Graded problems:

1. In discussing coordination numbers and deriving the permitted range of radius ratio, R_A / R_B, allowed for each (where R_A is the radius of the central ion and R_B is the radius of the surrounding ions) we skipped over 5-fold coordination without much attention. Were we being careless?

    Let us consider an arrangement of ions in which three *B* ions are arranged in a triangle around an *A* ion, and for which all four of these ions are coplanar. Let's now place a fourth and fifth *B* ion above and below the *A* ion in directions that are normal to the plane of the triangle. Voila! Five-fold coordination!! This is a nifty little polyhedron in the shape of a triangle (three-fold) bipyramid. There is no immediately apparent reason why this coordination polyhedron should not occur in crystal structures.

    a. Prepare a careful sketch of the polyhedron.
    b. If each of the spheres that represent the *B* cation are in contact with the *A* ion, will all of the *B-B* contacts along the edges of the polyhedron be of equal length?
    c. Derive values for the range of radius ratios R_A / R_B that are permitted for this configuration.
    d. Despite all of the above, and the fact that the polyhedron has a symmetry that is permitted in crystals, this grouping is almost <u>never</u> found to occur in ionic crystals! Can you explain why?

2.
    a. Determine the pairs of coordination numbers that would be permitted for a compound of stoichiometry AB_2 if *A* is surrounded only by *B* ions and vice versa, and if all *A* ions have the same coordination and all *B* ions do as well.
    b. Using the results of the calculations that we have performed for the range of radius ratios R_A / R_B that are permitted for various coordination numbers please establish the permitted range of radius ratios for each of the pairs of coordination numbers in part (A).
    c. Pauling lists 0.68 Angstroms for the radius of Ti^{4+} and 1.40 Angstroms for O^{2-}. What would you predict for the coordination numbers of the ions in TiO_2?

3. **Working with the First Law.** One mole of an ideal gas is compressed reversibly from 5L to 1 L at a constant pressure of 5 atm, and absorbs 2400 J of heat during this process.

   a. Calculate the work and internal energy change in this process.

Because the process is reversible, the work is simply:

$$dw = -PdV$$

$$w = -P\int_{5L}^{1L} dV = -(5atm)(1L - 5L)\left(\frac{8.3144\,J}{0.082057\,L \cdot atm}\right) = 2026J$$

The work is positive: work is done *on* the gas in this process. Next, the internal energy change is determined using the first law. Heat is absorbed by the gas in this process, so q is > 0:

$$dU = dq + dw$$

$$\Delta U = 2400J + 2026J = 4426J$$

   b. Determine the initial and final states (P, V, and T) of the gas.

The states are calculated using the ideal gas law:

Initial state:
$$P = 5atm$$
$$V = 5L$$
$$T = \frac{PV}{nR} = \frac{(5atm)(5L)}{(1mole)(0.082057\frac{L \cdot atm}{K \cdot mole})} = 305K$$

Final state:
$$P = 5atm$$
$$V = 1L$$
$$T = \frac{PV}{nR} = \frac{(5atm)(1L)}{(1mole)(0.082057\frac{L \cdot atm}{K \cdot mole})} = 60.9K$$

Note in proof on this problem: We haven't formally introduced the internal energy relation for the ideal gas in class yet (U = 1.5nRT). The heat absorption described for this process would clearly violate this relation- the internal energy is increasing while the temperature decreases. This was an error in the formulation of the problem; it does not affect the calculations you are asked to make, but this process would be an unstable change for a 'real' ideal gas.

   c. Now consider a roundabout means of moving the gas from the given initial state to the same final state, as illustrated below. Use a 3-step reversible process, first a constant volume drop in pressure, followed by a constant-pressure compression, followed last by a constant-volume rise in pressure (steps 1, 2, and 3 in the sketch below).

i. What is the internal energy change of this composite process (step 1 + step 2 + step 3)?

We know that internal energy is a state function. Thus, if we are moving from the same initial to the same final state in our composite process, then the internal energy change for the composite process must be the same as in our previous calculation: 4426 J. **The internal energy change does not depend on the path taken to move from the initial to final states because U is a state function**.

ii. Calculate the total heat transfer and work in this composite process (using P_2 as denoted in the diagram below) and use the calculation to prove that heat and work are not state functions.

Using the first law, we can relate the total internal energy change for the composite process to the heat and work transfers in each step:

$$dU = dq + dw$$

$$\Delta U_{total} = q_{step1} + w_{step1} + q_{step2} + w_{step2} + q_{step3} + w_{step3} = 4426 J$$

Because the process is reversible, we can determine the work terms in each step:

$$dw_{step1} = -PdV = 0$$

$$dw_{step2} = -PdV$$
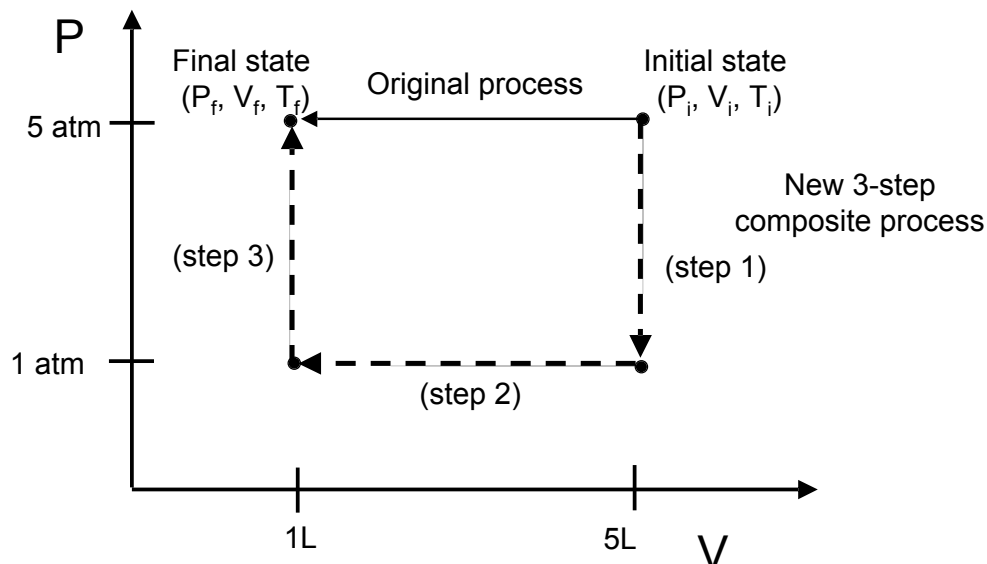
$$dw_{step3} = -PdV = 0$$

$$w_{step2} = -(1atm)(-4L)\left(\frac{8.3144}{0.082057 \cdot atm}\right)$$

$$w_{total} = w_{step2} = 405 J$$

…much less work is done in this composite process. Combining these equations, we obtain a final expression for the total heat transferred in the composite process:

$$q_{total} = q_{step1} + q_{step2} + q_{step3} = 4426J - w_{step2} = 4426 - \left[-(1atm)(-4L)\left(\frac{8.3144}{0.082057 L \cdot atm}\right)\right] = 4021J$$

The total heat transfer is also different from the original process. Thus we see that though the internal energy change is the same in both the original and composite processes, by taking a different path, the total heat and work performed are different. Since these functions show path dependence, they are **not** state functions.

The P-V diagram shows:

P axis (vertical), V axis (horizontal).

Final state (P_f, V_f, T_f) at 5 atm, 1L. Initial state (P_i, V_i, T_i) at 5 atm, 5L. "Original process" arrow from initial to final state.

New 3-step composite process: (step 1) down from initial state at 5L to 1 atm, (step 2) from 5L to 1L at 1 atm, (step 3) up from 1L at 1 atm to 5 atm.

Pressure marks: 5 atm, 1 atm. Volume marks: 1L, 5L.

4. **Heat vs. temperature**. You are designing a housing for a high-temperature apparatus, which serves to connect this heat-producing generator component to other parts of a larger system. The housing is in thermal contact with the generator (i.e., it can transfer heat with the generator). The generator must operate in cycles: at the start of each cycle, the system starts at a uniform temperature of 577°C, and produces heat. In each cycle, 29.4 kJ of this heat is passed to the housing- after which, the system is allowed to slowly cool back to 577°C (constant pressure conditions throughout). Your design team would like to use aluminum as the housing material as it is lightweight and inexpensive. The housing would be formed from 1 kg of aluminum. Relevant physical data for aluminum is provided below.

$$T_m = 932 \text{ K}$$

$$C_p^s = 20.7 + 12.4 \times 10^{-3} T \text{ J/mole K}$$

$$C_p^l = 29.0 \text{ J/mole K}$$

$$\Delta H_m = 10,500 \text{ J/mole}$$

Do you recommend that aluminum be used in this application? Explain your choice with thermodynamic calculations.

The 'resting' operating temperature of the system, 577°C = 850 K- which is only 82 K below the melting temperature of alumimum. Thus, our first concern is whether the housing would be heated to its melting point in the course of a cycle of operation (!). We are told how much heat is evolved to the housing per cycle and the mass of the housing. The total heat absorbed per mole of aluminum per cycle is:

$$q = \left(\frac{29,400\,J}{cycle}\right)\left(\frac{27\,g}{mole}\right)\left(\frac{1}{1,000\,g\,Al}\right) = 793.8\,\frac{J}{moleAl \cdot cycle}$$

We can compare this to the heat required to take the housing from its initial temperature at the start of the cycle (850 K) to its melting point (932 K):

$$q_{to\,T_m} = \int_{850}^{932} C_p\,dT = \int_{850}^{932}\left(20.7 + 12.4 \times 10^{-3}\,T\right)dT = 2603\,\frac{J}{moleAl}$$

Since the heat absorption per mole of Al in the cyclic process would not be enough to reach the melting temperature, we could state to first order that Al would be acceptable in this application.

5. **Super-cooled Silicon.** You have a sample of silicon that is super-cooled to 1670 K from a molten state, and then transferred to an adiabatic container at constant pressure. Calculate:

    a. The fraction of silicon that solidifies when the melt is placed in the adiabatic container

    b. the enthalpy change in this process

    c. the entropy change in this process

    d. the final temperature of the system at equilibrium

Data for Si: T_m = 1683 K

                ΔH_m = 50,630 J/mole

                C_p^s = 22.817 + 0.0038995T − 8.288x10^{-5}T^2 − 0.000354063T^{-2} J/mole K

                C_p^l = 27.19 J/mole K

Because we are calculating a change of state by a process involving heat transfer- here involving solidification of a liquid- it is very useful to make a qualitative (or quantitative) plot of the heat transfer for the system vs. temperature- and because we are at constant pressure, the heat transfer is simply the change in enthalpy of the system:

$$dH = dU + PdV + VdP = dq + VdP$$
$$dH = \left(dq\right)_P$$

Using this equality, we can plot relative changes in enthalpy over any temperature range of interest, provided we know the heat capacities and phase transitions occurring in that range. For example, I plot below the relative enthalpy change starting at T = 1500 K and heating a sample up past its melting point (shown by the black line):
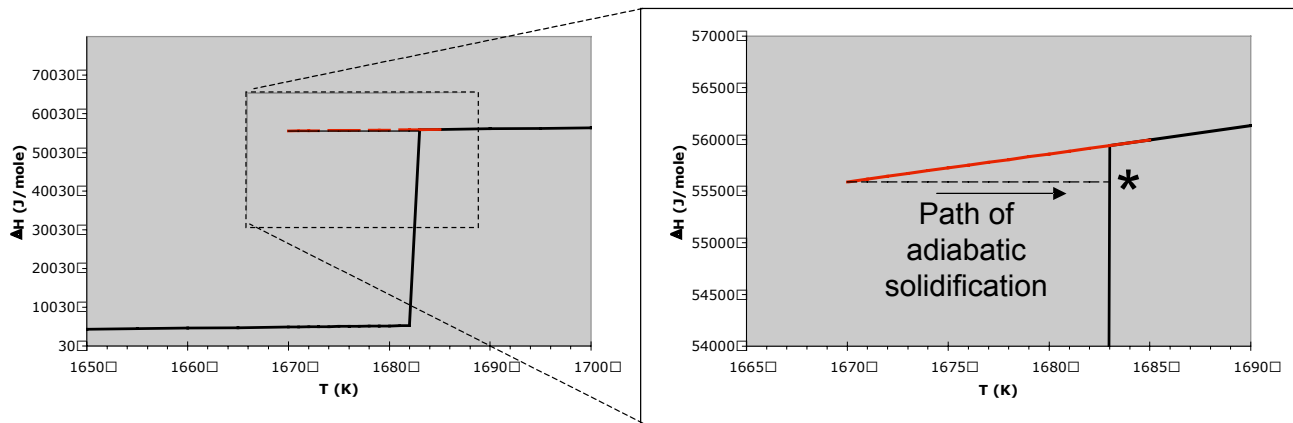
The plot is constructed by determining the enthalpy at each point using the constant pressure heat capacity. At 1500K, the silicon is in the solid state:

$$dH = dU + PdV + VdP = dq + VdP$$

$$dH = (dq)_P$$

$$\Delta H = \int dq = \int_{1500}^{T} C_P^S(T)dT = \int_{1500}^{T}\left(22.817 + 0.0038995T - 8.288 \times 10^{-5}T^2 - 3.54 \times 10^{-4}T^{-2}\right)dT$$

Note that it really doesn't matter what particular temperature I start the integration at, since I only care about the relative enthalpy change. The silicon melts at T = 1683K, and further heating occurs with the solid phase heat capacity. To calculate an enthalpy change from 1500K to 1700K, for example, I must account for the enthalpy of melting absorbed by the system to transform to the liquid state:

$$dH = dU + PdV + VdP = dq + VdP$$

$$dH = (dq)_P$$

$$\Delta H_{1500 \to 1700} = \int dq = \int_{1500}^{1683} C_P^S(T)dT + \Delta H_M + \int_{1683}^{1700} C_P^L(T)dT$$

Now, we are given the situation that a sample of molten (liquid) silicon is super-cooled- kept in the liquid state below the melting point, and the temperature is reduced to 1670K. The path of super-cooling is shown on the enthalpy change plot by the red line- a line whose slope is given by C_p^L since the Si remains in the liquid state. The sample is then allowed to equilibrate under adiabatic conditions. **A super-cooled or super-heated sample is not at equilibrium**: it is always unstable or metastable. Thus, our sample will be driven to transform to an equilibrium state consistent with the constraints on the system. The constraint in this case is that the system is contained adiabatically- no heat can enter or leave the system. This condition requires that the system can only move on our enthalpy change plot along a line of constant enthalpy (i.e., zero enthalpy change, zero heat transfer). This is denoted by the dotted line on the plots above. Thus, to reach an equilibrium state without releasing any heat, the system moves to the right along the dotted line to a point along the equilibrium curve at the phase transition (denoted by the asterisk). The final state of the system is a two-phase equilibrium: based on the position of the asterisk, it is clear that the system is mostly still liquid, with a small fraction of solid formed. The system cannot completely solidify, because

complete solidification would required that a substantial amount of heat be removed from the system.

We can now quantitatively answer the questions posed:

(a) The fraction of silicon in the solid state at equilibrium is determined by the amount of heat removed during super-cooling relative to the total enthalpy of melting. Graphically, the fraction of solid is the ratio $SC/\Delta H_m$ from the plot below. The value of the enthalpy change SC is determined using the heat capacity:

$$SC = \Delta H_{super-cooling} = \int dq = \int_{1670}^{1683} C_P^L(T)dT = \int_{1670}^{1683}(27.19)dT = 353.5 \frac{J}{mole}$$

$$f^S = \frac{SC}{\Delta H_m} = \frac{353.5}{50,630} = 0.0069$$

Thus we see that this modest degree of super-cooling leaves the system in nearly a total liquid state at the adiabatic equilibrium.
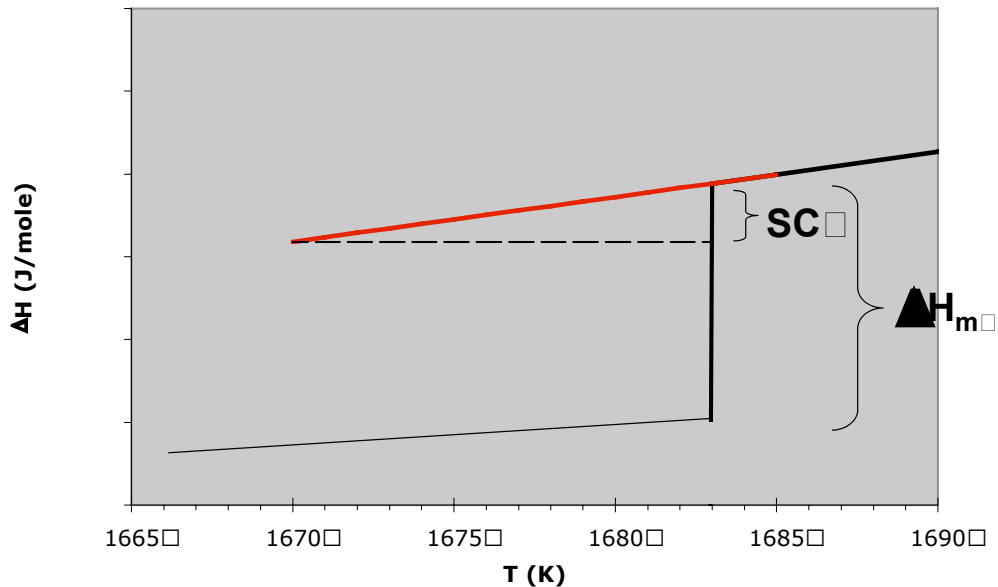
(b) We've already pointed out that the condition of an adiabatic process constrains the system to zero heat transfer. At constant pressure, zero heat transfer means $\Delta H = 0$ for the process.

(c) The entropy change is determined using the constant pressure heat capacity and our releationship between dq and S:

$$dq = TdS$$

$$\therefore \Delta S = \int \frac{dq}{T} = 0$$

Because this is an adiabatic process, there is no entropy change. We will later see with the introduction of the second law that the entropy is always constant during adiabatic processes. Why can't we plug into the relationship between Cp and S? i.e.:

$$C_{P} = T\left(\frac{\partial S}{\partial T}\right)_{P}$$

wrong!

$$\therefore \Delta S = \int_{1670}^{1683}\frac{C_P^L(T)}{T}dT = \int_{1670}^{1683}\frac{(27.19)}{T}dT = 27.19\ln\left(\frac{1683}{1670}\right) = 0.211\frac{J}{mole\cdot K}$$

… the error here is that we have used the heat capacity for the liquid- when we are in converting some of the liquid to solid! The heat capacity is not defined during the transformation, and we thus can't use this equation for an adiabatic transformation.

(d) The final temperature of the system is simply determined by the equilibrium point attainable under the adiabatic constraint: the melting temperature of the system. T_{final} = 1683K.