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**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 never found to occur in ionic crystals! Can you explain why?
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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.

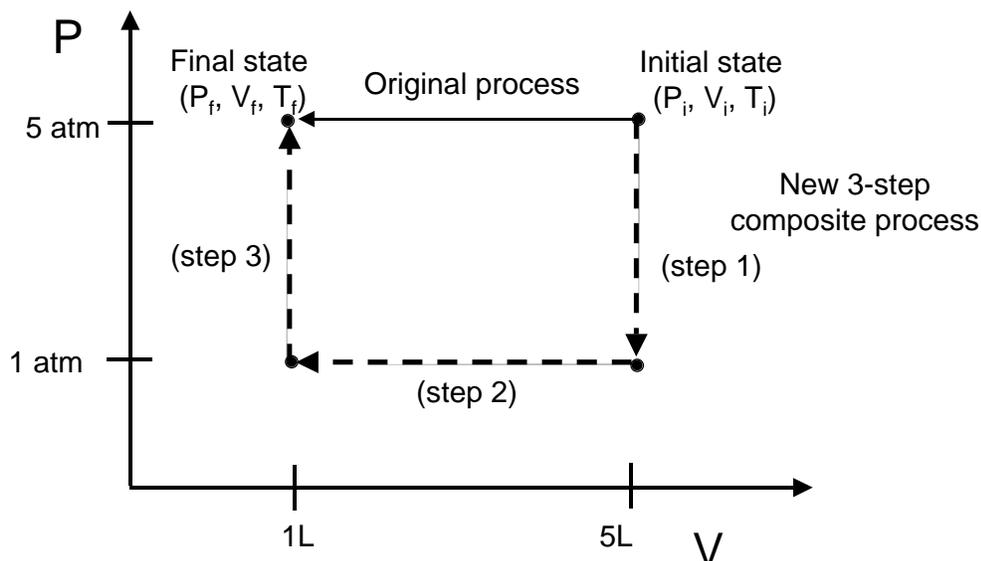
a. Calculate the work and internal energy change in this process.

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

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.



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.

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:
- The fraction of silicon that solidifies when the melt is placed in the adiabatic container
  - the enthalpy change in this process
  - the entropy change in this process
  - the final temperature of the system at equilibrium

Data for Si:  $T_m = 1683 \text{ K}$

$$\Delta H_m = 50,630 \text{ J/mole}$$

$$C_p^s = 22.817 + 0.0038995T - 8.288 \times 10^{-5} T^2 - 0.000354063 T^3 \text{ J/mole K}$$

$$C_p^l = 27.19 \text{ J/mole K}$$