

CHEM 120
Spring 2006
Pre-Exam Assignment 2

Name: _____

Instructions

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it.

Show all work for full credit! For the word problems write your final answer in a complete sentence. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

There are **8** pages, none blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

You may use the back of any page as additional workspace. Please indicate that you have done so.

| Problem | Possible Points | Points Received |
|---------|-----------------|-----------------|
| 1 | 30 | |
| 2 | 10 | |
| 3 | 12 | |
| 4 | 20 | |
| 5 | 20 | |
| Free | 8 | 8 |
| Total | 100 | |
| | Bonus | |
| | Grand Total | |

1. The mineral oldhamite (calcium sulfide) crystallizes in the NaCl lattice.

a. (10 Points) Using the data given below, calculate E_{lattice} for oldhamite. Note in the table IE standards for ionization energy and EA for electron affinity. The first electron affinity, EA_1 , is defined as ΔU for the following reaction: $A^-(g) \rightarrow A(g) + e^-$ and EA_2 is defined in a similar manner.

| | | | |
|----------------------|----------------|-------------------------|----------------|
| | <u>kJ/mole</u> | | <u>kJ/mole</u> |
| IE ₁ (Ca) | +589.7 | ΔH_f^0 (Ca, g) | +178.2 |
| IE ₂ (Ca) | +1145. | ΔH_f^0 (S, g) | +278.81 |
| EA ₁ (S) | +200.4 | ΔH_f^0 (CaS, s) | -473.21 |
| EA ₂ (S) | -532. | | |

b. (10 Points) Calculate E_{lattice} for oldhamite using the Born-Landé equation. Comment on any differences between this value and the one calculated using the Born-Haber cycle.

c. (10 Points) The unit cell of oldhamite is 5.689 \AA on a side. Calculate the ionic radius of each ion in oldhamite in \AA .

2. (10 Points) Given below are the ionic radii for the cations and anions in three different ionic compounds.

| Formula | r_{cation} (pm) | r_{anion} (pm) |
|------------------|--|---|
| SnO ₂ | 71. | 140. |
| AlP | 50. | 212. |
| BaO | 135. | 140. |

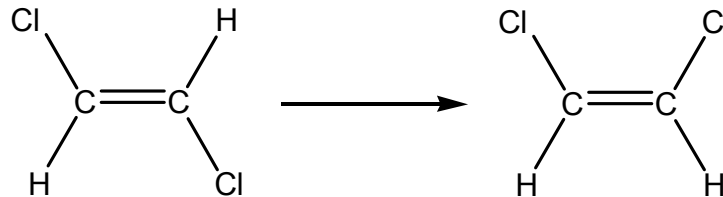
Each compound has either the NaCl, CsCl or the zincblende type cubic structure. Predict the type of structure formed (NaCl, CsCl or ZnS), the type and fraction of holes filled by the cations and estimate the density of each compound.

3. (12 Points) Consider the following melting point data.

| <u>Compound</u> | <u>Melting Point (°C)</u> | <u>Compound</u> | <u>Melting Point (°C)</u> |
|------------------|---------------------------|-------------------|---------------------------|
| NaF | 997 | NaCl | 801 |
| MgF ₂ | 1396 | MgCl ₂ | 708 |
| AlF ₃ | 1040 | AlCl ₃ | 190 |
| SiF ₄ | -90 | SiCl ₄ | -70 |
| PF ₅ | -94 | PCl ₃ | -91 |
| SF ₆ | -56 | SCl ₂ | -78 |
| F ₂ | -220 | Cl ₂ | -101 |

Account for the trends in melting points within the two series of compounds in terms of inter-particle forces. Be sure to comment on places where compounds with the same first atom have very different melting points (e. g., AlF₃ and AlCl₃), and where structural differences may be important (e. g., PF₅ and PCl₃).

4. Consider the isomerization of *trans*-1, 2-dichloroethane to *cis*-1, 2-dichloroethane, shown below.



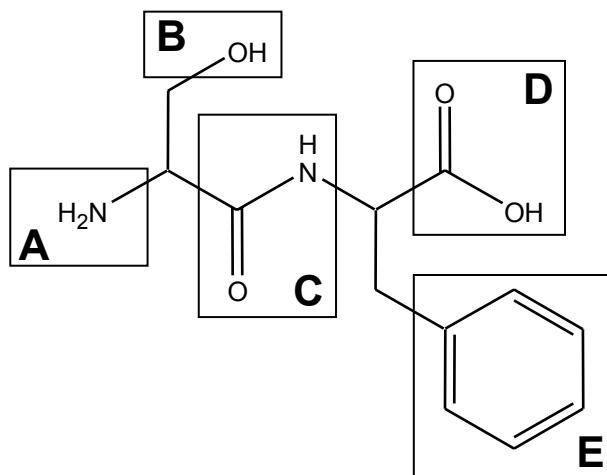
a. (4 Points) In the gas phase ΔH for the following reaction is expected to be 0, but it isn't. Explain why ΔH is predicted to be 0 in the gas phase and what it means when it is not 0.

b. (5 Points) Draw the reaction profile for this reaction. Label your graph.

c. (5 Points) Using the bond dissociation energies from Table 13.6, estimate E_a for this reaction. To do this you will need to consider what must happen to go from the reactant to the product in terms of bonds broken and formed.

e. (6 Points) Assuming that the pre-exponential factor is $1.00 \text{ M}^{-1} \cdot \text{hr}^{-1}$, what is the rate constant for this reaction at 298. K?

5. Consider the dipeptide shown below.



a. (14 Points) Fill in the following table.

| Functional Group | Functional Group's Name | Hybridization of Atoms in the Functional Group |
|------------------|-------------------------|--|
| A | | |
| B | | |
| C | | |
| D | | |
| E | | |

b. (6 Points) The functional group in box C has the C, O and N atoms all in the same plane and it is difficult to rotate around the C–N bond, despite the fact that it is a single bond. Draw another resonance structure for this functional group and use it to explain these observations.