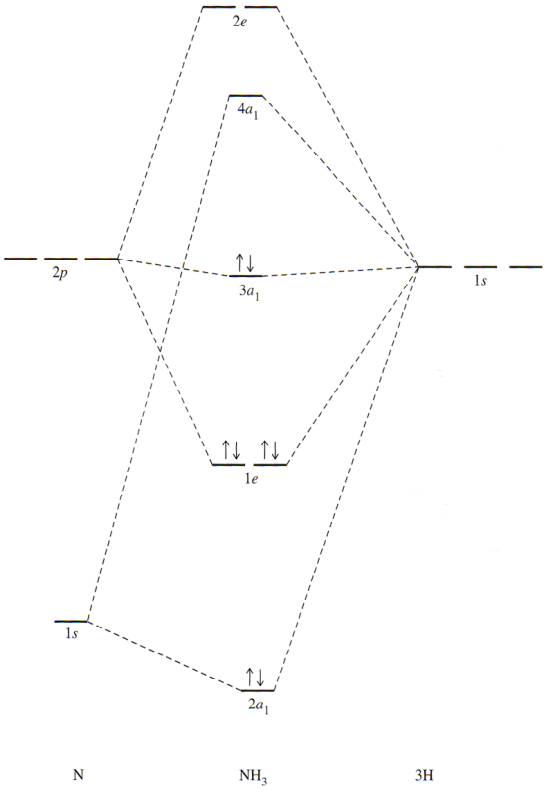
Inorganic Exam 2 **Name:**
Chm 451
28 October 2008

Instructions. Always show your work for full credit.

1. Ammonia has C_{3v} symmetry. The C_{3v} character table is shown below and the molecular orbital diagram for ammonia is given at right. Answer the following questions about the molecular orbital diagram for ammonia.

C_{3v}	E	2 C_3	3 σ_v	
A_1	1	1	1	z
A_2	1	1	-1	
E	2	-1	0	x, y



1(a) (3 pts) Sketch the set of H atomic orbitals that you would use to form your SALC set. (This is a 3-D ball and stick sketch.)

1(b) (3 pts) Determine the reducible representation for ammonia by using your sketch in (a):

C_{3v}	E	2 C_3	3 σ_v	
Γ				

1(c) (3 pts) Resolve the reducible representation into its irreducible components.

1(d) (3 pts) Sketch (balls and sticks) the MO labeled "$2a_1$" in the MO diagram.

1(e) (3 pts) What nitrogen orbital(s) are involved in forming the "1e" molecular orbital?

Circle: 2s $2p_x$ $2p_y$ $2p_z$

1(f) (3 pts) What is the bond order? Show work.

1(g) (3 pts) What orbital in the MO diagram represents the lone pair on ammonia? Use their labeling system: Circle: $2a_1$ 1e $3a_1$ $4a_1$ 2e

2. (4 pts) Just from your knowledge of symmetry, how would you expect the s and p orbitals to transform in a D_{3h} geometry? (You did this with BF_3) To answer the question, fill in "s," "$2p_x$," "$2p_y$," and "$2p_z$ in the table below.

D_{3h}	E	$2C_3$	$3\ C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	
A_1"	1	1	1	-1	-1	-1	
A_2"	1	1	-1	-1	-1	1	
E"	2	-1	0	-2	1	0	

3. (5 pts) Which of these are Lewis bases? Circle all that are.

NH_3 BF_3 Al^{+3} H_2O F^-

4. (5 pts) Circle the strongest Bronsted-Lowry acid in each pair.

(a) HF or HCl

(b) H_3AsO_3 or H_3AsO_4

(c) NaH_2AsO_3 or Na_2HAsO_3

(d) HAt or HAtO

(e) HIO_2 or HIO_3

5. (4 pts) Use hard-soft acid-base theory to predict the preferred direction for the equilibrium in each of the following. Do this by sketching in long/short arrows: $\xrightleftharpoons{}$ or $\xleftharpoons{}$ or $\rightleftharpoons$

LiCl + AuI [ ] LiI + AuCl

2 CuSCN + $Ca(NO_3)_2$ [ ] 2 $CuNO_3$ + $Ca(SCN)_2$

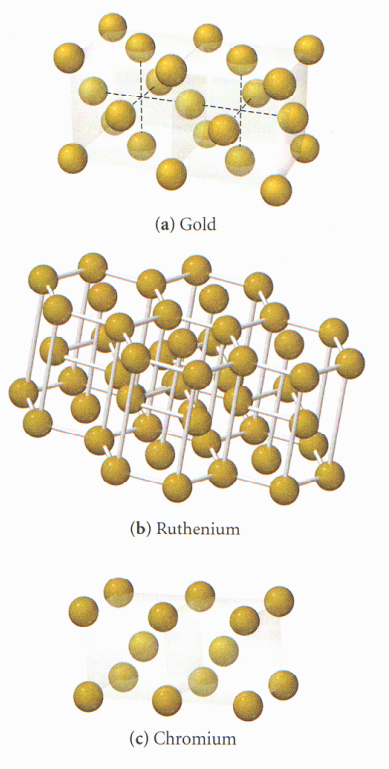
6. (5 pts) Nickel crystallizes in a fcc lattice. Its density is 8.90 g/cm^3. What is the atomic radius of nickel in pm? Show all work.

7. (6 pts) In the pictures given at right, gold, ruthenium and chromium are depicted. In each case, more than one unit cell is shown. Identify the unit cell that each exhibits.

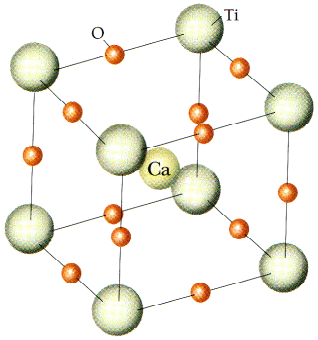
(a) Gold

(b) ruthenium

(c) chromium



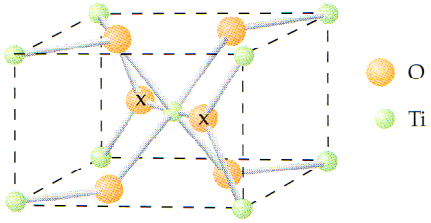
8(a) (3 pts) Perovskite contains calcium, titanium and oxygen ions. They are labeled in the figure at right. (Note that the relative sizes of the ions is misleading.) What is the empirical formula for perovskite?



8(b) (2 pts) What is the oxidation state of titanium in perovskite?

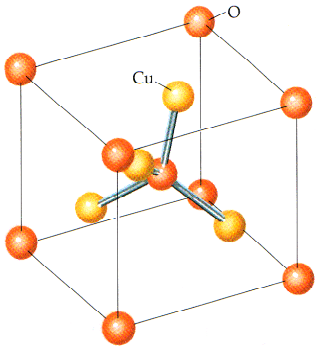
9. Rutile crystallizes in the structure shown at right. This is an important and common structure.

9(a) (3 pts) What sublattice is exhibited by the titanium ions shown in green? Hint: It is body-centered, but not body-centered cubic. Note: I will accept two answers here as there is some ambiguity.

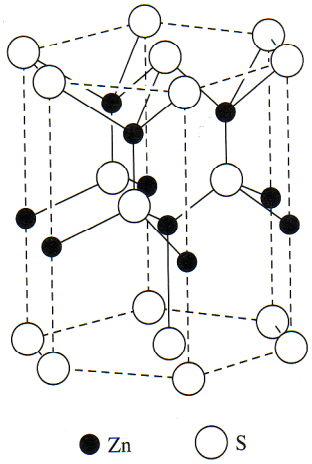


9(b) (3 pts) What is the <u>empirical formula</u> for rutile? Note: The oxides marked with "x" are entirely inside the unit cell shown. The other oxides are centered in faces.

10. (3 pts) Cuprite, shown at right, is a semiconductor consisting of copper and oxide ions and is shown at right. Many other compounds crystallize in this structure including the important semiconductor gallium arsenide. What is the <u>empirical formula</u> for cuprite?



11. Wurtzite consists of zinc(II) and sulfide ions and crystallizes in the structure shown at right.



11(a) (3 pts) What unit cell do the sulfur ions use for their sublattice?

11(b) (3 pts) Is this one of the close-packed lattices?

11(c) (4 pts) What sort of holes and what fraction of those holes are occupied by the zinc ions? Hint: There are two ways to do this. Keep in mind that the empirical formula must work out for zinc(II) sulfide.

12. Lattice energy.

12(a) (2 pts) What is the definition of "lattice energy"? Answer by way of an example, say potassium bromide. It is acceptable to simply write the balanced chemical equation.

12(b) (6 pts) Calculate the lattice energy for calcium fluoride. Given: sublimation energy for calcium metal is +178 kJ/mol, the ionization energies for calcium are E_{i1} = 590 kJ/mol and E_{i2} = 1145 kJ/mol. The F_2 bond energy is 158 kJ/mol and the energy associated with electron affinity for fluorine:

$$F(g) + e^- \rightarrow F^-(g)\ \Delta H = -328\ kJ/mol.$$

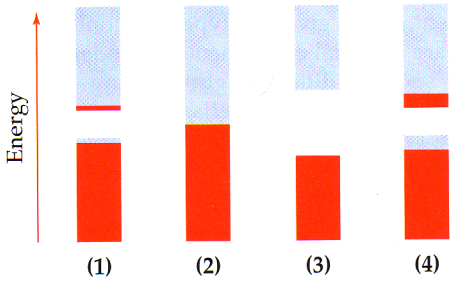
The heat for formation for calcium fluoride is –1228 kJ/mol.

13(a) (2 pts) Why does MgO have a larger lattice energy than NaCl, even though both form similar fcc-style lattices?

13(b) (1 pt) What is the general relationship between lattice energy and predicted solubility in water?

Solubility [increases/decreases] as the lattice energy increases.

14. Consider the diagrams shown at right.



14(a) (1 pt) What does each blue and red column represent?

14(b) (1 pts) What does the blue region represent? What does the red region represent?

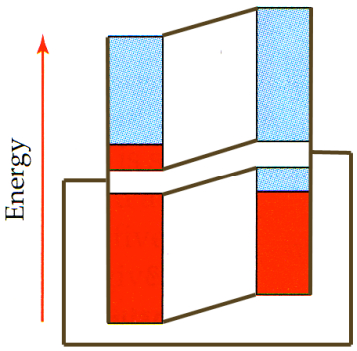
14(c) (1 pt) Which blue/red column(s) represent(s) an insulator? Circle: (1) (2) (3) (4)

14(d) (1 pt) Which blue/red column(s) represent(s) metal conductor? Circle: (1) (2) (3) (4)

14(e) (1 pt) Which blue/red column(s) represent(s) a semiconductor? Circle: (1) (2) (3) (4)

14(f) (2 pts) Why is there some red in the upper part of Figures (1)? What causes that?

15. Consider the sketch for a diode shown at right.

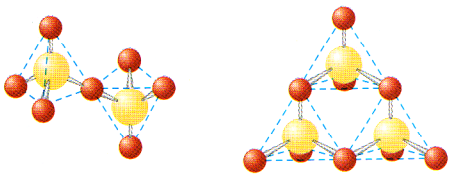


15(a). (1 pts) Label the n-type and p-type parts of the diode.

15(b) (1 pt) Add an arrow to show the allowed direction of electron flow.

15(c) (2 pts) Suppose that the band gap corresponds to an energy associated with visible light, say red light, what would be the result of adding a battery in a forward bias arrangement? What would happen?

16. (4 pts) Give the formula for each of these two silicates. Silicon in yellow; oxygen in red. Include charge!



Inorganic Exam 2 **Name:**
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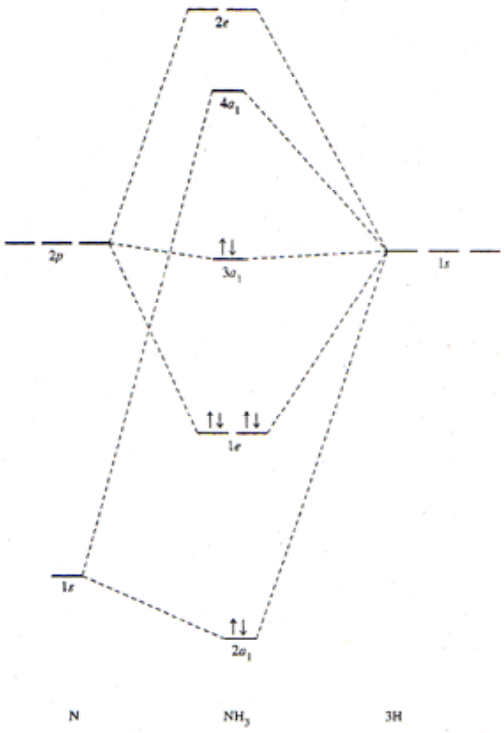
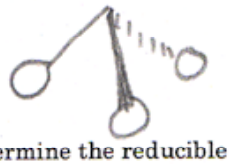
1. Ammonia has C_{3v} symmetry. The C_{3v} character table is shown below and the molecular orbital diagram for ammonia is given at right. Answer the following questions about the molecular orbital diagram for ammonia.

C_{3v}	E	2 C_3	3 σ_v	
A_1	1	1	1	z
A_2	1	1	-1	
E	2	-1	0	x, y



1(a) (3 pts) Sketch the set of H atomic orbitals that you would use to form your SALC set. (This is a 3-D ball and stick sketch.)



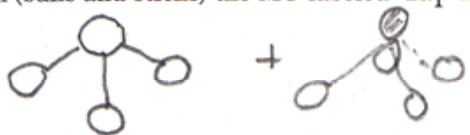
1(b) (3 pts) Determine the reducible representation for ammonia by using your sketch in (a):

C_{3v}	E	2 C_3	3 σ_v	
Γ	3	0	1	

1(c) (3 pts) Resolve the reducible representation into its irreducible components.

A_1 1 1 1
E 2 −1 0
Γ 3 0 1

1(d) (3 pts) Sketch (balls and sticks) the MO labeled "$2a_1$" in the MO diagram.



1(e) (3 pts) What nitrogen orbital(s) are involved in forming the "1e" molecular orbital?

Circle: 2s (2p_x) (2p_y) 2p_z

1(f) (3 pts) What is the bond order? Show work.

BO = (# bonding elect − # antibond)/2 * # bonds = $\frac{6-0}{2\cdot 3} = 1$

1(g) (3 pts) What orbital in the MO diagram represents the lone pair on ammonia? Use their labeling system: Circle: $2a_1$ 1e (3a_1) $4a_1$ 2e

2. (4 pts) Just from your knowledge of symmetry, how would you expect the s and p orbitals to transform in a D_{3h} geometry? (You did this with BF_3) To answer the question, fill in "s," "$2p_x$," "$2p_y$," and "$2p_z$ in the table below.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	s
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	p_x p_y
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	p_z
E''	2	-1	0	-2	1	0	

3. (5 pts) Which of these are Lewis bases? Circle all that are.

NH_3 BF_3 Al^{+3} H_2O F^-

4. (5 pts) Circle the strongest Bronsted-Lowry acid in each pair.

(a) HF or HCl

(b) H_3AsO_3 or H_3AsO_4

(c) NaH_2AsO_3 or Na_2HAsO_3

(d) HAt or HAtO

(e) HIO_2 or HIO_3

5. (4 pts) Use hard-soft acid-base theory to predict the preferred direction for the equilibrium in each of the following. Do this by sketching in long/short arrows: ⟶ or ⟵ or ⟷

$LiCl + AuI \quad [\leftarrow] \quad LiI + AuCl$

$2\,CuSCN + Ca(NO_3)_2 \; [\leftarrow] \; 2\,CuNO_3 + Ca(SCN)_2$

6. (5 pts) Nickel crystallizes in a fcc lattice. Its density is 8.90 g/cm^3. What is the atomic radius of nickel in pm? Show all work.

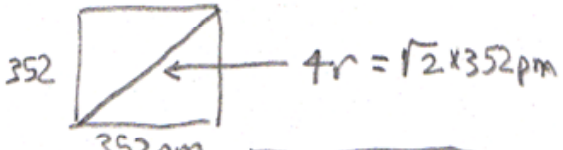
$d = m/V$

$V = m/d = \dfrac{4\,Ni}{\text{unitcell}} \dfrac{58.69\,g\,Ni}{mol\,Ni} \dfrac{1\,mol\,Ni}{6.02\times10^{23}\,Ni} \dfrac{cm^3}{8.90\,g} \dfrac{10^{-6}\,m^3}{1\,cm^3} \dfrac{1\,pm^3}{10^{-36}\,m^3}$

(fcc) (AM) (N_A) (d)

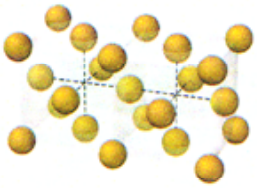
$= 4.39\times10^7\,pm^3$

$e = \sqrt[3]{V} = 352\,pm$



$r = 125\,pm$

7. (6 pts) In the pictures given at right, gold, ruthenium and chromium are depicted. In each case, more than one unit cell is shown. Identify the unit cell that each exhibits.



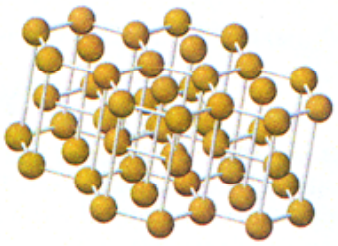
(a) Gold

(a) Gold

fcc or ccp

(b) ruthenium

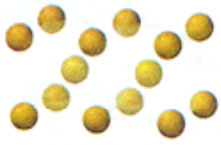
hcp



(b) Ruthenium

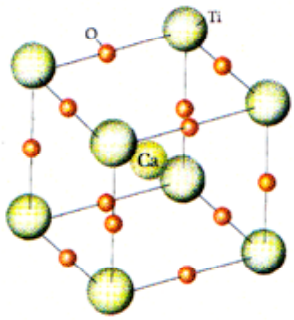
(c) chromium

body-centered cubic



(c) Chromium

8(a) (3 pts) Perovskite contains calcium, titanium and oxygen ions. They are labeled in the figure at right. (Note that the relative sizes of the ions is misleading.) What is the empirical formula for perovskite?

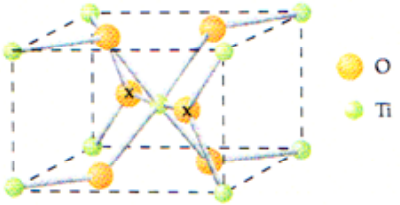


$CaTiO_3$

8(b) (2 pts) What is the oxidation state of titanium in perovskite?

+4

9. Rutile crystallizes in the structure shown at right. This is an important and common structure.



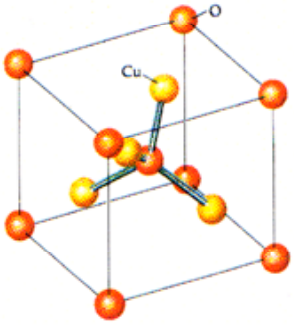
9(a) (3 pts) What sublattice is exhibited by the titanium ions shown in green? Hint: It is body-centered, but not body-centered cubic. Note: I will accept two answers here as there is some ambiguity.

body-centered tetragonal or body-centered orthorhombic

9(b) (3 pts) What is the <u>empirical formula</u> for rutile? Note: The oxides marked with "x" are entirely inside the unit cell shown. The other oxides are centered in faces.

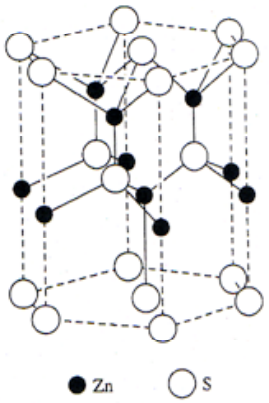
TiO_2

10. (3 pts) Cuprite, shown at right, is a semiconductor consisting of copper and oxide ions and is shown at right. Many other compounds crystallize in this structure including the important semiconductor gallium arsenide. What is the <u>empirical formula</u> for cuprite?



Cu_2O

11. Wurtzite consists of zinc(II) and sulfide ions and crystallizes in the structure shown at right.



11(a) (3 pts) What unit cell do the sulfur ions use for their sublattice?

hcp

11(b) (3 pts) Is this one of the close-packed lattices?

yes

11(c) (4 pts) What sort of holes and what fraction of those holes are occupied by the zinc ions? Hint: There are two ways to do this. Keep in mind that the empirical formula must work out for zinc(II) sulfide.

Zn^{+2} in tetrahedral holes

2 tetrahedral holes : 1 S^{-2} ion

∴ ½ of the tetrahedral holes are occupied.

12. Lattice energy.

12(a) (2 pts) What is the definition of "lattice energy"? Answer by way of an example, say potassium bromide. It is acceptable to simply write the balanced chemical equation.

$$K^+(g) + Br^-(g) \longrightarrow KBr(s)$$

12(b) (6 pts) Calculate the lattice energy for calcium fluoride. Given: sublimation energy for calcium metal is +178 kJ/mol, the ionization energies for calcium are E_{i1} = 590 kJ/mol and E_{i2} = 1145 kJ/mol. The F_2 bond energy is 158 kJ/mol and the energy associated with electron affinity for fluorine:

$$F(g) + e^- \rightarrow F^-(g) \quad \Delta H = -328 \text{ kJ/mol.}$$

The heat for formation for calcium fluoride is –1228 kJ/mol.

$Ca(s) \rightarrow Ca(g)$ $\quad \Delta H = +178$ kJ

$Ca(g) \rightarrow Ca^{+1}(g) + e^-$ $\quad +590$

$Ca^+(g) \rightarrow Ca^{+2}(g) + e^-$ $\quad +1145$

$F_2(g) \rightarrow 2F(g)$ $\quad +158$

$2F(g) + 2e^- \rightarrow 2F^-(g)$ $\quad 2 \times -328$

$Ca^{+2}(g) + 2F^-(g) \rightarrow CaF_2(s)$ $\quad \Delta H_{LE}$

$Ca(s) + F_2(g) \rightarrow CaF_2(s)$ $\quad \Delta H_f = -1228$ kJ/mol

$$\Delta H_{LE} = -2643 \text{ kJ/mol}$$

13(a) (2 pts) Why does MgO have a larger lattice energy than NaCl, even though both form similar fcc-style lattices?

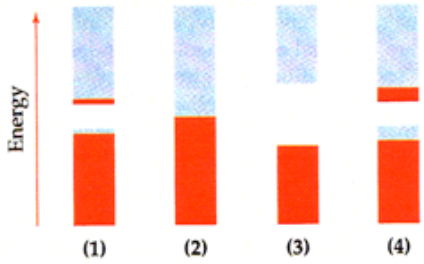
Lattice energy $\propto q^+ * q^-$

$\therefore (+2)(-2) > (+1)(-1)$

13(b) (1 pt) What is the general relationship between lattice energy and predicted solubility in water?

Solubility [increases/decreases] as the lattice energy increases.

14. Consider the diagrams shown at right.



14(a) (1 pt) What does each blue and red column represent?

molecular orbitals

14(b) (1 pts) What does the blue region represent? What does the red region represent?

blue – empty MOs

red – empty MOs

14(c) (1 pt) Which blue/red column(s) represent(s) an insulator? Circle: (1) (2) (3) (4)

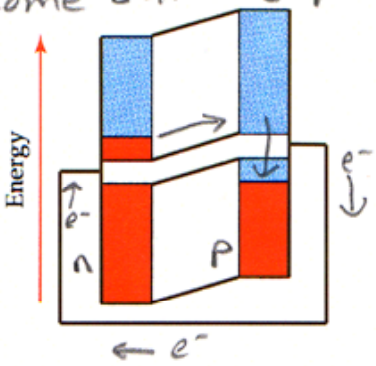
14(d) (1 pt) Which blue/red column(s) represent(s) metal conductor? Circle: (1) (2) (3) (4)

14(e) (1 pt) Which blue/red column(s) represent(s) a semiconductor? Circle: (1) (2) (3) (4)

14(f) (2 pts) Why is there some red in the upper part of Figures (1)? What causes that?

These electrons are in excited states due to Thermal excitation (temperature) which provides enough energy to overcome band gap.

15. Consider the sketch for a diode shown at right.



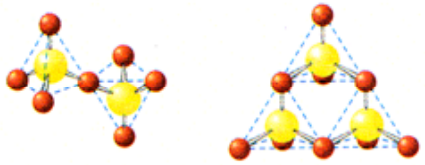
15(a). (1 pts) Label the n-type and p-type parts of the diode.

15(b) (1 pt) Add an arrow to show the allowed direction of electron flow.

15(c) (2 pts) Suppose that the band gap corresponds to an energy associated with visible light, say red light, what would be the result of adding a battery in a forward bias arrangement? What would happen?

A red LED would result

16. (4 pts) Give the formula for each of these two silicates. Silicon in yellow; oxygen in red. Include charge!



$Si_2O_7^{-6}$ $Si_3O_9^{-6}$ or SiO_3^{-2}