

DESTROY

ANSWER KEY

CHEMISTRY S1404
PROFESSOR J. MORROW

SECOND EXAM

7/29/99

PRINT NAME, LAST: _____

FIRST: _____

I.D.# : _____

 MAXIMUM POINT VALUE IS IN PARENTHESIS

- | | | |
|--------------|---------------|--------------|
| 1. _____(6) | 9. _____(10) | 17. _____(6) |
| 2. _____(9) | 10. _____(20) | 18. _____(6) |
| 3. _____(10) | 11. _____(6) | 19. _____(6) |
| 4. _____(20) | 12. _____(6) | 20. _____(6) |
| 5. _____(6) | 13. _____(6) | 21. _____(6) |
| 6. _____(15) | 14. _____(10) | 22. _____(6) |
| 7. _____(12) | 15. _____(6) | 23. _____(6) |
| 8. _____(8) | 16. _____(6) | 24. _____(6) |

COLUMN TOTALS: (MAXIMUM)

| | | |
|------------|------------|------------|
| _____ (86) | _____ (70) | _____ (48) |
|------------|------------|------------|

EXAM TOTAL (186 pts) _____

| |
|-------|
| _____ |
|-------|

 OUT OF 100

1)

Ionization Energies (kJ/mol)

| | Fe | |
|--------|-------|------|
| First | | 759 |
| Second | 1561 | |
| Third | | 2957 |
| Fourth | _____ | 4175 |

A compound, ilmenite, (FeTiO_3) is composed of either Fe^{2+} and Ti^{4+} ions OR Fe^{3+} and Ti^{3+} ions. Which combination, (Fe^{2+} and Ti^{4+}) or (Fe^{3+} and Ti^{3+}) is more reasonable. (6 pts) SHOW WORK

Fe^{3+} and Ti^{3+} requires 9897 kJ to form
 Fe^{2+} and Ti^{4+} requires 11,115 kJ to form

ANSWER IS: Fe^{3+} and Ti^{3+}

2) Give the electronic configuration ($1s^2$ etc) and the number of unpaired electrons (UE) in each of the following gaseous atoms/ions. (9 pts - 3 pts each: 2 pts/1 pt)

Cu $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^9$ UE = 1
OR $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

Cu^+ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^9$ UE = 2
OR $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^{10}$ UE = 0

Cu^{2+} $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^9$ UE = 1

3) An ionic crystalline solid, MX_3 , has a cubic unit cell. Which of the following arrangements of the ions is consistent with the stoichiometry of the compound? (10 pts)

- i) M^{3+} ions at the corners, X^- ions at the face centers.
- ii) M^{3+} ions at the corners, X^- ions at the body center.
- iii) X^- ions at the corners, M^{3+} ions at the face centers.
- iv) X^- ions at the corners, M^{3+} ions at the body center.
- v) M^{3+} ions at the corners and the body center, X^- ions at the face centers.

ANSWER IS: i

- 4) Magnetite, Fe_3O_4 ($231.54 \frac{\text{g}}{\text{mol}}$), has a density of $4.897 \frac{\text{g}}{\text{cm}^3}$. It is an orthorhombic crystal with $a = b = 11.86 \text{ \AA}$ and $c = 16.75 \text{ \AA}$. How many formula weight units of Fe_3O_4 are there per unit cell? How many Fe^{2+} ions and how many Fe^{3+} ions are there per unit cell? (20 pts) SHOW WORK

The number of formula weight units is:

- i) 12 ii) 15 iii) 24 iv) 30 v) 36

$$\frac{\text{molecules}}{\text{uc}} = \left(\frac{\text{molecules}}{\text{mol}}\right) \left(\frac{\text{mol}}{\text{g}}\right) \left(\frac{\text{g}}{\text{cm}^3}\right) \left(\frac{\text{cm}^3}{\text{\AA}^3}\right) \left(\frac{\text{\AA}^3}{\text{uc}}\right)$$

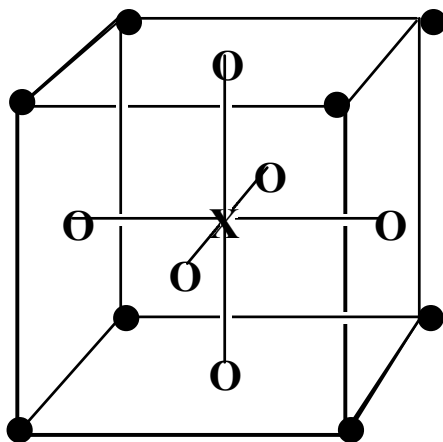
$$\frac{\text{molecules}}{\text{uc}} = (6.022 \times 10^{23}) \left(\frac{1}{231.54}\right) (4.897) (10^{-24}) (16.75) (11.86)^2 = 30$$

(12 pts) # of Formula weights: 30

(4 pts) # of Fe^{2+} ions: 30

(4 pts) # of Fe^{3+} ions: 60

- 5) Perovskite is a material containing calcium, titanium, and oxygen. The cubic unit cell is shown below.



$\times = \text{Ti}^{4+}$

$\circ = \text{O}^{2-}$

$\bullet = \text{Ca}^{2+}$

Ionic radii: $\text{Ti}^{4+} = 0.360 \text{ \AA}$; $\text{O}^{2-} = 1.450 \text{ \AA}$

density = 4.759 g/cm^3 Molar mass = 135.96 g/mol

Calculate the unit cell edge length in \AA . (6 pts)

$$\text{unit cell edge length} = 2(0.360 \text{ \AA}) + 2(1.450 \text{ \AA})$$

ANSWER IS: 3.62 \text{ \AA}

- 6) Osmium is one of the world's most expensive elements. The abundance of osmium is 2×10^{-4} ppm (parts per million) and it has a melting point of

3045°C. Last year one kilogram of this element sold for 78 *million* dollars. Aside from all of this fascinating information, osmium crystallizes in a face centered cubic lattice. The atomic radius of osmium is 1.352 Å, and its molar mass is $190.2 \frac{\text{g}}{\text{mol}}$. (15 pts)

a) Calculate the density of osmium. (10 pts) SHOW WORK

$$\text{FOR fcc unit cell, } a = (8^{1/2})r = (2.829)(1.352) = 3.824 \text{ \AA} \quad (3 \text{ pts})$$

$$\frac{\text{g}}{\text{cm}^3} = \left(\frac{\text{g}}{\text{mol}}\right) \left(\frac{\text{mol}}{\text{molecule}}\right) \left(\frac{\text{molecules}}{\text{uc}}\right) \left(\frac{\text{uc}}{\text{\AA}^3}\right) \left(\frac{\text{\AA}^3}{\text{cm}^3}\right)$$

$$\text{density} = (190.2) \left(\frac{1}{6.022 \times 10^{23}}\right) (4) \left(\frac{1}{3.824}\right)^3 (10^{24}) = 22.59 \frac{\text{g}}{\text{cm}^3} \quad (7 \text{ pts})$$

ANSWER IS: 22.59

b) Calculate its molar volume ($\frac{\text{cm}^3}{\text{mol}}$). (5 pts)

$$\frac{\text{cm}^3}{\text{mol}} = \left(\frac{\text{cm}^3}{\text{g}}\right) \left(\frac{\text{g}}{\text{mol}}\right) = \left(\frac{1}{22.59}\right) (190.2) = 8.42 \frac{\text{cm}^3}{\text{mol}}$$

ANSWER IS: 8.42

7) Give the hybridization for each underlined atom in the following ions. Also give the actual spatial appearance of the ion. If the ion cannot exist, write CNE, in space provided. (ie. sp² / trigonal)
Group numbers: N (5), Cl (7), S (6), F (7) (12 pts - 3 pts each)

i) IF₄⁺ sp³d / seesaw

ii) SF₅⁺ sp³d / trigonal bipyramid

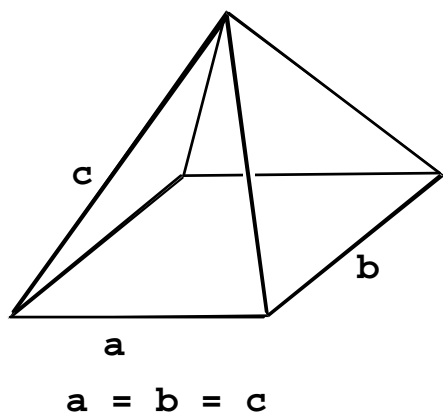
iii) NF₄⁻ CNE

iv) BF₄⁺ CNE

- 8) State how many of each of the following types of elements of symmetry exist in chlorofluoromethane. (8 pts)



- 9) State how many of each of the following types of elements of symmetry exist in square based pyramid below. (10 pts)



center of symmetry, 0

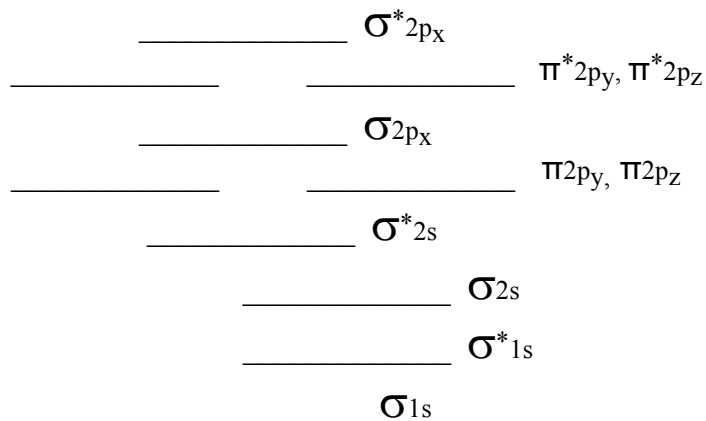
two fold axis of rotation, 0

three fold axis of rotation, 0

four fold axis of rotation, 1

planes of symmetry, 4

Use the MO correlation diagram below (where needed) to answer questions 10, 11, and 12.



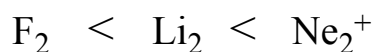
- 10) Predict the apparent bond order, relative bond length, and number of unpaired electrons in the following species; CO, BN, and BeC. Where relative values are compared, use < or > otherwise use the calculated numerical values. (20 pts)

| | CO | BN | BeC |
|-------------------------------------|----|----|-----|
| <u>Bond order</u> | 3 | 2 | 1 |
| <u>Bond Length</u> | < | < | |
| <u>Bond enthalpy</u> | > | > | |
| <u>Number of unpaired electrons</u> | 0 | 0 | 2 |

- 11) If light of the proper wavelength is used an electron in the π_{2py} molecular orbital is excited to the π^*_{2py} . What is the bond order after this transition in BeC? (6 pts)

$$\text{bond order} = 0$$

- 12) List the following in order of increasing bond length: Li_2 , Ne_2^+ , and F_2 . (6 pts)

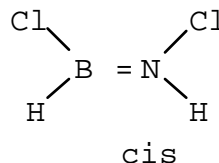
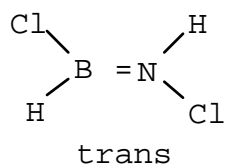


- 13) The bond order of each of the following, C-H, O-H, and F-H, is 1. List them in order of decreasing bond enthalpy. (6 pts)



14) The molecule BNH_2Cl_2 exists in two forms, a cis form and a trans form.

GIVEN: Bond enthalpies (kJ/mol): B=N (511); N-N (163); B-N (212);
N-H (388); N-Cl (381); B-H (551); Cl-Cl (243); B-Cl (349)



Calculate the energy per molecule ($\frac{\text{J}}{\text{molecule}}$), required to convert the trans form to the cis form. (10 pts)

i) 8.48×10^{-19} ii) 4.97×10^{-19} iii) 3.52×10^{-19} iv) 2.67×10^{-19}

$$\mathcal{E} \left(\frac{\text{J}}{\text{molecule}} \right) = \left(\frac{\text{kJ}}{\text{mol}} \right) \left(\frac{\text{J}}{\text{kJ}} \right) \left(\frac{\text{mol}}{\text{molecule}} \right) = (511-212)(10^3) \left(\frac{1}{6.022 \times 10^{23}} \right)$$

GIVE 4 pts FOR EITHER i or iii ANSWER IS: ii

THE FOLLOWING PERIODIC TABLE MAY BE OF USE IN ANSWERING THE REMAINING PROBLEMS.

Group Number

| | I _A | II _A | III _A | IV _A | V _A | VI _A | VII _A | Inert gas |
|---|----------------|-----------------|------------------|-----------------|----------------|-----------------|------------------|-----------|
| 2 | Li 1.0 | Be 1.5 | B 2.0 | C 2.5 | N 3.0 | O 3.5 | F 4.0 | |
| 3 | Na 0.97 | Mg | Al 1.5 | Si | P 2.1 | S 2.5 | Cl 3.0 | |
| | K 0.90 | Ca | Ga | Ge | As | Se 2.4 | Br 2.8 | |
| 5 | Rb 0.87 | Sr | In | Sn | Sb | Te | I 2.5 | |

Beneath most symbols are electronegativity values. Please use them where necessary in answering this question.

15) List the following atoms in order of decreasing 2nd ionization

energy: O, S, and K. (6 pts)



ACTUAL VALUES (kJ): 147 133 98

16) List the following in order of decreasing radius.

- Na⁺, Mg⁺, and K⁺. (6 pts) $Mg^+ > K^+ > Na^+$
- 17) List the ions S²⁻, P³⁻, and N³⁻, in order of increasing ionic radius, that is, the largest is last. (6 pts) $N^{3-} < S^{2-} < P^{3-}$
- 18) List the following ions in order of decreasing ionic radius. Li⁺, Be³⁺, and B⁺ (6 pts) $B^+ > Li^+ > Be^{3+}$
- 19) List the following gases in order of decreasing molecular bond enthalpy P₂, S₂, and Cl₂. Lowest goes last. (6 pts) $P_2 > S_2 > Cl_2$
- 20) List the following atoms in order of decreasing 3rd ionization energy. Li, Na, and Al (6 pts) $Li > Na > Al$
ACTUAL VALUES (kJ): 510 301 117
- 21) Which of these molecules is/are non-polar ; IF₃, BF₃, NF₃, SF₄, XeF₄? (6 pts)
ANSWER: BF₃, XeF₄
- 22) Circle the stronger acid in each of the following pairs.
- i) H₂S₂O₃ or *H₂S₄O₆* (3 pts)
- ii) HIO₃ or *HClO₃* (3 pts)
- 23) Match up the following bond enthalpies (in kJ/mol), 163, 360, 412, and 436, with the indicated molecules; (6 pts)
- H-H 436 C-H 412 C-O 360 N-N 163
- 24) In a multi-electron atom, how many electrons can have the following sets of quantum numbers? (6 pts - 2 pts each)
- i) n = 3, m_λ = 0, m_s = - $\frac{1}{2}$ 3
- ii) n = 4, m_λ = -2, m_s = + $\frac{1}{2}$ 2
- iii) n = 4, m_λ = +2 4