
Graded problems:

1. **5-fold coordination structures.** We have omitted 5-fold coordination from our consideration of the connection between coordination number and the range of permitted radius ratios for the ions that are involved. This was done in spite of the fact that there is a coordination geometry for a 5-fold coordination polyhedron that has an acceptable crystallographic symmetry.

Consider a trigonal bipyramidal coordination polyhedron of anions, B , about a central cation A (i.e. a pair of apical neighbors above and below a planar triangular group).

- a. Are all edges of this polyhedron of the same length in this configuration when the cation is in contact with all surrounding anions?
 - b. Which edge is the critical anion-anion separation?
 - c. Determine the range of radius ratios that is permitted for this coordination.
 - d. Do you have a suggestion for why this polyhedron is quite rare in structures in comparison with tetrahedral or octahedral coordination?
2. **Perovskite structures.** Oxides that have the so-called Perovskite structure type (or a closely-related distorted version thereof) are presently under active study for their extraordinarily large piezoelectric response. These materials see wide application in capacitors (because of a very large dielectric constant), sensors, and actuators.

One material in this family is barium titanate, BaTiO_3 . In the structure the Ba^{2+} ion is at the center of a cube, the Ti^{4+} ions are at the corners, and O^{2-} resides at the middle of each of the cell edges.

- a. What are the coordination numbers of Ba^{2+} and Ti^{4+} ?
- b. Is Pauling's rule concerning the sum of bond strengths satisfied?
- c. Are both of the cations in contact with O^{2-} ? (Please use the appropriate Shannon-Prewitt ionic radii if or when you need to employ specific ionic sizes).
- d. Consider a two-dimensional plot in which the y -axis is R_A and the x -axis is R_B . Is there a locus in this field in which both A and B contact O^{2-} ? What do you think might happen to the structure outside of/away from this locus?

3. **Transforming materials.** Elemental manganese has several phase transitions among different solid states in the temperature range 800-1500 K. The heat capacity of Mn can be modeled by the polynomial expression:

$$C_p = a + bT + cT^{-2} \text{ (J/mole K)}$$

Constants for the heat capacity of manganese, along with relevant temperature and enthalpies of transformation are:

Phase	Stable Temperature range (K)	a	b	c	ΔH_{trans} (J/mole)
\square	298-993	21.6	.0159	0	-
$\square \rightarrow \square$	-	-	-	-	2010
\square	993-1373	34.9	0.0028	0	-
$\square \rightarrow \square$	-	-	-	-	2300
\square	1373-1409	44.8	0	0	-
$\square \rightarrow \square$	-	-	-	-	1800
\square	1409-1517	47.3	0	0	-
$\square \rightarrow \text{liquid}$	1517- T_b	-	-	-	129,580
liquid	T_b -	46.0	-	-	-

- a. Using this data, calculate the entropy change for heating 1 mole of Mn from 860K to 1400K at constant pressure.
- b. Suppose 1 mole of Mn is super-cooled (cooled below its stable solidification temperature without transformation to the solid) to a temperature of 1000K, then *adiabatically* allowed to solidify in its stable form at constant pressure. Determine what final phase is formed, the fraction that has solidified, and the final temperature of the system.

(Eqn 1)
$$H_{T_M}^L - H_{1000K}^L = \int_{1000}^{T_M} C_P^L dT$$

(Eqn 2)
$$H_{T_M}^L - H_{T_{\text{final}}}^{\square} = \Delta H_m + \int_{1409}^{T_M} C_P^{\square} dT + \Delta H_{\square\square\square} + \int_{1373}^{1409} C_P^{\square} dT + \Delta H_{\square\square\square} + \int_{T_{\text{final}}}^{1373} C_P^{\square} dT$$

4. **Why is it hard to make measurements at constant volume?** We have discussed in class that experimentally, C_v is difficult to measure due to thermal expansion. Let's quantify this difficulty: Suppose you have 1 mole of iron that has a volume of 7.31 cm^3 at 293 K.

Determine the pressure that would have to be applied after this material is heated to 298 K (only 5 degrees warmer!) to compress it to the volume it had at 293K- thus maintaining constant volume.

Data for Fe: $\alpha = 6.3 \times 10^{-5} \text{ K}^{-1}$
 $\beta = 1.10 \times 10^{-6} \text{ atm}^{-1}$ at 298K

Optional Problems:

5. **Pauling's fourth rule.** Demonstrate the validity of Pauling's fourth rule that concerns sharing of elements of coordination polyhedra by computing the distance between the central cations, A , in terms of R_A and R_B when cubic coordination polyhedra share:
- Corners
 - Edges
 - Faces

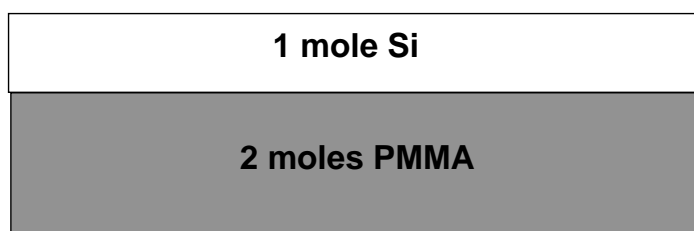
Note: There will be degrees of freedom in the orientation of the polyhedra for some of these linkages. If such is the case, please consider the geometry that results in *maximum* separation of the cations.

6. **Difference in heat capacities for an ideal gas.** We have discussed that for most solids, C_p and C_v are nearly equal at very low temperatures, and as the temperature rises, their values diverge due to thermal expansion under constant pressure conditions. However, the ideal gas shows a different behavior: derive the difference $C_p - C_v$ for the ideal gas.
7. **Phase changes to maintain cool temperatures.** Cooling systems can be designed around the use of phase transitions as sinks for heat at a constant temperature. In these systems, a material is used which undergoes a phase transition near the desired use temperature. If you were to design a cooling system designed to maintain a temperature between 0°C and 20°C, which of the materials below would you choose for the heat absorbing component and why?

Material	C_p^{solid} (kJ/kg K)	T_m (K)	ΔH_m (kJ/kg)	C_p^{liquid} (kJ/kg K)
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Water	2.09	273	336	4.18
Tetradecane (CH ₃ -(CH ₂) ₁₂ -CH ₃)	1.68	278.8	227	2.18
CaCl ₂ •6H ₂ O+CaBr ₂ •6H ₂ O	1.52	287	140	2.01
Glycerol	1.62	291	192	2.37

8. **Equilibrating the temperature of materials.** Suppose you are designing a new microchip, which will utilize an electrically insulating polymer, poly(methyl methacrylate) (PMMA), as a base, with a single crystal silicon film grown atop. The completed chip becomes heated such that 1 mole of the Si crystal reaches a temperature of 50°C, while 2 moles of the PMMA underlayer remain near room temperature- at 25°C. If the chip is then powered down (no more heating) and the two components can together be considered an isolated system at constant volume (no heat transfer to the surrounding air), they will equilibrate to a common final temperature.



The heat capacities for these materials are approximately constant in this temperature range:

$$C_V^{\text{PMMA}} = 130.8 \text{ J/mole K}$$

$$C_V^{\text{Si}} = 19.99 \text{ J/mole K}$$

- What final temperature will the materials reach?
- Calculate the entropy change in the PMMA film and in the Si crystal, and the total entropy change for the whole system.