

Chemistry 6011 (Fall 2016)

Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds

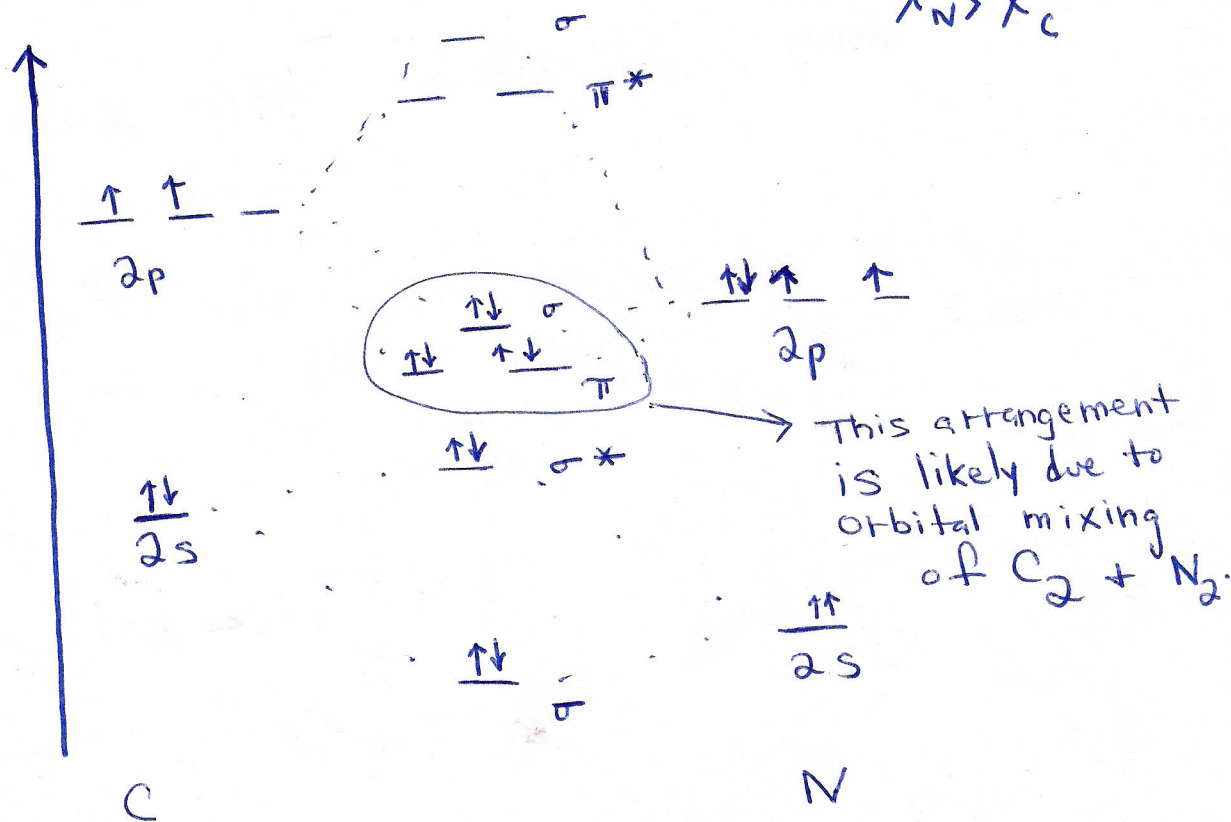
Exam 2

Name:

Show your work for maximum credit.

1. (20 points)

a. Draw a molecular orbital diagram for the bonding in  $\text{CN}^-$ .



b. What is the bond order in  $\text{CN}^-$ ?

$$\text{B.O.} = \frac{1}{2} [\text{bonding} - \text{antibonding}] = \frac{1}{2} (8 - 2) = \underline{3}$$



c. How many unpaired electrons are there in  $\text{CN}^-$ ?

No unpaired  $e^-$

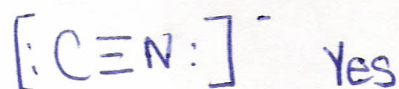
d.  $\text{CN}^-$  has a lower bond dissociation energy than the isoelectronic CO (887 kJ/mol vs 1072 kJ/mol). Suggest an explanation.

$\text{CN}^-$  vs CO

Higher  $\Delta\chi$  and therefore greater ionic resonance character contribution

Also the bonding  $e^-$  in the molecular orbitals of CO would be more stabilized due to O being higher  $\chi$  than N

e. Draw a Lewis structure for  $\text{CN}^-$ , including resonance structures and formal charges. Does the bond order you get by this valence bond model agree with the one you got by using molecular orbital theory?



$$\text{B.O.} = 3$$

f. If you made the neutral molecule, CN, would the bond length get longer or shorter than  $\text{CN}^-$ ?

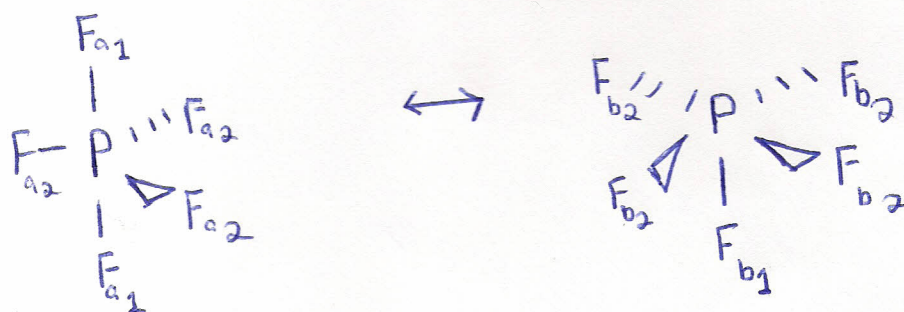
You would remove one  $e^-$  ~~bonding~~ from a bonding MO. Increase in bond length due to decrease in bond order relative to  $\text{CN}^-$ .

a. (10 points) The  $^{19}\text{F}$  NMR spectrum for  $\text{PF}_5$  is not what is expected based on the molecular structure of the compound. The compound undergoes a structural rearrangement that is faster than the NMR time scale. Raynaud, Maron, Daudey, and Jolibois (*ChemPhysChem* **2006**, 7, 407-413) have performed an ab initio molecular dynamics simulations study that allows us to understand this rearrangement process and to get mechanistic insight. They have calculated the chemical shifts that would be observed for  $\text{PF}_5$  if a low enough temperature could be achieved to detect the distinct structures during the rearrangement by  $^{19}\text{F}$  NMR.

a. Explain the calculated  $^{19}\text{F}$  NMR spectral data for  $\text{PF}_5$  below.

	$\text{F}_{a1}$ $\delta$ (ppm)	Integration for $\text{F}_{a1}$	$\text{F}_{a2}$ $\delta$ (ppm)	Integration for $\text{F}_{a2}$
Structure a	-62.71	2	-71.47	3

	$\text{F}_{b1}$ $\delta$ (ppm)	Integration for $\text{F}_{b1}$	$\text{F}_{b2}$ $\delta$ (ppm)	Integration for $\text{F}_{b2}$
Structure b	-117.70	1	-38.45	4

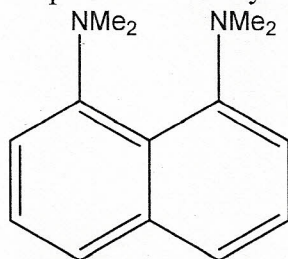


b. What is the name for this structural rearrangement process?

Berry pseudorotation

3. (15 points)

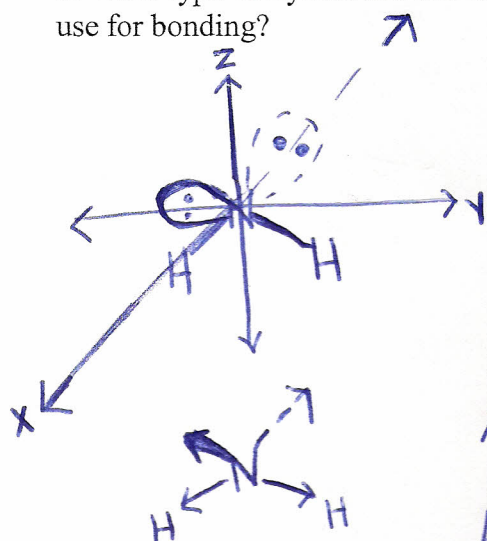
a. Show what would happen if you placed the superbases 1,8-bis(dimethylamino)naphthalene in a solution of ammonia. Assume that the superbases can only accept one proton.



1,8-bis(dimethylamino)naphthalene



b. What type of hybrid orbitals would the nitrogen in the conjugate partner form of ammonia use for bonding?



4 vectors for 4 e<sup>-</sup> pairs → 4 irred. rep.

C <sub>2v</sub>	E	C <sub>2</sub> (z)	σ <sub>v</sub> (xz)	σ <sub>v</sub> (yz)
Γ <sub>red</sub>	4	0	2	2

+1: unmoved

0: moved

$$A_1 = \frac{1}{4} [4(1)(1) + 0 + 2(1)(1) + 2(1)(1)] = 2$$

$$A_2 = \frac{1}{4} [4 + 0 - 2 - 2] = 0$$

$$B_1 = \frac{1}{4} [4 + 0 + 2 - 2] = 1$$

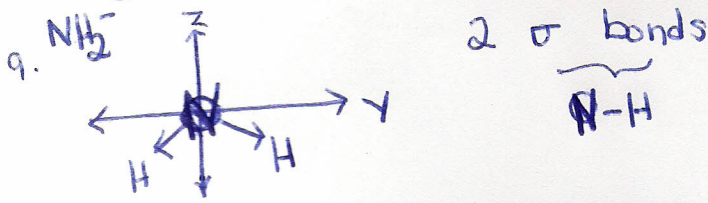
$$B_2 = \frac{1}{4} [4 + 0 - 2 + 2] = 1$$

$$\Gamma_{\text{red}} = 2A_1 + 1B_1 + 1B_2$$

$a_1 \Rightarrow s, p_z, d_{z^2}$   
 $b_1 \Rightarrow p_x, d_{xz}$   
 $b_2 \Rightarrow p_y, d_{yz}$

} No d-orbitals in N.  
 Hybridization: sp<sup>3</sup>

c. Use group theory to determine the **molecular orbitals** formed by the **conjugate partner** of **ammonia** (see part a) to create **molecular orbitals**. Make sure to construct the molecular orbital diagram for this molecule and determine/analyze the bond order.



$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
red	2	0	0	2

$\Gamma_{red} = 1A_1 + 1B_2 \Rightarrow$  Symmetries

b.  $a_1$ : s,  $p_z$

$b_2$ :  $p_y$

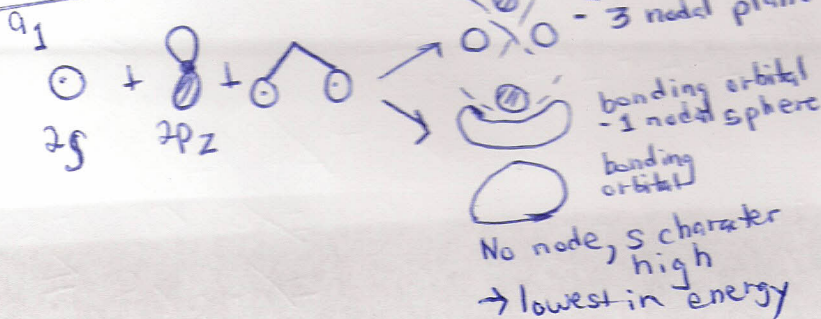
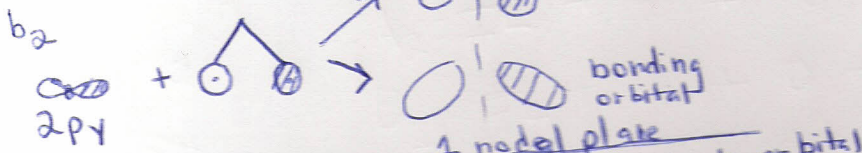
atomic orbitals of N

LGOs:

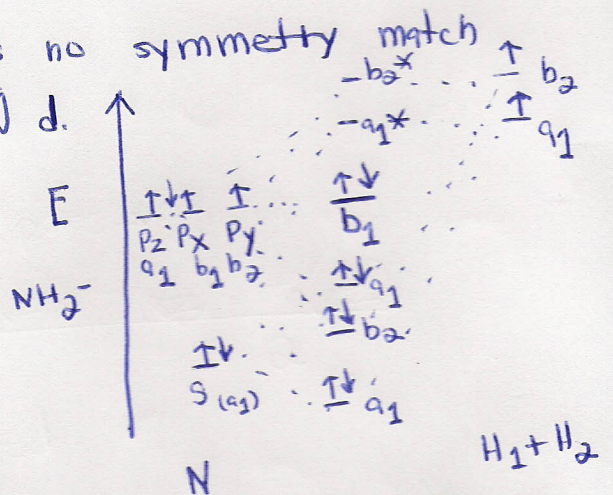


c. symmetry matching

2 nodal planes  
antibonding orbital  
highest in energy due to more repulsion



$b_1$ :  $p_x$  has no symmetry match  
 $\therefore$  Nonbonding

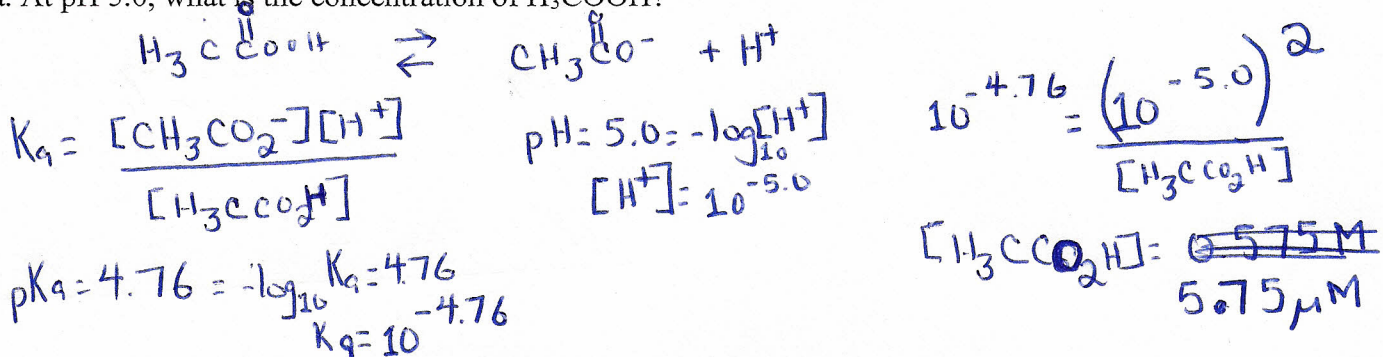


Bond order =  $\frac{6}{2} = 3$

• But there are only 2 N-H bonds.  
• The higher energy  $a_1$  molecular orbital can be treated like a nonbonding one because it has a higher N  $p_z$  character.  
Need two nonbonding orbitals to account for the two lone pairs.

4. (5 points) You are given an aqueous solution of the monoprotic acid, acetic acid ( $\text{H}_3\text{COOH}$ ,  $\text{pK}_a = 4.76$ ).

a. At pH 5.0, what is the concentration of  $\text{H}_3\text{COOH}$ ?



b. Is the ionization of the acid thermodynamically favorable?

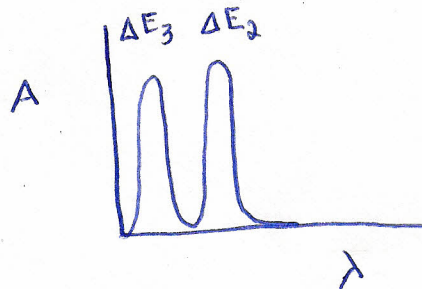
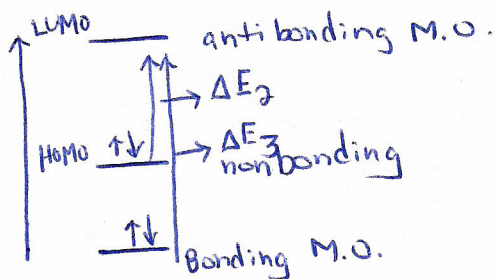
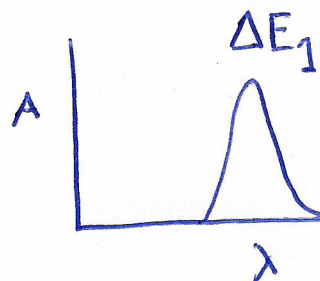
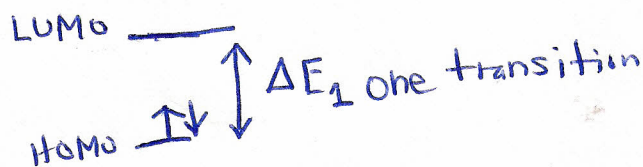
No,  $K < 1$ .

c. Determine the  $\text{pK}_b$  of the conjugate base of formic acid.

$$\text{pK}_w = \text{pK}_a + \text{pK}_b \quad \text{pK}_b = \text{pK}_w - \text{pK}_a = 14 - 4.76 = 9.24$$

5. (5 points) Predict the UV-vis spectrum of  $\text{BF}_3$  in hexane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) and in diethylether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ). Thoroughly explain your prediction with visuals and words.

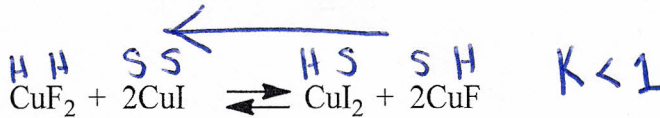
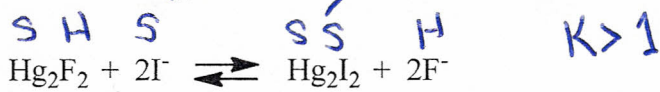
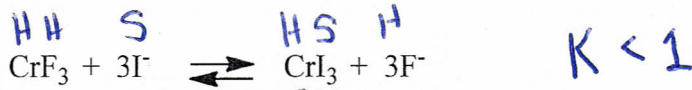
a.  $\text{BF}_3 + \text{hexane} \rightarrow \text{No adduct}$



$$\Delta E_3 > \Delta E_2 > \Delta E_1$$

$\Delta E_3$ : Charge transfer  
 $\Delta E_2$ : Adduct transfer

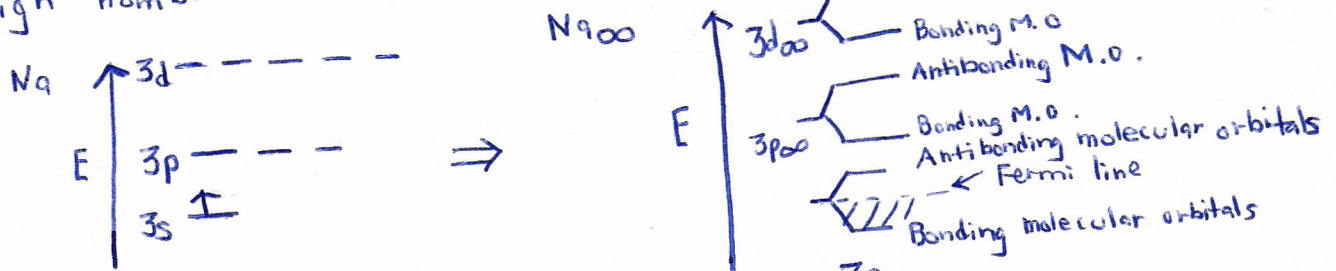
6. (5 points) For each of the following chemical equations, predict whether the equilibrium constant is greater than 1 or less than 1. Explain your choice.



7. (15 points) The following pertain to conductivity.

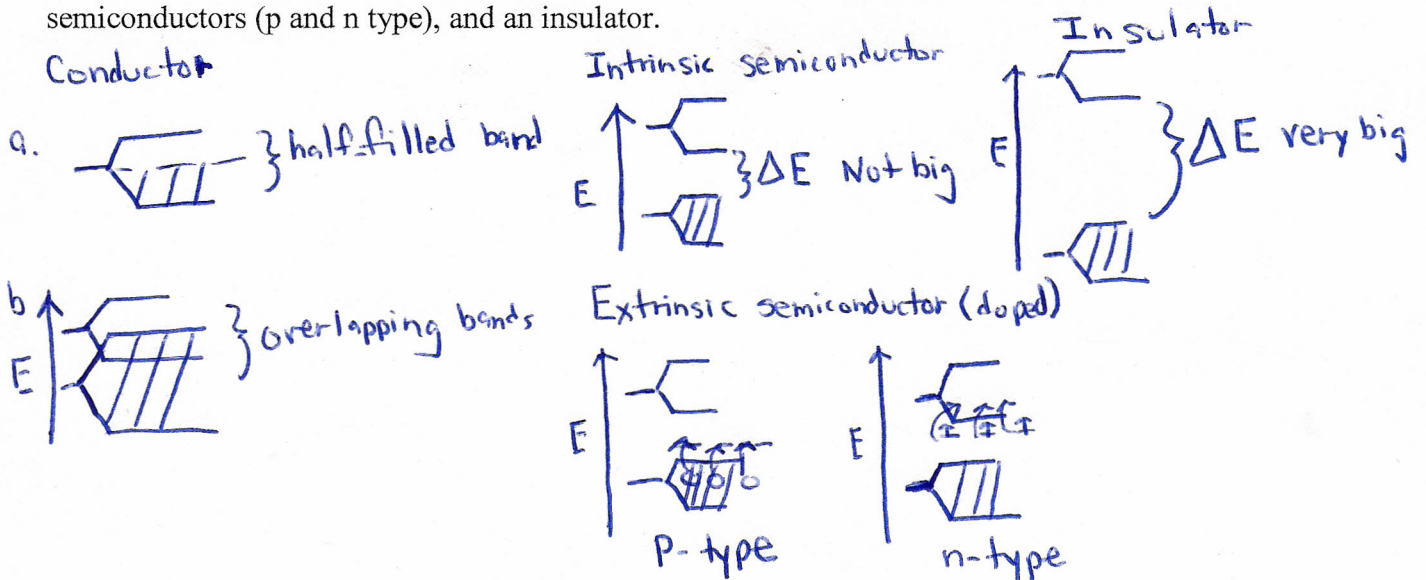
a. Briefly describe Band Theory.

Band theory conceptualizes atomic orbitals as bands when considering compounds of elements ~~where~~ in which there is a high number of these elements, for instance a mole quantity.



The bands of orbitals can be used to determine whether a compound is a conductor, semiconductor, or insulator.

b. Use band gap drawings to illustrate a conductor, an intrinsic semiconductor, extrinsic semiconductors (p and n type), and an insulator.



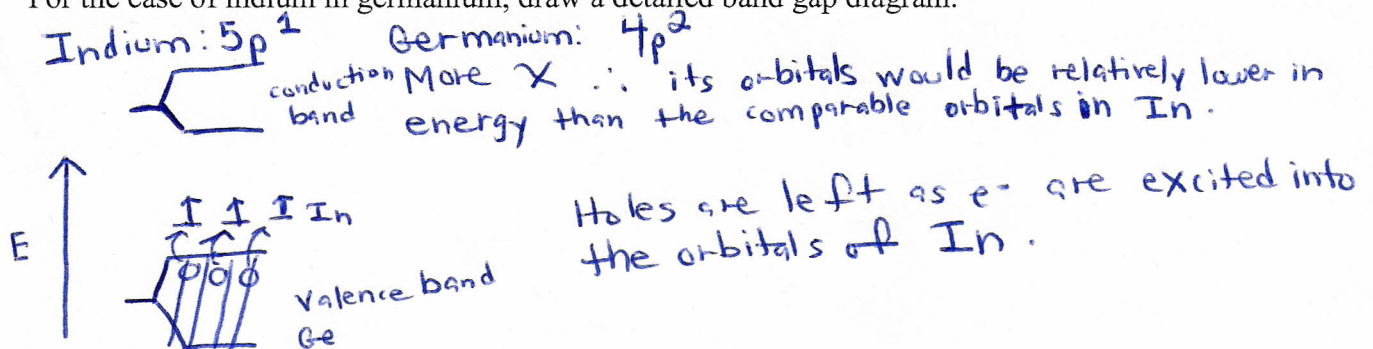
c. How could you use the band gap for Si(s) to distinguish between a semiconductor ( $1.94 \times 10^{-19} \text{ J}$ ) and an insulator?

If a material has a band gap  $<$  Si(s) band gap  $\Rightarrow$  semiconductor  
 $>$  " " "  $\Rightarrow$  insulator

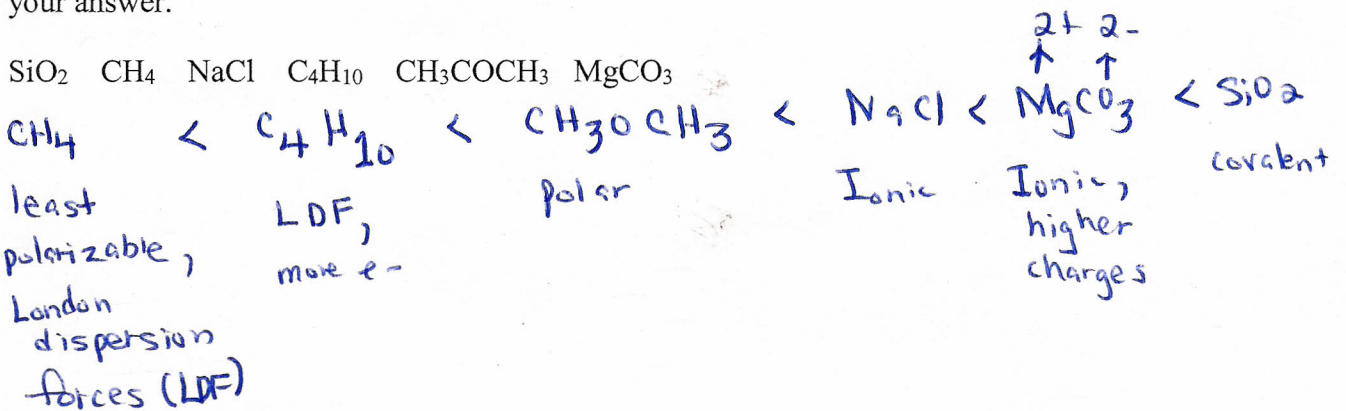
d. Of the following doped semiconductors, which will be p-type or n-type?

- i. arsenic in germanium n-type: As has more  $e^-$  in the valence shell than Ge.
- ii. germanium in silicon Neither
- iii. indium in germanium p-type: In has fewer valence  $e^-$  than Ge.

For the case of indium in germanium, draw a detailed band gap diagram.

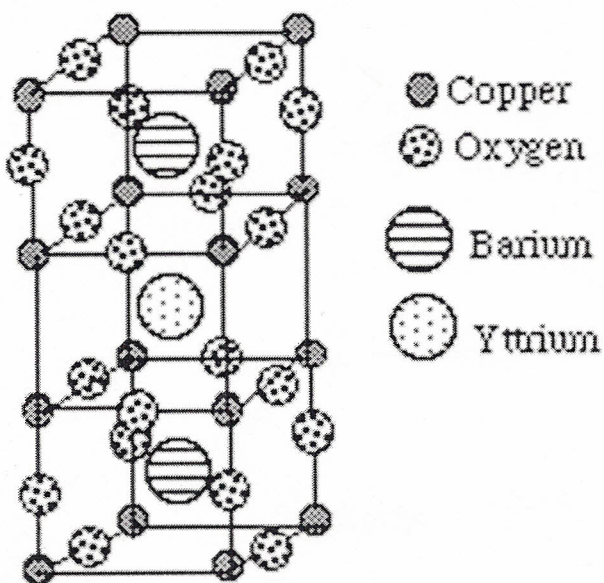


8. (5 points) Arrange the following materials in order of increasing melting point. Briefly justify your answer.



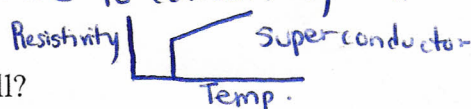


9. (10 points) Shown below is **one** unit cell for the YBCO superconductor.



a. What is a superconductor?

Superconductors are metal whose conductivity changes abruptly near liquid He temperatures ( $< 10\text{ K}$ ). At or below the critical temperature ( $T_c$ ) the resistance to conductivity falls to zero.



b. How many  $\text{Cu}^{2+/3+}$  ions lie within one unit cell?

8 corners:  $8 \times (\frac{1}{8}) = 1$

8 edges:  $8 \times (\frac{1}{4}) = 2$

3 per cell

c. How many  $\text{Ba}^{2+}$  ions lie within one unit cell?

1

d. How many  $\text{Y}^{3+}$  ions lie within one unit cell?

1

e. How many  $\text{O}^{2-}$  ions lie within one unit cell?

12 edges:  $12 \times (\frac{1}{4}) = 3$

8 faces:  $8 \times (\frac{1}{2}) = 4$

7 per cell

f. What is the empirical formula for the YBCO superconductor?



g. With respect to the  $\text{Cu}^{2+/3+}$  ions, in what type of hole is  $\text{Ba}^{2+}$  located?

Cubic

10. (10 points) Under ambient conditions AgCl crystallizes in the NaCl lattice. Under high pressure (11 GPa), AgCl transitions from the NaCl lattice to the CsCl lattice.

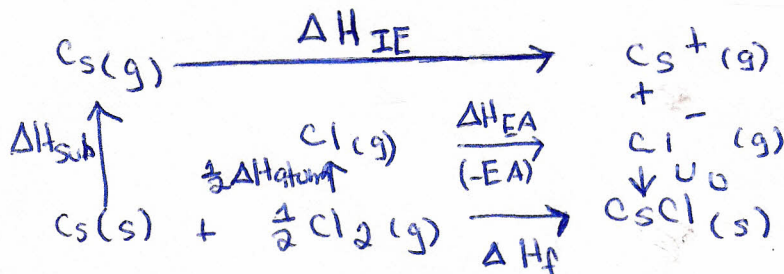
a. What are the differences between the NaCl and CsCl lattices?

CsCl consists of two interpenetrating simple cubic lattices. Both  $\text{Cs}^+$  +  $\text{Cl}^-$  fill cubic holes and have coordination numbers of 8.

NaCl consists of two interpenetrating face center cube lattices. Both ~~Na~~  $\text{Na}^+$  +  $\text{Cl}^-$  fill octahedral holes and have coordination numbers of 6.

b. Calculate the enthalpy of formation of  $\text{AgCl}$  in the typical CsCl lattice and in the NaCl lattice.

Ag should have been but let's go with CsCl



$$\begin{aligned}
 \Delta H_f &= \Delta H_{sub}(\text{Cs}) + \Delta H_{IE}(\text{Cs}) + \frac{1}{2} \Delta H_{atom}(\text{Cl}_2) + \Delta H_{EA}(\text{Cl}) + \Delta U \\
 &= (79 + 375.7 + \frac{1}{2}(244) - 349 + \Delta U_{lattice}) \frac{\text{kJ}}{\text{mol}} \\
 &= 227.7 \frac{\text{kJ}}{\text{mol}} + \Delta U_{lattice \text{ type}}
 \end{aligned}$$

$$\Delta U = \frac{120,200 \text{ J } z^+z^-}{r_0} \left( 1 - \frac{34.5 \text{ pm}}{r_0} \right) \frac{\text{kJ}}{\text{mol}}$$

CsCl lattice c.N. = 8  $r_0 = r_+ + r_- = 173 + 165 = 338 \text{ pm}$

$\Delta U = -638.6 \text{ kJ/mol}$   $\therefore \Delta H_f = -410.9 \text{ kJ/mol}$

NaCl lattice c.N. = 6

$r_0 = r_+ + r_- = 181 + 167 = 348 \text{ pm}$

$\Delta U = -622.3 \text{ kJ/mol}$   
 $\therefore \Delta H_f = -394.6 \text{ kJ/mol}$

Extra Credit:

a. The 2016 Nobel Prize in Chemistry was awarded to who and for what accomplishment?

Jean Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa for the design and synthesis of molecular machines.

b. The lattice energy for AgCl is -916.3 kJ/mol and that of NaCl (-769 kJ/mol) and KCl (-698 kJ/mol) are lower. The  $K_{sp}$  for AgCl is  $1.77 \times 10^{-10}$ , for NaCl is 36, and for KCl is 21.7. It is said that when AgCl dissolves, the species AgCl (aq) should exist in solution in addition to the ions  $Ag^+$ (aq) and  $Cl^-$ (aq). Try to rationalize these properties of AgCl.

AgCl has a higher covalent character. This makes it more difficult to dissociate in solution (low  $K_{sp}$ ) and is the reason why there ~~is~~ should be some amount of solubilized molecular AgCl.

