Name_____**Key**_____

Chem 370 - Spring, 2019
Test II - Part 1
April 22, 2019

1. (30 points; 3 points each) Circle the correct answer to each of the following.

a. Which one of the following aqueous solutions would be acidic?

$Ba(NO_3)_2(aq)$ $KNO_3(aq)$ $Ca(NO_3)_2(aq)$ **$Al(NO_3)_3(aq)$** $NaNO_3(aq)$

b. Which one of the following would have the lowest proton affinity, defined as the enthalpy of the reaction, $HA(g) \rightarrow H^+(g) + A^-(g)$, and therefore be inherently most acidic?

H_2 PH_3 H_2S GeH_4 **HBr**

c. *On the basis of the solvent system concept*, which one of the following reactions would result in an *acidic* solution? **The first reactant is the solvent in each case.**

$BrF_3 + NaF \rightarrow Na^+ + [BrF_4]^-$

$ICl + PCl_5 \rightarrow [PCl_4]^+ + [ICl_2]^-$

$ClF_3 + PtF_5 \rightarrow [ClF_2^+] + [PtF_6^-]$

$ClF_3 + NOF \rightarrow [NO]^+ + [ClF_4]^-$

$ICl + NaCl \rightarrow Na^+ + [ICl_2]^-$

d. Which one of the following acids is strongest in water?

H_3PO_4 HOCl **$HClO_3$** H_3PO_2 H_2SO_3

e. Which one of the following has the ground state configuration $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2(\pi^*_{2p})^2$?

NO^- C_2 C_2^{2-} N_2 NO^+

f. Which one of the following has a double bond and is diamagnetic?

NO^- **C_2** C_2^{2-} N_2 O_2^{2+}

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g. Which of the following statements concerning close-packed structures is *not true*?

i. Cubic close-packed (ccp) and hexagonal close packed (hcp) have the maximum packing efficiency of 74.05%

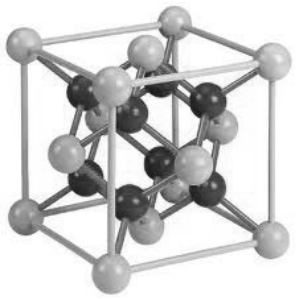
ii. Both ccp and hcp structures have as many octahedral holes as they have tetrahedral holes.

iii. Both ccp and hcp structures have CN12 for every atom

iv. If *r* is the radius of the atoms comprising a close-packed structure, an interstitial atom whose radius is 0.35*r* would most probably occupy an octahedral hole, but not a tetrahedral hole.

v. A body-centered cubic structure of like atoms is not close-packed and results in a lower packing efficiency.

h. The calcium fluoride (fluorite) structure is shown below, in which gray spheres represent Ca^{2+} ions, and black spheres represent F^- ions.



How many CaF_2 formula units (*Z*) does the fluorite structure contain?

1 2 3 **4** 8

i. Which one of the following best describes the structure of fluorite (shown above)?

triclinic simple cubic body-centered cubic **face-centered cubic** rhombahedral

j. Which one of the following ionic compounds has the *largest* lattice energy?

ScN NaF Na_2O ZnS CaO

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2. (16 points; 4 points each lettered part) Fill in the blanks with the correct answers.

a. Give the electronic configuration in the form $t_{2g}^{\ n}e_g^{\ m}$ for the metal ion in each of the following ML_6 octahedral complexes, where M is a transition-metal ion and L is a unidentate ligand.

d^7 high-spin $\boldsymbol{t_{2g}^{\ 5}e_g^{\ 2}}$ d^7 low-spin $\boldsymbol{t_{2g}^{\ 6}e_g^{\ 1}}$

b. Give the spin-only magnetic moments (B.M.) expected for octahedral complexes with metal ions having the following configurations.

d^7 high-spin **3.87 B.M.** d^7 low-spin **1.73 B.M.**

c. For the complexes described in parts a and b, give the expressions for the crystal (ligand) field stabilization energies (CFSE) in terms of Δ_o and P.

d^7 high-spin $\boldsymbol{-0.8\Delta_o + 2P}$ d^7 low-spin $\boldsymbol{-1.8\Delta_o + 3P}$

d. How many unpaired electrons would each of the following Co^{2+} complexes have?

$[CoCl_4]^{2-}$ **3** $[Co(CN)_6]^{4-}$ **1**

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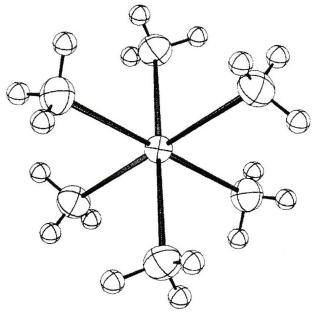
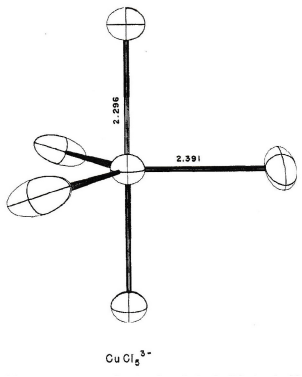
3. (12 points) X-ray structure determination of crystalline $[Cr(NH_3)_6][CuCl_5]$ shows that the compounds consists of octahedral $[Cr(NH_3)_6]^{3+}$ cations (O_h) and trigonal bipyramidal $[CuCl_5]^{3-}$ anions (D_{3h}).[1]





a. (3 points) Show the CFT splitting of the *d* orbitals on Cr^{3+} in the octahedral $[Cr(NH_3)_6]^{3+}$ cation. Label the levels by Mulliken symbol and specific *d* orbitals, and fill the scheme with the appropriate number of electrons, using up and down arrow notation, ↿⇂.

___ ___ e_g $(d_{z^2}, d_{x^2-y^2})$

1 1 1 t_{2g} (d_{xz}, d_{yz}, d_{xy})

b. (7 points) With the aid of the attached D_{3h} character table, determine the CFT splitting scheme of the *d* orbitals on Cu^{2+} in the trigonal bipyramidal $[CuCl_5]^{3-}$ anion. Label the levels by Mulliken symbol and specific *d* orbitals, and fill the scheme with the appropriate number of electrons, using up and down arrow notation, ↿⇂.

1 a_1' (d_{z^2})

↿⇂ ↿⇂ e' $(d_{x^2-y^2}, d_{xy})$

↿⇂ ↿⇂ e'' (d_{xz}, d_{yz})

c. (2 points) Both ions in $[Cr(NH_3)_6][CuCl_5]$ are paramagnetic. What would be the predicted spin-only magnetic moment in Bohr magnetons for this compound?

μ = (3.87 B.M. + 1.73 B.M.)/2 = 2.80 B.M.

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[1]K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **1968**, 1111.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)