3.012 Quiz 1 **3.012**
09.23.04 **Fall 2004**
100 points total

Structure (50 points total):

1. . (16 points). Let's consider an ionic compound of composition A_2B_3 in which the coordination number C_{NA} of every cation is the same, and similarly, the coordination of every anion C_{NB} is the same. In addition, only anions are nearest neighbors of the cations and vice versa.

   a. What are the allowed pairs of coordination numbers C_{NA} and C_{NB} for phases of this stoichiometry?

   b. Derive the range of radius ratios for which a structure of this composition is permitted if the coordination of **A** is octahedral (six-fold). Please indicate clearly the geometry of the coordination on which your calculation is based.

2. (16 points) There is an alternative six-fold coordination besides octahedral: a trigonal prism. This arrangement would be symmetrical- an equilateral triangle of **B** ions in the same orientation above and below the central cation- and could readily be fit into a structure.

   a. One can immediately state that this configuration is less likely than octahedral coordination in an ionic structure. Why?

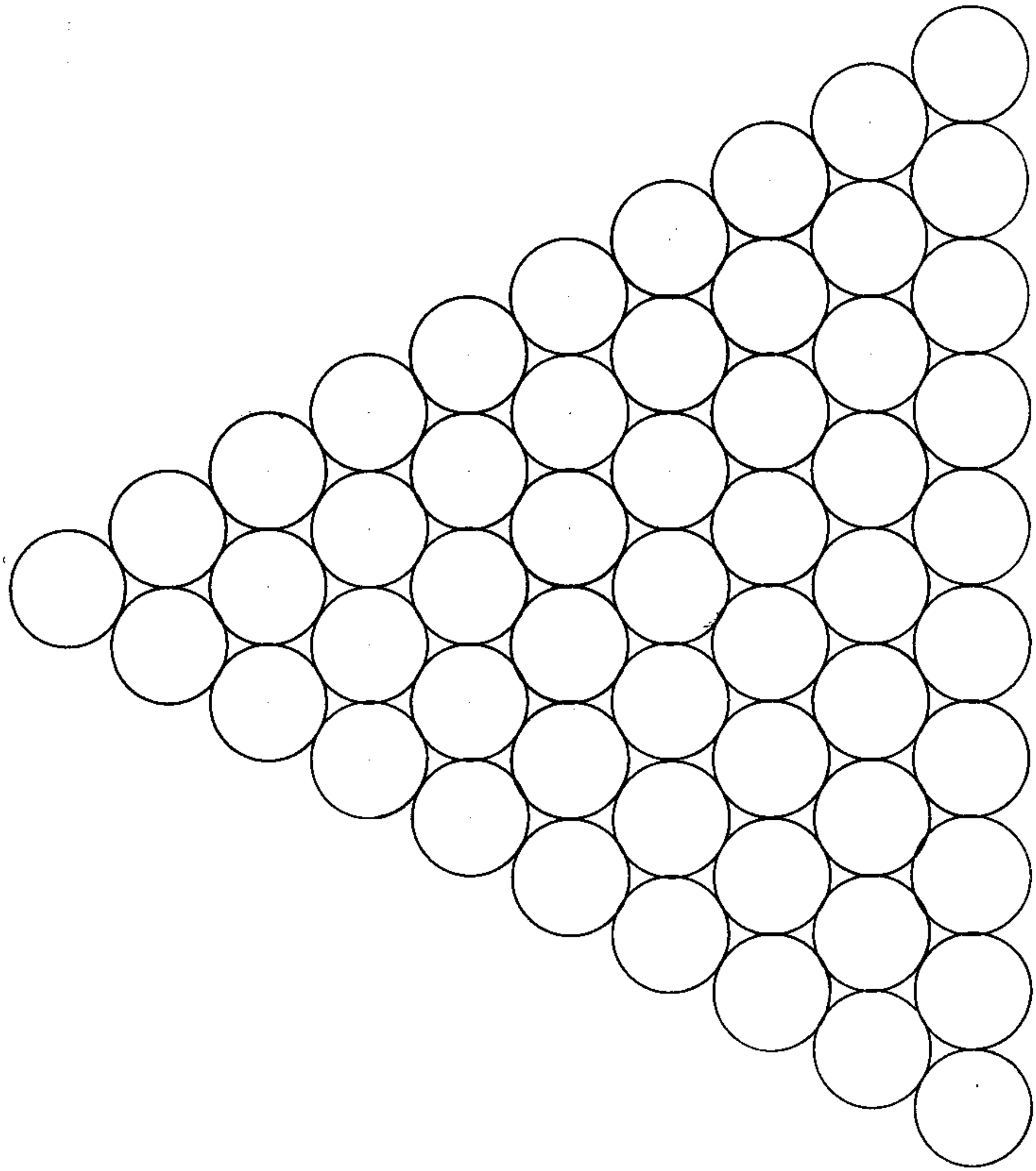
   b. In spite of the above observation, let's compute the critical radius ratio for trigonal prismatic coordination assuming, as usual, that this occurs when the **A** and **B** ions remain in contact and the surrounding anions just touch along all edges of the polyhedron.

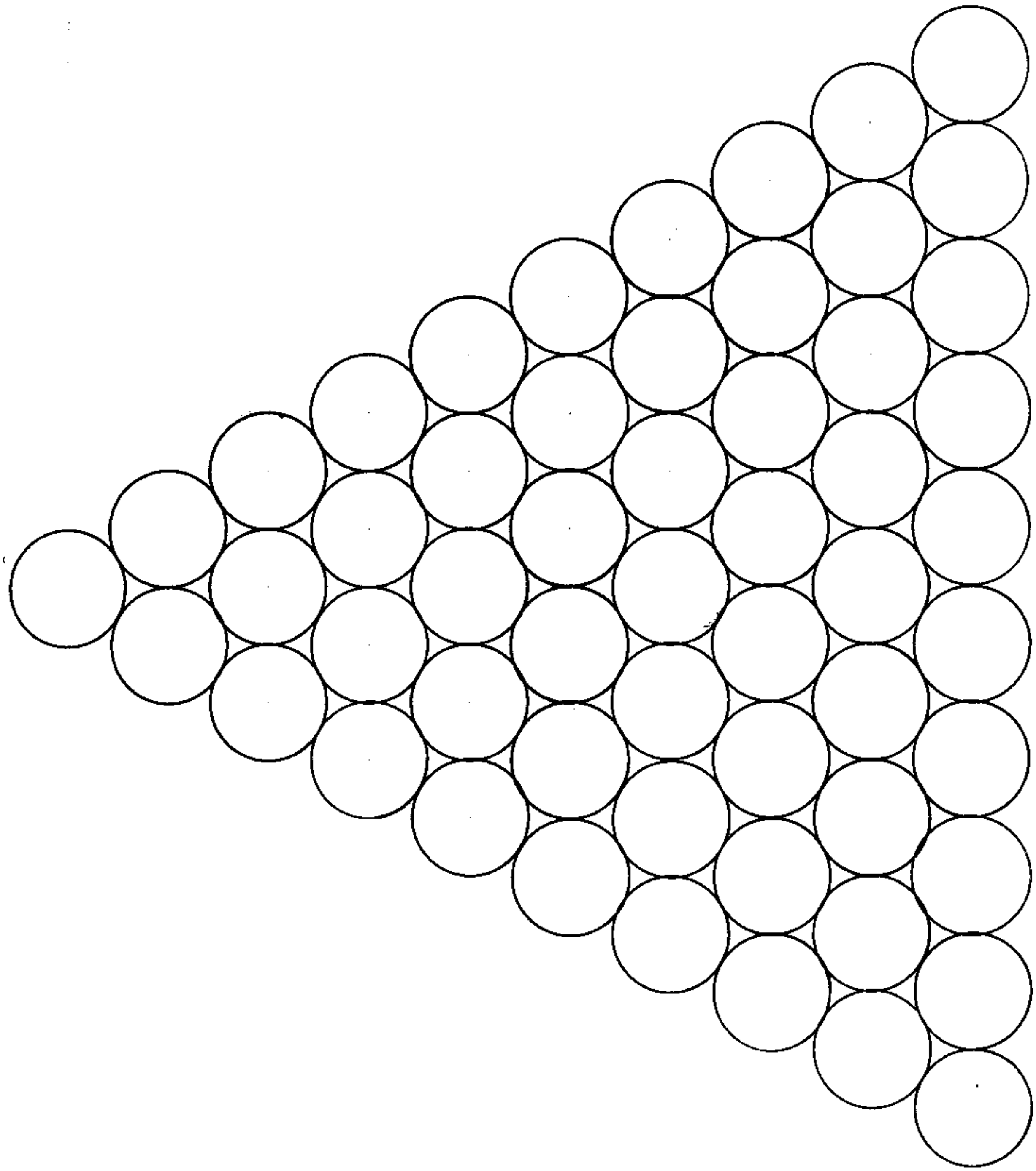
(18 points) Let us consider the structure of AL_2O_3, which conforms to your considerations in the above problems. The larger oxygen anions are arranged in close-packing in this structure. Let us consider one pair of such layers.

c. How many octahedral and tetrahedral sites per anion are present between this pair of sheets?

d. Quite independent of ionic sizes, show that Pauling's rule concerning the summation of bond strength makes it quite unlikely (if not impossible) that the tetrahedral interstices are occupied in the structure of Al_2O_3.

e. The sheets of oxygen anions stack in a close-packed sequence. If some or all of the octahedral sites are occupied between each pair of successive layers, and the same fraction of available octahedral sites are occupied between each pair of layers, deduce a likely pattern of site occupancies for Al^{3+} between the pair of layers that you considered in part 3(a). Pauling's rule on bond strength summation may be of use. A number of drawings for circles in close packing are provided on the following sheets for scratch work and presentation of your final prediction for this part of the problem.





Thermodynamics (50 points total):

3. Consider a thermodynamic system consisting of 1 mole of the material examined in problem 3- (alumina, Al_2O_3)- in the solid state, reversibly heated at a constant pressure of 1 atm from 20°C to 200°C in an oven. Solid alumina is the stable phase throughout this temperature range. **Be sure to show your work in each part- this makes it possible to give partial credit**.

   Thermodynamic data for Al_2O_3:

   $$C_P^s = 106.6 + 0.0178T - 28.5 \times 10^5 T^{-2} \left(\frac{J}{mole \cdot K} \right)$$

   T_m = 2327 K

   Alumina has no structural phase transitions in the temperature range of interest.

   a. (4 points) What type of system is this? (State your assumptions.)

   b. (8 points) Determine the heat transferred to the system in this process.

c. (8 points) If the internal energy of the system increases by 33,500J in this process, what is the reversible work performed? Is this work ***done on*** the system or ***done by*** the system?

d. (8 points) What is the enthalpy change in the system during this process?

e. (8 points) What is the entropy change in the system?

f. (8 points) If the system is now returned to its initial pressure, temperature, and volume by a series of stepwise compression and cooling steps, what will the internal energy change for the total return process be? State why.

g. (6 points) Finally, consider 1 mole of a sample of *aluminum* (heat capacity given below), which receives the same quantity of heat (at constant pressure) that was transferred to the Al_2O_3 sample above. (Solid aluminum is stable up to 932K). Without performing a detailed calculation, state whether the Al sample will have the same final temperature as the alumina sample, a lower temperature, or a higher temperature. Explain why in one or two sentences.

$$C_P^s = \left(20.7 + 0.0124T\right)\left(\frac{J}{mole \cdot K}\right)$$