

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.

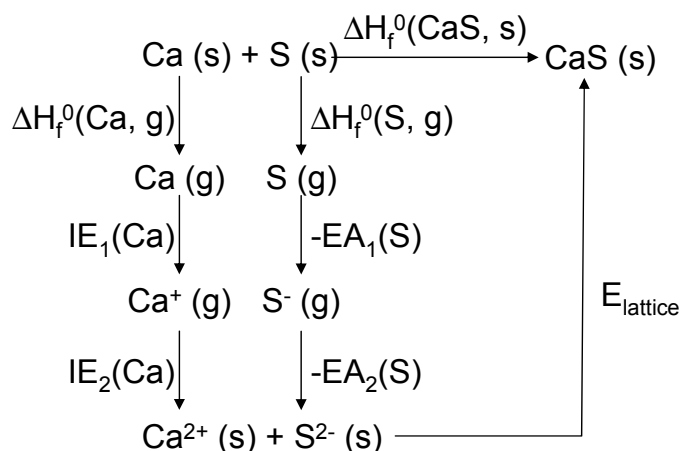
You may use the back of any page as additional workspace. Please indicate that you have done so.

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>
$IE_1(\text{Ca})$	+589.7	$\Delta H_f^0(\text{Ca}, g)$	+178.2
$IE_2(\text{Ca})$	+1145.	$\Delta H_f^0(\text{S}, g)$	+278.81
$EA_1(\text{S})$	+200.4	$\Delta H_f^0(\text{CaS}, s)$	-473.21
$EA_2(\text{S})$	-532.		

Construct Born-Haber cycle for CaS (shown below).



Setting up the equation that describes the cycle yields

$$\Delta H_f^0(\text{Ca}, g) + IE_1(\text{Ca}) + IE_2(\text{Ca}) - \Delta H_f^0(\text{S}, g) - EA_1(\text{S}) - EA_2(\text{S}) + E_{\text{lattice}} = \Delta H_f^0(\text{CaS}, s)$$

Substituting in the appropriate values gives

$$178.2 + 589.7 + 1145. + 278.1 - 200.4 + 532) \text{ kJ/mole} + E_{\text{lattice}} = -473.21 \text{ kJ/mole}$$

$$E_{\text{lattice}} + 2522.6 \text{ kJ/mole} = -473.21 \text{ kJ/mole}$$

$$E_{\text{lattice}} = -2996. \text{ kJ/mole}$$

The lattice energy of CaS is -2996. kJ/mole.

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.

Start with the Born-Landé equation.

$$E_{\text{lattice}} = -\frac{NA|z_+||z_-|e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

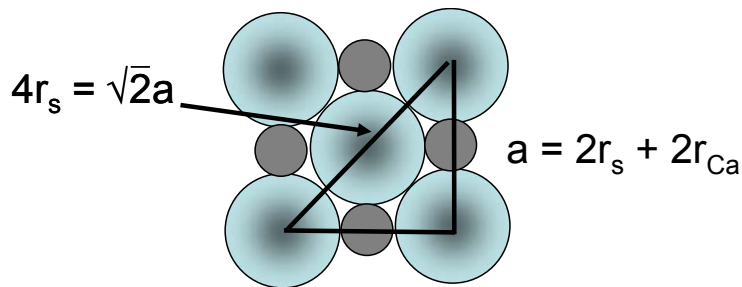
Calculate r_0 from the ionic radii (99. pm for Ca^{2+} and 184. pm for S^{2-}) given in the text. Both Ca^{2+} and S^{2-} have the [Ar] electronic configuration so n for both equals 9 and the average n is also 9. The Madelung constant for NaCl is 1.7476. Substituting these values into the Born-Landé equation gives the following.

$$E_{\text{lattice}} = -\frac{(6.022 \times 10^{23})(1.7476)(2)(2)(1.602 \times 10^{-19})^2}{4(3.1415)(8.854 \times 10^{-12})(283. \times 10^{-12})} \left(1 - \frac{1}{9}\right) = -3.05 \times 10^3 \text{ kJ/mole}$$

The predicted lattice energy of CaS is -3.05×10^3 kJ/mole. This predicted value is in reasonable agreement with the experimental value calculated with the Born-Haber cycle. We conclude, therefore, that CaS is primarily an ionic compound with only a small amount of covalency.

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

The NaCl structure has a face-centered lattice of anions with cations in all the octahedral holes.



$$4r_s = \sqrt{2}a \quad \text{and} \quad a = 2r_s + 2r_{\text{Ca}}$$

$$r_s = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2}(5.689 \text{ \AA})}{4} = 2.011 \text{ \AA}$$

$$r_{\text{Ca}} = \frac{a - 2r_s}{2} = \frac{5.689 \text{ \AA} - 2(2.011 \text{ \AA})}{2} = 0.8331 \text{ \AA}$$

The ionic radius of S^{2-} is 2.011 Å and the ionic radius of Ca^{2+} is 0.8331 Å.

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.

Calculate the radius ratio for each compound and then consult the table in the notes for limiting values of radius ratio for each structure.

Compound	Radius Ratio	Possible Structures
SnO ₂	$\frac{r_{\text{Sn}}}{r_{\text{O}}} = \frac{71. \text{ pm}}{140. \text{ pm}} = 0.51$	zincblende, NaCl, rutile
AlP	$\frac{r_{\text{Al}}}{r_{\text{S}}} = \frac{50. \text{ pm}}{212. \text{ pm}} = 0.24$	zincblende
BaO	$\frac{r_{\text{Ba}}}{r_{\text{O}}} = \frac{135. \text{ pm}}{140. \text{ pm}} = 0.964$	CsCl, NaCl, rutile

We next consider the stoichiometry of each lattice to eliminate some of the possible structures. Zincblende has the stoichiometry CA, so we can eliminate it as a possibility for SnO₂. The rutile structure has the formula CA₂, so we can eliminate it as a possibility for BaO. Normally we would also eliminate the NaCl structure for SnO₂ for the same reasons. However, the problem says that rutile is not a possibility. So, we are forced to accept SnO₂ has the NaCl structure. Although this doesn't seem to work, we can make it work if we place Sn in only half of the octahedral holes, which will make the stoichiometry SnO₂. *In reality SnO₂ crystallizes in the rutile structure, as we would predict based on the stoichiometry.* For BaO we cannot determine whether it crystallizes in the CsCl or the NaCl lattice because both match the compound's stoichiometry, although the radius ratio is closer to CsCl. Based on that fact (and the wording of the problem), we will assume that BaO has the CsCl structure (*although it is really the NaCl structure*).

The structures of each compound are as follows.

<i>Compound</i>	<i>Structure</i>	<i>Formula Units/Cell</i>	<i>Molar Mass (g/mole)</i>
SnO ₂	NaCl, cubic close pack array of O ²⁻ with Sn ⁴⁺ in half the octahedral holes	2	150.71
AlP	Zincblende, cubic close pack array of P ³⁻ with Al ³⁺ in half the tetrahedral holes	4	57.955
BaO	CsCl, cubic array of O ²⁻ with Ba ²⁺ in the center of each unit cell	1	153.33

To determine the density of each compound we need to know how many formula units are in each cell and the volume of the unit cell.

For the NaCl structure there are 8 oxygens on the corners (counting 1/8 each) and 6 in the center of each face (counting as 1/2 each) for a total of 4 oxygens. There are 12 octahedral holes on each edge (count 1/4 each) and one hole in the center, for a total of 4. If only half of the holes are occupied by Sn⁴⁺, then there are only 2 Sn⁴⁺ per unit cell, or 2 SnO₂ formula units. For the zincblende structure there are 4 formula units per cell (from the notes). And for the CsCl structure there is 1 formula unit per unit cell. These results are summarized above.

For the NaCl cell, we know that the cations and anions touch along the unit cell edge. So the edge, a , is equal to $2r_A$ (radius of the anion) plus $2r_C$ (radius of the cation).

$$V = a^3 = (2r_A + 2r_C)^3$$

The volume of the CsCl unit cell is different because we need to use the body diagonal (where the cations and anions touch). The body diagonal is equal to both $\sqrt{3}a$ and $2r_C + 2r_A$, where r_C is the cation's radius and r_A is the anion's radius. The volume in terms of the ionic radii is thus

$$V = a^3 = \left(\frac{2r_C + 2r_A}{\sqrt{3}} \right)^3$$

Similarly, the length of the zincblende unit cell can be determined to be

$$V = a^3 = \left(\frac{4r_C + 4r_A}{\sqrt{3}} \right)^3$$

The volume of the SnO₂ unit cell is

$$V = (2r_A + 2r_C)^3 = (2 \cdot 71 \cdot 10^{-12} \text{ m} + 2 \cdot 140 \cdot 10^{-12} \text{ pm})^3 = 7.51_5 \times 10^{-29} \text{ m}^3 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 7.51_5 \times 10^{-23} \text{ cm}^3$$

The volume of the AlP unit cell is

$$V = \left(\frac{4 \cdot 50 \cdot 10^{-12} \text{ m} + 4 \cdot 212 \cdot 10^{-12} \text{ m}}{\sqrt{3}} \right)^3 = 2.2_1 \times 10^{-28} \text{ m}^3 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 2.2_1 \times 10^{-22} \text{ cm}^3$$

The volume of the BaO unit cell is

$$V = \left(\frac{2r_C + 2r_A}{\sqrt{3}} \right)^3 = \left(\frac{2 \cdot 135 \cdot 10^{-12} \text{ m} + 2 \cdot 140 \cdot 10^{-12} \text{ m}}{\sqrt{3}} \right)^3 = 3.20_1 \cdot 10^{-29} \text{ m}^3 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 3.20_1 \cdot 10^{-23} \text{ cm}^3$$

The mass of each unit cell are calculated as follows.

$$\left(\frac{2 \text{ formula units SnO}_2}{1 \text{ unit cell}} \right) \left(\frac{1 \text{ mole}}{6.02214 \times 10^{23} \text{ formula units}} \right) \left(\frac{150.71 \text{ g}}{1 \text{ mole}} \right) = 5.0052 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}$$

$$\left(\frac{4 \text{ formula units AlP}}{1 \text{ unit cell}} \right) \left(\frac{1 \text{ mole}}{6.02214 \times 10^{23} \text{ formula units}} \right) \left(\frac{57.955 \text{ g}}{1 \text{ mole}} \right) = 3.8494_6 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}$$

$$\left(\frac{1 \text{ formula unit BaO}}{1 \text{ unit cell}} \right) \left(\frac{1 \text{ mole}}{6.02214 \times 10^{23} \text{ formula units}} \right) \left(\frac{153.33 \text{ g}}{1 \text{ mole}} \right) = 2.5461 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}$$

The densities are as follows.

$$\text{SnO}_2: \frac{5.0052 \times 10^{-22} \text{ g}}{7.51_5 \times 10^{-23} \text{ cm}^3} = 6.66 \frac{\text{g}}{\text{cm}^3}$$

$$\text{AlP: } \frac{3.8494_6 \times 10^{-22} \text{ g}}{2.2_1 \times 10^{-22} \text{ cm}^3} = 1.7 \frac{\text{g}}{\text{cm}^3}$$

$$\text{BaO: } \frac{2.5461 \times 10^{-22} \text{ g}}{3.20_1 \times 10^{-23} \text{ cm}^3} = 7.95 \frac{\text{g}}{\text{cm}^3}$$

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	714
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).

The compounds fall broadly into two groups: ionic (MP > 1000 °C) and molecular (MP < 1000 °C).

Within the ionic group we expect that the MP should increase as charge increases and as the ionic radius decreases (E_{lattice} increases in both cases). For the compounds NaF and MgF₂ we see that when the charge on the cation increases (from +1 in NaF to +2 in MgF₂) and the cation's size decreases (the Mg²⁺ ion is smaller than the Na⁺ ion), the MP increases. Between the series (NaF, MgF₂, AlF₃ versus NaCl, MgCl₂, AlCl₃) we see a decrease in the melting point, as we expect for a decrease in E_{lattice} resulting from the presence of the larger Cl⁻ ion.

For AlF₃ and the series NaCl, MgCl₂ and AlCl₃ we see the MP decrease as charge increases and cation size decreases. As this runs counter to our expectations for ionic compounds, this must be a manifestation of the covalent nature of these primarily ionic bonds. As the cation's charge increases, covalency increases because the high charge of the cation distorts the electron cloud of the anion more to itself and results in the electrons being more shared than localized on the anion. This effect should be accentuated when the anion has more electrons (anion is more "polarizable"). Fluoride is small and holds its electrons tightly while the larger chloride does not. So, chloride's electrons are more easily distorted toward the cation and the bond has a higher degree of covalency. As covalency increases, the solid will act less like an infinite lattice of ions and more like a lattice of individual groupings of particles. These groupings will have strong interactions between particles in the group and weaker interactions between groupings (i. e., they behave more like molecular compounds). Because the groups have weaker interactions between them, the melting point will be lower than expected.

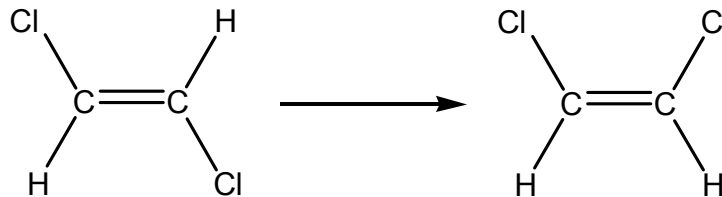
Within the covalent group we expect dispersion forces and dipole-dipole interactions to be important. F₂ and Cl₂ are linear, non-polar molecules that have only dispersion forces as their intermolecular interactions. They have the fewest number

of electrons of any of the molecular compounds, and as dispersion forces are proportional to the number of electrons, we expect them to have the weakest intermolecular interactions and the lowest MP. By the same reasoning F_2 has a lower melting than Cl_2 because it has fewer electrons.

Within the SiF_4 , PF_5 , SF_6 series we see an increase in the MP as the molar mass (number of electrons) increases between SiF_4 and SF_6 and between PF_5 and SF_6 , as expected. PF_5 appears to be anomalously low. This molecule is predicted to have a trigonal bipyramidal structure, while SiF_4 is tetrahedral and SF_6 is octahedral. The lower MP implies weaker interactions between PF_5 molecules and also implies that the trigonal bipyramidal structure must be more compact (less surface area over which dispersion forces can act) or that molecules with this structure cannot pack as tightly together in the solid state. In either case, the result should be a lower MP.

The MP of $SiCl_4$ is higher than that of SiF_4 , consistent with an increase in the number of dispersion forces with an increase in the number of electrons. For the rest of the series ($SiCl_4$, PCl_3 , SCl_2) the molar mass decreases (169.90, 137.33, 102.97, respectively). We expect that the molar mass should decrease simply based on the lower dispersion forces. Based on the general rule of dispersion forces causing about 1 K change in MP for every g/mole, we would expect PCl_3 to have a MP of $-100\text{ }^\circ\text{C}$ and SCl_2 to have a MP of $-137\text{ }^\circ\text{C}$ (calculated from the MP of $SiCl_4$). The MP of PCl_3 is fairly close to this estimate. So even though PCl_3 is a polar molecule, the dipole-dipole interactions must be fairly weak. This is understandable given the similar electronegativities of P and Cl which means that the P-Cl bond is relatively non-polar and thus the molecule is not as polar as NH_3 with which it is isoelectronic and isostructural. The MP of SCl_2 is significantly higher than predicted based on dispersion forces alone. This bent molecule is expected to be polar, and in this case, it appears that the dipole-dipole interactions are more important than in PCl_3 leading to a higher MP than expected.

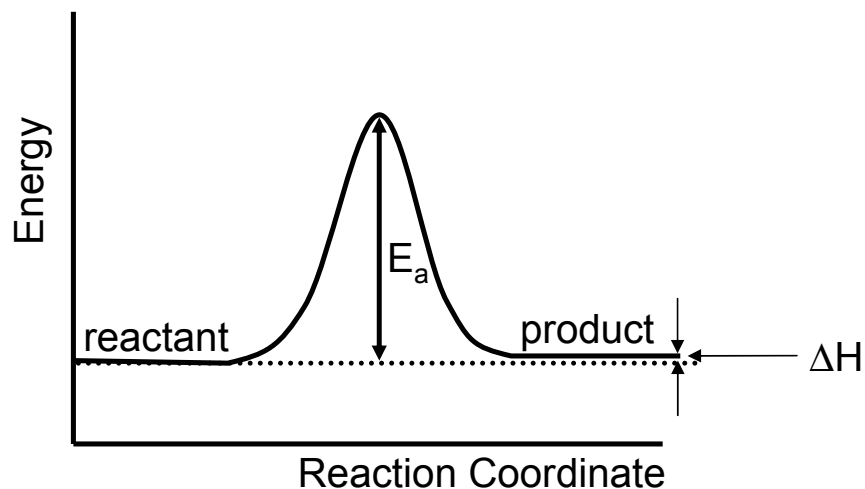
4. Consider the isomerization of *trans*-1, 2-dichloroethane to *cis*-1, 2-dichloroethane, shown below.



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.

In this reaction, the bonds broken are exactly the same as the bonds formed (no matter how we do the reaction). Therefore based simply on bond dissociation energies, we expect ΔH for this reaction to be 0 ($\Delta H = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$). Since it is not, we must assume that there is something else occurring that we have not considered.

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.

If we break the C=C we will need to input 614 kJ/mole.

If we break a C-Cl and a C-H bond, we will need to add $339. + 413 = 752.$ kJ/mole.

If we break the C=C and replace it with a C-C single bond, the overall E_a would be $614. - 347 = 267.$ kJ/mole. Doing this means we are then free to rotate around the C-C single bond

As the rate of reaction will be fastest for the pathway that has the lowest E_a , we would expect the activation energy to be approximately 267. kJ/mole.

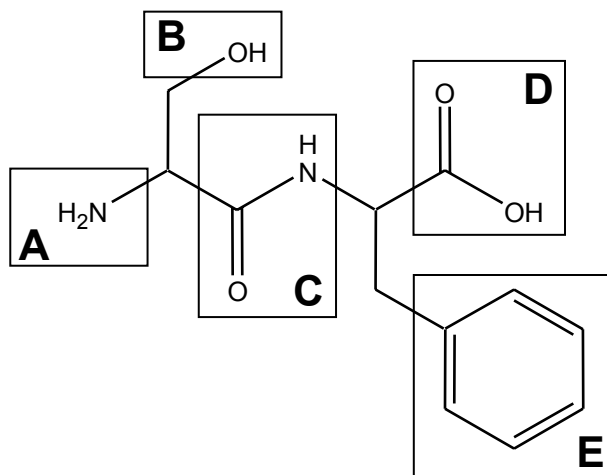
d. (6 Points) Assuming that the pre-exponential factor is $1.00 \text{ M}^{-1}\cdot\text{hr}^{-1}$, what is the rate constant for this reaction at 298. K?

Start with the Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

Substituting in any of the E_a values from part c (remember to use $R = 8.314$ kJ/mole) may give you an exponent that your calculator can't handle because it leads to a number that is too small. The result is simply that, because the activation energy for rotation around a C=C is so high, the rate of isomerization is very low (essentially zero).

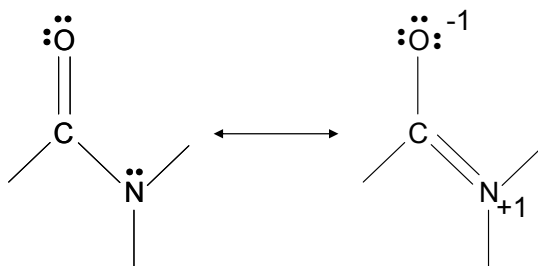
5. Consider the dipeptide shown below.



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

Functional Group	Functional Group's Name	Hybridization of Atoms in the Functional Group
A	amine	sp^3
B	alcohol	sp^3
C	amide	C sp^2 , O sp^2 , N sp^3
D	carboxylic acid	C sp^2 , O sp^2 (double bond) and sp^3
E	phenyl ring	sp^2

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.



The two resonance structures for an amide are shown above. The second one, although it separates charge, does put a double bond between the C and the N. This resonance structure introduces some double bond character into the C–N bond. We showed in question 4d that a double bond is difficult to rotate about (because one must break a C–C bond). So, adding double bond character to a single bond will severely hinder rotation about that bond.