Chem 130 – Third Exam

Name_______________________________

On the following pages you will find questions covering various topics ranging from the structure of solid-state materials, the chemistry of acid-base and oxidation-reduction reactions, and metal-ligand complexes. Read each question carefully and consider how you might approach the problem before you put pen or pencil to paper. If you aren't sure how to start a question, move to another problem; working on a new question may suggest an approach to that more troublesome problem. For problems requiring a written response, be sure that your answer is written in complete sentences and that it directly and clearly answers the question.

Partial credit is willingly given on all problems so be sure to answer all questions!

Question 1 _____/20	Question 5 _____/6
Question 2 _____/14	Question 6 _____/18
Question 3 _____/12	Question 7 _____/18
Question 4 _____/12	

Total __________

Potentially useful equations and constants:

$c = \lambda\nu$ $\quad E = h\nu$ $\quad KE = h\nu - BE$ $\quad \frac{1}{\lambda} = 1.09737\times10^{-2}\ \text{nm}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ $\quad V = \frac{kq_1q_2}{d}$

$$FC_a = V_a - N_a - \frac{B_a}{2} \qquad \delta_a = V_a - N_a - B_a\left(\frac{EN_a}{EN_a + EN_b}\right)$$

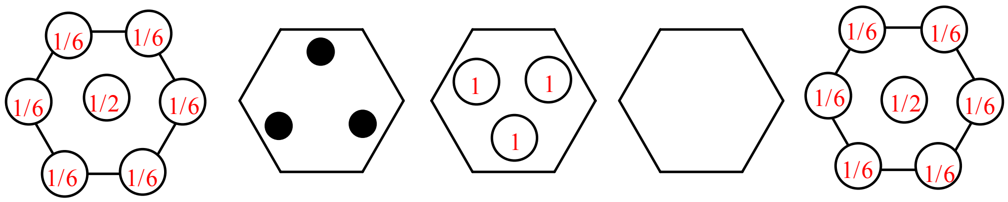
$$OX_a = V_a - N_a - B_a \times (0\ \text{if least EN}; 1\ \text{if most EN})$$

$$c = 2.998\times10^{8}\ \text{m/s} \qquad h = 6.626\times10^{-34}\ \text{Js} \qquad N_A = 6.022\times10^{23}\ \text{mol}^{-1}$$

$$K_a \times K_b = K_w \text{ for conjugate acid/base pair}$$

Some potentially useful tables are on an additional handout.

Question 1. Shown below are five cross-sections through the unit cell an ionic solid. Anions are shown as open circles (○) and cations are shown as solid circles (●).



How many anions are in this unit cell? Clearly show how you arrived at this answer by *labeling above each anion with its contribution to the unit cell.*

Each anion is labeled above with its contribution to the unit cell. There are 6 anions in the unit cell.

How many cations are in this unit cell? Clearly show how you arrived at this answer by *labeling above each cation with its contribution to the unit cell.*

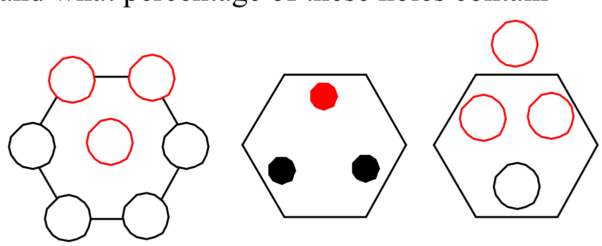
The three cations in the second layer are wholly in this unit cell; thus, there are 3 cations in the unit cell.

If each anion has a charge of -1, what is the charge on each cation? Clearly explain your answer in one sentence.

The six anions, each with a charge of -1, provide a total charge of -6. The three cations must provide a total charge of +6; thus, the cations each have a charge of +2.

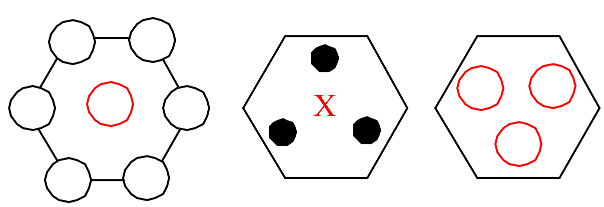
In what type of hole does each cation sit and what percentage of these holes contain cations?

Each cation sit in an octahedral hole, of which there are six; thus, 50% of the holes are occupied. This is shown here by the red anions and cations. Note that one of the anions is from an adjacent unit cell.



In addition to the holes occupied by cations, there is another type of hole in the anion's lattice. What type of hole is this? Place an **X** in a one of the layers shown below such that it clearly marks one of these holes. In addition, shade the anions coordinated to this hole.

There also are tetrahedral holes, as shown here by the red X and the red anions.



Question 2. Consider the following three acids. Place an **S** below the strongest of the acids and a **W** below the weakest of the acids. Briefly explain your reasoning in two or three sentences. In your answer, be sure to provide a chemically relevant reason for your rankings.

H_2Se	H_2S	HF
S		**W**

The strength of an X-H bond is determined by both the size of X and by its electronegativity, with size being the more important factor when comparing compounds in the same group. A larger X means a longer X-H bond, which, in turn, is easier to break and makes for a better acid. Selenium is larger than sulfur, which is larger than fluorine; thus, H_2Se is the strongest acid and HF is the weakest acid.

Consider the following three bases. Place an **S** below the strongest of the bases and a **W** below the weakest of the bases. Briefly explain your reasoning in two or three sentences. In your answer, be sure to provide a chemically relevant reason for your rankings.

BrO_2^-	BrO^-	ClO_2^-
	S	**W**

This is easiest to decipher by considering the conjugate acids, $HBrO_2$, HBrO, and $HClO_2$, where H is bound to an oxygen. The strength of an acid increases when more electronegative constituents pull electron density away from the O-H bond, which weakens the bond and makes ionization easier. Between $HClO_2$ and $HBrO_2$, the greater EN of chlorine makes $HClO_2$ a stronger acid. Between HBrO and $HBrO_2$, the extra oxygen makes $HBrO_2$ the stronger acid; thus, BrO^- is the strongest base and ClO_2^- is the weakest base.

Question 3. Ammonium acetate is an interesting compound because it contains both a weak acid, NH_4^+, and a weak base, CH_3COO^-. When NH_4CH_3COO*(s)* dissolves in water the following acid-base reaction may occur:

$$NH_4^+(aq) + CH_3COO^-(aq) \leftrightarrows NH_3(aq) + CH_3COOH(aq)$$

Will the resulting solution contain more NH_4^+ or more NH_3? The K_a for CH_3COOH and the K_b for NH_3 are each 1.75×10^{-5}. In one to three sentences, provide a convincing explanation for your choice. You may supplement your answer with a calculation, but it is not necessary to do so! A calculation without an accompanying written explanation will receive little partial credit.

The solution will have more NH_4^+ than NH_3. An acid-base reaction is favorable when a stronger acid and a stronger base react to make a weaker acid and a weaker base. The K_a and K_b values for NH_3 and CH_3COOH are 1.75×10^{-5} and the K_a and K_b values for NH_4^+ and CH_3COO^- are $1.00\times10^{-14}/1.75\times10^{-5}$, or 5.7×10^{-10}. NH_4^+ and CH_3COO^- are the weaker acid and the weaker base; thus, the reaction will not happen to any appreciable extent and there will be more NH_4^+ than NH_3. K_a for the reaction is 1.9×10^{-17}.

Question 4. Metals such as Au and Pt are very unreactive, which is one reason why they are valuable. In 800 AD the Islamic alchemist Jabir Ibn Hayyan discovered that Pt, which does not dissolve in HCl or in HNO_3, will dissolve in a mixture of these acids. This mixture is more commonly known as *aqua regia*. Given the following standard state reduction potentials

$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	$E^o = 1.188$ V
$HNO_3(aq) + 3H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	$E^o = 0.96$ V
$PtCl_4^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4Cl^-(aq)$	$E^o = 0.755$ V
$2HCl(aq) + 2e^- \rightarrow H_2 + 2Cl^-(g)$	$E^o = 0.00$ V

write a reaction showing how Pt dissolves in *aqua regia*.

The reaction is $2HNO_3 + 6H^+ + 3Pt + 12Cl^- \rightarrow 2NO + 3PtCl_4^{2-} + 4H_2O$.

In one to three sentences, provide a convincing explanation for your choice. You may supplement your answer with a calculation, but it is not necessary to do so! A calculation without an accompanying written explanation will receive little partial credit.

A redox reaction occurs when a strong oxidizing agent and a strong reducing agent react to make a weaker oxidizing agent and a weaker reducing agent. Stronger oxidizing agents have more positive reduction potentials and stronger reducing agents have less positive reduction potentials. Pt by itself (first reaction) is too weak of a reducing agent to react with HNO_3, but Pt in the presence of Cl^- (third reaction) can react with HNO_3. The E^o for the reaction is 0.96 + (-0.755) = 0.205 V, which is favorable.

For your reaction, what is the oxidizing agent and what is the specific change in oxidation state that is occurring?

The oxidizing agent is HNO_3 with nitrogen changing oxidation state from +5 to an +2.

Question 5. Provide the name for the coordination compound $(NH_4)_4[Fe(ox)_3]$ where "ox" is the oxalate anion, $C_2O_4^{2-}$.

Each NH_4^+ contributes a charge of +1, for a total of +4 and each oxalate contributes a charge of -2, for a total of -6; the iron, therefore, has an oxidation state of +2. The compound is ammonium trioxalatoferrate(II)

Provide the chemical formula for the coordination compound

hexaminecobalt(III) pentachlorocuprate(II)

Each ion has a net charge of -3; thus, the formula is $[Co(NH_3)_6][CuCl_5]$.

Question 6. The table below contains data for a series of coordination compounds. Fill in the missing blanks. If you wish, use the boxes below the table to annotate you work.

	Empirical Formula	# ions	# Cl^- ppt as AgCl	Oxidation State for Pt	Coordination Number for Pt	Chemical Formula
a	$PtCl_4{\bullet}6NH_3$	5	4	+4	6	$[Pt(NH_3)_6]Cl_4$
b	$PtCl_4{\bullet}4NH_3$	3	2	+4	6	$[Pt(NH_3)_4Cl_2]Cl_2$
c	$PtCl_4{\bullet}2NH_3$	0	0	+4	6	$Pt(NH_3)_2Cl_4$
d	$PtCl_4{\bullet}2KCl$	3	0	+4	6	$K_2[PtCl_6]$
e	$PtCl_2{\bullet}NH_3{\bullet}KCl$	2	0	+2	4	$K[Pt(NH_3)Cl_3]$
f	$2PtCl_2{\bullet}4NH_3$	2	0	+2/+2	4/4	$[Pt(NH_3)_4][PtCl_4]$

a. These values follow directly from the formula.	b. Four chlorides means that Pt must have an ox. state of +4. Two of the chlorides must be bound to Pt, giving a CN of 6.	c. No ions means that all chlorides are bound to Pt.
d. Both potassiums are cations; thus, all chlorides are bound to Pt. Four chlorides means that the Pt must have an oxidation state of +4.	e. All chlorides are bound to Pt; thus, there are two ions—a potassium cation and the Pt complex anion.	f. The two oxidation states and two coordination numbers mean that there is a Pt cation and a Pt anion.

Question 7. The ligand nitrite may bind either through its nitrogen ($–NO_2^-$) or through one of its oxygens ($–ONO^-$). In the boxes below, draw all possible geometric and linkage isomers for the octahedral coordination compound $Pt(NH_3)_2(NO_2)Cl_3$. Do not include optical isomers in your answers. Be careful to draw each unique isomer only once. There may be more spaces than answers! Use the back of your this page for your initial work and places your answers only here. Please note that I will not be evaluating work on the back side of this page.

The three chlorides can be in either a facial or a meridional arrangement. In the meridional arrangement (top row), the two ammonias can be cis- or trans- to each other and the nitrite can be bound through its N or O. In the facial arrangement (bottom row) the nitrite can be bound through its N or O. Thus, there are six possible arrangements.