.080 kg of a non-volatile solute is dissolved in 1.0 mole of the liquid the new vapor pressure is 26.66 kPa. What is the molar mass of the solute? Assume that the solution is ideal.

Raoult’s Law: \( p_A = x_A p_A^* \) or \( x_A = p_A / p_A^* \)

\[
x_A = \frac{26.66 \text{ kPa}}{40.00 \text{ kPa}} = 0.666
\]

\[
x_A = \frac{n_A}{n_A + n_B}
\]

\[
0.666 = \frac{1}{1 + n_B}
\]

\[
n_B = \frac{1}{0.666} - 1 = 0.5 \text{ mole}
\]

Molar Mass = 80 g / 0.5 mole = 160 g/mole
4) The molar volume of a binary solution is given by: \( V_m = x_1 V_{m1} + x_2 V_{m2} \).

Show that: \( V_{m1} = V_m - x_2 \left( \frac{\partial V_m}{\partial x_2} \right) \) and \( V_{m2} = V_m + (1 - x_2) \left( \frac{\partial V_m}{\partial x_2} \right) \).

\[
\begin{align*}
V_m &= x_1 V_{m1} + x_2 V_{m2} \\
V_m &= (1 - x_2) V_{m1} + x_2 V_{m2} \\
V_m &= V_{m1} + x_2 (V_{m2} - V_{m1}) \\
\frac{\partial V_m}{\partial x_2} &= (V_{m2} - V_{m1}) \\
V_m &= V_{m1} + x_2 \left( \frac{\partial V_m}{\partial x_2} \right) \\
V_{m1} &= V_m - x_2 \left( \frac{\partial V_m}{\partial x_2} \right) \\
\frac{\partial V_m}{\partial x_2} &= (V_{m2} - V_{m1}) \\
V_m &= x_1 V_{m1} + x_2 V_{m2} \\
V_m &= x_1 V_{m1} + (1 - x_1) V_{m2} \\
V_m &= V_{m2} + x_1 (V_{m1} - V_{m2}) \\
V_{m2} &= V_m - x_1 (V_{m1} - V_{m2}) \\
V_{m2} &= V_m + (1 - x_2) \left( \frac{\partial V_m}{\partial x_2} \right)
\end{align*}
\]
5) The osmotic pressure of an aqueous solution of bovine serum albumin with \( \rho_B = 0.0200 \text{ g/cm}^3 \) is 6.1 torr at 0 °C. Estimate the molecular weight of this protein.

\[
\Pi = [B]RT \\
\Pi = (\rho_B/M)RT \\
M = (\rho_B/\Pi)RT
\]

\[
M = (0.02 \text{ g/cm}^3 \times 1000 \text{ cm}^3/\text{L} \times 6.1 \text{ torr} \times 1 \text{ atm}/760 \text{ torr}) \\
\times (8.205 \times 10^{-2} \text{ L-atm/K-mol}) (273 \text{ K})
\]

\[
M = 55,820 \text{ g/mole}
\]
6) By measuring the equilibrium in the liquid and vapor phases of an acetone(A) – ethanol(E) solution at 57 °C and 1.00 atm it was found that \( x_A = 0.4 \) (liquid phase) when \( y_A = 0.516 \) (vapor phase). Calculate the activities and the activity coefficients of both components in this solution on the Raoult’s Law basis. The vapor pressures of the pure components are \( p_A^* = 786 \) torr and \( p_E^* = 551 \) torr.

\[
y_A = \frac{p_A}{p_{\text{total}}} = 0.516 = \frac{p_A}{760 \text{ torr}}
\]

\[
p_A = 392 \text{ torr}
\]

\[
p_E = 368 \text{ torr}
\]

\[
a_A = \frac{p_A}{p_A^*} = \frac{392 \text{ torr}}{786 \text{ torr}} = 0.499
\]

\[
a_E = \frac{p_E}{p_E^*} = \frac{368 \text{ torr}}{551 \text{ torr}} = 0.668
\]

\[
y_A = \frac{a_A}{x_A} = \frac{0.499}{0.4} = 1.248
\]

\[
y_E = \frac{a_E}{x_E} = \frac{0.668}{0.6} = 1.113
\]
Useful formulae:

\[ \Delta U = q + w; \quad dw = -p \text{d}V, \quad dq = T \text{d}S \]
\[ \Delta H = \Delta U + \Delta(PV) \]
\[ C_v = (\frac{\partial U}{\partial T})_V \quad C_p = (\frac{\partial H}{\partial T})_p \]
\[ C_p - C_v = nR \]
\[ \alpha = (1/V)(\frac{\partial V}{\partial T})_p \quad \kappa_T = -(1/V)(\frac{\partial V}{\partial p})_T \]
\[ \mu_T = (\frac{\partial H}{\partial p})_T \]

ideal gas: \( p = nRT/V \)

van der Waals gas: \( p = \frac{nRT}{(V-b)} - \frac{an^2}{V^2} \)

1 L-atm = 101.325 J \quad 1 J = 1 kg-m^2/sec^2 \quad 1 N = 1 kg-m/sec^2

\[ R = 8.314 \text{ J/K-mol} = 8.205 \times 10^{-2} \text{ L-atm/K-mol} \]

\[ z = f(x,y); \quad \text{Total Differential of } z: \quad \text{d}z = \frac{\partial z}{\partial x} d\sigma \]

\[ dU = T \text{d}S - pdV \quad dH = T \text{d}S + VdP \]
\[ dA = -pdV - SdT \quad dG = VdP - SdT \]

\[ T = (\frac{\partial U}{\partial S})_V = (\frac{\partial H}{\partial S})_p \quad (\frac{\partial T}{\partial S})_V = -(\frac{\partial p}{\partial S})_V \]
\[ -P = (\frac{\partial U}{\partial V})_S = (\frac{\partial A}{\partial V})_T \quad (\frac{\partial T}{\partial p})_S = (\frac{\partial V}{\partial p})_T \]
\[ V = (\frac{\partial H}{\partial P})_S = (\frac{\partial G}{\partial P})_T \quad (\frac{\partial p}{\partial T})_V = (\frac{\partial S}{\partial V})_T \]
\[ -S = (\frac{\partial A}{\partial T})_V = (\frac{\partial G}{\partial T})_p \quad (\frac{\partial V}{\partial T})_p = -(\frac{\partial S}{\partial P})_T \]

Chemical Potential: \( \mu = G_m \) \quad (\frac{\partial \mu}{\partial T})_p = -S_m \quad (\frac{\partial \mu}{\partial p})_T = V_m \n
\[ \frac{dp}{dT} = \Delta_{trs}S/\Delta_{trs}V = \Delta_{trs}H/T\Delta_{trs}V \]
\[ \frac{d\ln(p)}{dT} = \Delta_{trs}H/RT^2 \]

Surface Tensiton: \( \gamma, \quad \text{d}w = \gamma \text{d}\sigma \)

Partial Molar Properties: \( X_j = (\frac{\partial X_j}{\partial n_j})_{p,T,n_j} \)
\[ \mu_j = (\frac{\partial G}{\partial n_j})_{p,T,n_i \neq j} = (\frac{\partial U}{\partial n_j})_{S,V,n_i \neq j} = (\frac{\partial H}{\partial n_j})_{p,S,n_i \neq j} = (\frac{\partial A}{\partial n_j})_{V,T,n_i \neq j} \]
\[ \sum_{i} n_i \text{d}x_j = 0 \quad \mu_j = \mu^0 + RT \ln(p/p^0) \]
\[ \rho_A = x_A \rho_A^* \quad \rho_B = x_B \rho_B^* \quad \mu_A = \mu_A^* + RT \ln(x_A) \]
\[ a_A = \rho_A / \rho_A^* \quad \gamma_A = a_A / x_A \quad \mu_A = \mu_A^* + RT \ln(a_A) \]

\[ \Delta G_{MIX} = nRT(x_A \ln(x_A) + x_B \ln(x_B)) \]
\[ \Pi = [B]RT \]