EXAM TWO PART ONE

CHM 451 (INORGANIC CHEMISTRY)

DR. MATTSON 1 NOVEMBER 2012 NAME:

Instructions: This exam has two parts. In Part One, only a pencil and a non-programmable calculator may be used. When you have completed Part 1, turn it in and obtain Part Two. In Part Two, your data sheet (on the periodic table) and a non-programmable calculator may be used. Show your work for credit whenever a box is provided.

Acid-base concepts.

1. (2 pts) Predict the product(s) of this Lewis acid-base reaction:

   $AlCl_3 + NH_4F \longrightarrow$

2. (2 pts) Identify the Bronsted-Lowry acid and base in the reaction:

   $HC_2H_3O_2 + HI \longrightarrow H_2C_2H_3O_2^+ + I^-$

3. (2 pts) Methanol has an autodissociation $pK_{solvent}$ value of 18.9. Write the equilibrium expression. Box the acid and circle the base (Sounds like a sporting event.)

4. (2 pts) NaF has a solubility in water of 4.2 g/100 mL while NaCl's is 35.7 g/mL. Use the concept of hard-soft acid bases to explain this phenomenon.

5. (1 pt) Acetic acid would have the largest K_a value in

   A. 100% sulfuric acid

   B. water

   C. liquid ammonia.

6. (2 pts) Baking soda contains aluminum sulfate and sodium bicarbonate. When the aluminum sulfate comes in contact with water water, $Al(H_2O)_6^{+3}(aq)$ is formed. This ion is acidic with a $K_a = 1.2 \times 10^{-5}$. Write the equilibrium expression showing how $Al(H_2O)_6^{+3}(aq)$ functions as a monoprotic acid.

7. (1 pt each) Liquid SbF_5 can function as a solvent.

7a. Write the equilibrium that is established when some NaF is added to $SbF_5(l)$.

7b. Is NaF an acid or a base in this solvent?

A. an acid B. a base C. Neither

8. (3 pts) Circle the strongest acid of each pair

(a) HF or HCl

(b) $HClO_2$ or $HClO_4$

(c) LiH or H_2O

9. (3 pts) Circle the "hard acid" of each pair

(a) H^+ or Ag^+

(b) Fe^{+2} or Fe^{+3}

(c) Ni^{+2} or Pt^{+2}

Solid state concepts.

10. Palladium exists as a solid in a fcc arrangement of atoms. The atomic radius, r, of palladium is 137.5 pm.

10a. (1 pt) How many atoms of Pd are present in each unit cell?

10b. (3 pts) What is the relationship between the length of each unit cell edge, e, and the atomic radius?

Answer: e =

10c. (3 pts) What is the volume of a unit cell of Pd in units of cm^3?

10d. (3 pts) What is the calculated density of Pd in units of g/cm^3?

10e. (1 pt) How would the density of Pd be different if Pd existed as a bcc unit cell instead of a fcc? It would be

A. greater B. smaller C. the same

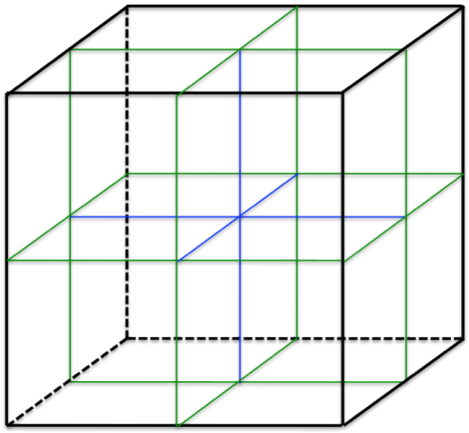
10f. (1 pt) How would the density of Pd be different if Pd existed as a hcp unit cell instead of a fcc?

A. greater B. smaller C. the same

11. (4 pts) What sort of holes and how many of each exist in a fcc lattice?

12. (3 pts) What is the percent empty space in any fcc lattice? Given: $V_{sph} = {}^4/_3\pi r^3$

13a. (2 pts) Locate one of the tetrahedral holes occurring in an fcc lattice using the figure below. Label it "T" Draw lines to show how it connects to nearest neighboring atoms/ions.



13b. (2 pts) Locate one of the octahedral holes in the figure above. Label it "O"

14. (3 pts) Which member of each pair has the largest lattice energy?

a. LiCl or Na_2O

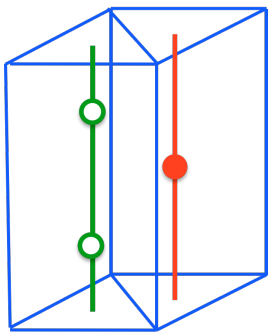
b. MgO or $MgCl_2$

c. MgO or Na_2O

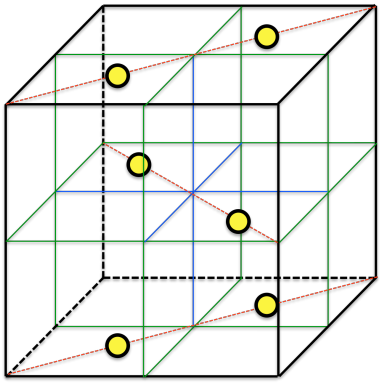
15. (1 pt ea) One unit cell of the hcp lattice is shown below.

15a. What is designated by the red circle?

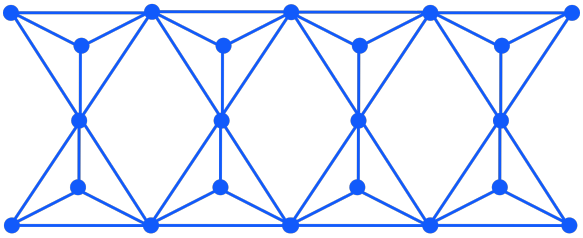
15b. What is designated by the green circles?



16. (3 pts) The mineral rutile features titanium ions in a bcc arrangement with oxide ions in the locations shown in yellow below. The oxide ions lie along the two red line that go from corner to corner and along the other red line that goes from edge-center to edge-center. What is the formula of rutile?



17. (3 pts) A polymeric silicate we have not seen before is shown below. The pattern continues indefinitely. What is the empirical formula of the silicate?



18. (5 pts) The tetragonal unit cell has which of these symmetry elements? Circle all that apply.

A. C_4

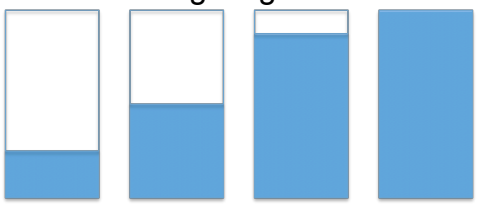
B. $\perp C_2$

C. σ_v

D. σ_h

E. i

19. (1 pt ea) The molecular orbital diagram for macroscopic samples of metals can be represented using diagrams such as:



A B C D

19a. Which one of these could represent scandium?

A B C D

19b. Which MO diagram is most likely to represent a high melting element?

A B C D

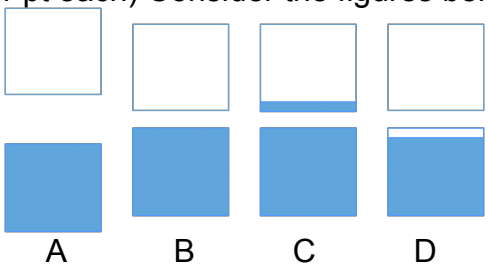
19c. Which of these has the largest bond order?

A B C D

19d. Which of these elements would be the poorest conductor as shown?

A B C D

20. (1 pt each) Consider the figures below.



A B C D

20a. Which is the most likely to be an insulator?

A B C D

20b. Which is most likely to be silicon doped with antimony?

A B C D

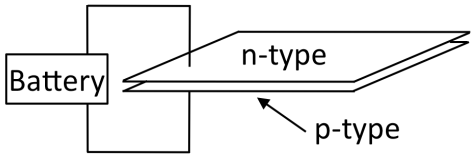
20c. Which is most likely to be silicon doped with indium?

A B C D

20d. Which is most likely to be a the best conductor?

A B C D

21. (1 pt each) A pn-junction is constructed as shown.



21a. Sketch the electron flow in a forward bias arrangement.

21b. Using the figures given in Problem 20, which figure represents the n-type portion of the pn-junction?

A B C D

BONUS (3 pts) How many space-defining ions exist within the following unit cells?

a. face-centered orthorhombic

b. base-centered monoclinic

c. rhombohedron

This ends Part 1. Check your work and turn this portion of the exam in and receive Part 2. In Part 2, you can use the special exam yellow periodic table with whatever notes you've made on the periodic table.

EXAM TWO PART TWO

CHM 451 (INORGANIC CHEMISTRY)

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Instructions: In Part Two, your data sheet (on the periodic table) and a non-programmable calculator may be used. Always show your work!

1. (6 pts) Use the method of radius ratio to predict the bonding arrangement used in:

   a. NaBr, r_{cation} = 116 pm and r_{anion} = 182 pm

   b. TiO_2, r_{cation} = 56 pm and r_{anion} = 124 pm

   c. BaS, r_{cation} = 149 pm and r_{anion} = 170 pm

2. The density of pure palladium is 12.0 g/cm^3. As stated in Part 1, palladium forms a fcc solid. Palladium absorbs molecular hydrogen, H_2, with a release of energy. The hydrogen breaks into atoms and the hydrogen atoms occupy the octahedral holes within palladium.

   2a. (2 pts) What is the volume of one mole of palladium in units of cm^3?

   2b. (2 pts) What is the formula of palladium hydride if every octahedral hole is occupied?

2c. (2 pts) What is the volume of 0.5 moles of H_2 gas at 25 ^oC and 1.0 atm? (This corresponds to 1.0 mole of H atoms) Use the ideal gas law, PV = nRT, R = 0.0821 L atm/mol K to perform this calculation.

2d. (2 pts) Divide the volume of 0.5 mol H_2 gas by the volume of 1 mole of palladium. Watch the volume units so they cancel! This gives you the volume of hydrogen that can be absorbed by one volume of palladium metal. Expect to be surprised!

2e. (2 pts) Palladium hydride is actually a non-stoichiometric hydride, meaning that the formula is not a ratio of simple integers. That means we can have decimals in our formula, Pd_aH_b. If in reality, only 70% of the octahedral holes are occupied by hydrogen (as a maximum), what is the formula Pd_aH_b if a = 1? (Note that b is not an integer.)

3. The mineral zinc blende features sulfide ions in a fcc sub-lattice and zinc ions in half of the tetrahedral holes. The mineral wurtzite has sulfide ions in a hcp sub-lattice and zinc ions in half of the tetrahedral holes.

3a. (4 pts) What is the formula of each mineral?

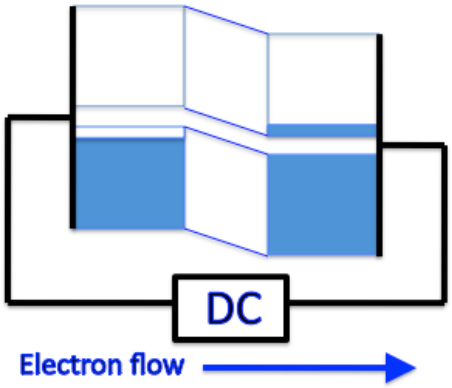
3b. (1 pt) Would there be a preference for either fcc or hcp if the zinc ion were a different size?

A. Yes B. No C. More information needed

4. (5 pts) Calculated the lattice energy for CaS(s), given the following information?

ΔH_f^o for Ca(g)	+178 kJ/mol
Subsequent ionization energies for calcium:	
1^{st}:	+590 kJ/mol
2^{nd}:	+1145 kJ/mol
3^{rd}:	+4912 kJ/mol
4^{th}:	+6491 kJ/mol
5^{th}:	+8153 kJ/mol
ΔH_f^o for S(g)	+277 kJ/mol
Electron affinity for S(g)	-200 kJ/mol
Electron affinity for S^-(g) ($S^-(g) + e^- \rightarrow S^{-2}(g)$)	+456 kJ/mol
ΔH_f^o for CaS(s)	-482.4 kJ/mol

5. (3 pts) This diagram shows how a diode could be used as a light-emitting diode, or LED. Using a single arrow, indicate the source of the light on the diagram.



6. (3 pts) What is the radius of an octahedral hole, $r_{oct\ hole}$, in terms of the radius of the space defining spheres, r?

Answers:

1. $AlCl_3 + NH_4F \longrightarrow NH_4^+ + AlCl_3F^-$

2. The Bronsted-Lowry acid is HI and the base is $HC_2H_3O_2$.

3. $2\ CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$
The acid is $CH_3OH_2^+$ and the base is CH_3O^-

4. NaF is a better match of hard acid + hard base and these compounds are often less soluble than hard-soft or soft-hard.

5. C

6. $Al(H_2O)_6^{+3} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{+2}$

7. $SbF_5 + F^- \rightleftharpoons SbF_6^-$; 7b. B

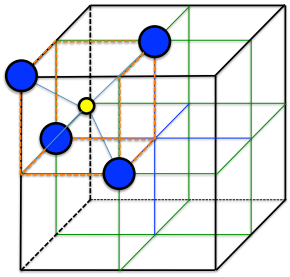
8. (a) HCl; (b) $HClO_4$; (c) H_2O

9. (a) H^+; (b) Fe^{+3}; (c) Ni^{+2}

10a. 4; 10b. $e = 2 \times 2^{0.5} r$; 10c. $5.88 \times 10^{-23}\ cm^3$; 10d. $12.02 g/cm^3$; 10e. B; 10f. C

11. 4 octahedral holes and 8 tetrahedral holes; 12. 26%

13a. One (of 8) of the tetrahedral holes is shown in yellow:



13b. The octahedral holes are along all 12 edge centers and the body-center position for a total of 4.

14. a. Na_2O; b. MgO; c. MgO

15a. The red circle is an atom from the B layer (ABAB); 15b. The green circles are octahedral holes.

16. TiO_2; 17. $Si_2O_5^{-2}$; 18. All 5 (A-E)

19a. A; 19b. B; 19c. B; 19d. D

20a. A; 20b. C; 20c. D; 20d. C

21a. Electron flow is counter-clockwise in this diagram; 21b. C; BONUS a. 4; b. 2; c. 1

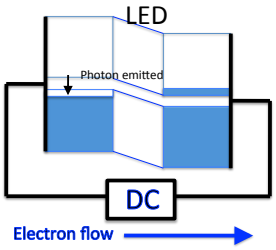
Part Two 1a. Small ions in octahedral holes; 1b. Small ions in octahedral holes; 1c. Large ions form simple cube and small ions are in body-centered positions (CsCl lattice)

2a. $8.87\ cm^3$; 2b. PdH; 2c. 12.2 L; 2d. 1350; 2e. $PdH_{0.7}$

3a. ZnS for both; 3b. no

4. $\Delta H_{lattice} = -2930$ kJ

5.



6. $r = 0.414 \times r_{oct\ hole}$