Chem 130 – Key for Third Exam

Name_____

On the following pages are eight questions that consider topics ranging from precipitation–solubility, acid–base, and oxidation–reduction reactions to metal–ligand complexes and coordination compounds. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer one question, then move on to another question; working on a new question may suggest an approach to the one that is more troublesome. If a question requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question.

Question 1 _____/12	Question 5 _____/12
Question 2 _____/12	Question 6 _____/6
Question 3 _____/12	Question 7 _____/17
Question 4 _____/12	Question 8 _____/17

Total _____/100

Potentially useful equations and constants:

$$c = \lambda \nu \qquad\qquad E = h\nu = hc/\lambda$$

$$KE = h\nu - W \qquad\qquad \frac{1}{\lambda} = 1.09737 \times 10^{-2} \text{ nm} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$FC_a = V_a - N_a - \frac{B_a}{2} \qquad\qquad V \propto \frac{Q_+ Q_-}{d}$$

$$AVEE = \frac{xIE_s + yIE_p + zIE_d}{x + y + z} \text{ (valence shell electrons only)}$$

$$\delta_a = V_a - N_a - B_a \left(\frac{EN_a}{EN_a + EN_b} \right) \qquad\qquad c = 2.998 \times 10^8 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ Js} \qquad\qquad N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

Other potentially useful information is available as separate handouts.

Problem 1. The formation of a precipitate—or the lack thereof—is a common technique for identifying the presence or the absence of an ion in a sample. Suppose you have a solution that might contain one or more the following four cations: Ag^+, K^+, Ba^{2+}, and Cu^{2+}. To identify which ions are present in your sample, you carry out the following sequential set of tests. *First*, you add a solution of HCl to your sample and observe that a precipitate forms. *Second*, after centrifuging, you remove the supernatant solution, add to it a solution of H_2SO_4, and observe that nothing happens. *Finally*, you add a solution of Na_2CO_3 to the same supernatant solution and observe that a precipitate forms. Based on these three tests, identify which cations **must be present** in your sample, identify which **must be absent** in your sample, and identify for which cations you have **insufficient information** to reach a conclusion. For each cation, explain how you know that your conclusion is correct.

must be present	must be absent	insufficient information
Ag^+ and Cu^{2+}	Ba^{2+}	K^+

The precipitate that forms when we add HCl is AgCl; thus, Ag^+ is present in the sample. After removing AgCl from the supernatant, a failure to form a precipitate when we add H_2SO_4 means there is no Ba^{2+} in the sample because otherwise $BaSO_4$ would precipitate. The precipitate that forms when we add Na_2CO_3 is $CuCO_3$ as we know that Ba^{2+} is not in the sample and we already removed any Ag^+. We have insufficient information for K^+ because it has no possible reactions with HCl, H_2SO_4, or Na_2CO_3 that could confirm its presence or its absence.

Problem 2. For each of the following pairs of acids, circle the one that is the stronger acid and, for each pair, defend your choice in 1–2 sentences.

H_2S vs. **HCl** Because S and Cl are in the same row and of reasonably similar size, electronegativity is more important than size in determining bond strength; Cl is more electronegative than S, making the H–Cl bond weaker and making HCl the stronger acid.

PH_4^+ vs. NH_4^+ Because P and N are in the same column, size is more important than electronegativity in determining bond strength; P has a greater radius than S, making the H–P bond weaker and making **PH_4^+** the stronger acid.

$HSeO_3$ vs. **$HSeO_4$** (for both, hydrogen is bound to oxygen) The greater the number of oxygens, the more positive the oxidation state on Se, which is +5 for $HSeO_3$ and +7 for $HSeO_4$; the more positive the oxidation state, the more electrons are pulled toward Se and away from the H–O bond making $HSeO_4$ the stronger acid.

Problem 3. Some of the earliest matches were made by preparing a mixture of white phosphorous, P_4, and potassium chlorate, $KClO_3$, glued to the end of wooden stick. When rubbed across a piece of sandpaper, the oxidation-reduction reaction

$$3P_4(s) + 10\textbf{KClO}_3(s) \rightarrow 3P_4O_{10}(s) + 10KCl(s)$$
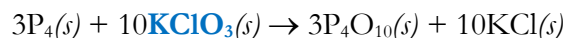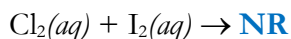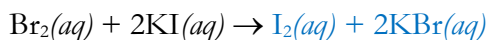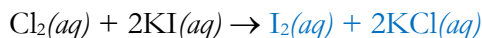
produced a flame. Draw a circle around the reactant that is the oxidizing agent. To support your answer, identify the specific element that is oxidized and the specific element that is reduced, and, for each, report the change in its oxidation state.

The oxidation states are as follows: P in P_4 is 0; K in $KClO_3$ is +1, Cl in $KClO_3$ is +5, O in $KClO_3$ is –2; P in P_4O_{10} is +5; O in P_4O_{10} is –2; K in KCl is +1; and Cl in KCl is –1. Note that K has only a +1 ion and that oxygen is almost always –2. The oxidizing agent is $KClO_3$ as the chlorine in this compound is reduced from +5 to –1; phosphorous is oxidized from 0 to +5.

Problem 4. The following two reactions are known to occur:

$$Br_2(aq) + 2NaI(aq) \rightarrow I_2(aq) + 2NaBr(aq)$$

$$Cl_2(aq) + 2NaBr(aq) \rightarrow Br_2(aq) + 2NaCl(aq)$$
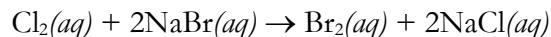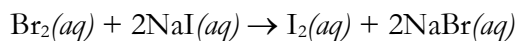
Based on these observations, predict the products of the following reactions, writing NR if no reaction is expected.

$Cl_2(aq) + 2KI(aq) \rightarrow I_2(aq) + 2KCl(aq)$

$Br_2(aq) + 2KI(aq) \rightarrow I_2(aq) + 2KBr(aq)$

$Cl_2(aq) + I_2(aq) \rightarrow$ **NR**

In the space below, defend your predictions in 2–5 sentences.

The two known reactions show us that Br_2 is a stronger oxidizing agent than I_2 and that Cl_2 is a stronger oxidizing agent than Br_2. Based on this, we know that Cl_2 is the strongest oxidizing agent and I_2 is the weakest oxidizing agent. We also know that I^- is the strongest reducing agent and that Cl^- is the weakest reducing agents. The first two of the three possible reactions take place because the reactants are stronger oxidizing agents and stronger reducing agents than are the products. The last of the possible reactions does not occur because both reactants are oxidizing agents and an oxidation–reduction reaction requires an oxidizing agent and a reducing agent.

Problem 5. You can make a simple weather predictor by soaking a piece of filter paper in a solution of $CoCl_4^{2-}$ and letting the paper dry. On a sunny day with low humidity, the paper is pink due to the color of the tetrahedral $CoCl_4^{2-}$ metal-ligand complex. When the humidity increases—and the chance for rain increases—the paper turns blue as water molecules replace the chloride ions in $CoCl_4^{2-}$, forming the octahedral $Co(H_2O)_6^{2+}$ metal-ligand complex. The color in each case is the result of the splitting of cobalt's d-orbitals into two groups, one of higher energy and one of lower energy. The difference in energy is defined as Δ_o for an octahedral complex and as Δ_t for a tetrahedral. Based on the color of the two complexes, is the value for Δ_o bigger or smaller than that for Δ_t? Explain your reasoning in 1–3 sentences. *Note: The supplemental sheet shows the arrangement of d-orbitals for both an octahedral and a tetrahedral metal-ligand complex.*

We know that the blue $Co(H_2O)_6^{2+}$ metal-ligand complex absorbs light with a wavelength of approximately 610 nm and that the pink $CoCl_4^{2-}$ metal-ligand complex absorbs light with a wavelength of approximately 525 nm. We also know that energy—and Δ_o and Δ_t are energies—is inversely proportional to wavelength; thus, the octahedral $Co(H_2O)_6^{2+}$ metal-ligand complex has a smaller energy than does the tetrahedral $CoCl_4^{2-}$ metal-ligand complex, which means that Δ_o is smaller than Δ_t.

Problem 6. What is the name for the coordination compound $[Co(NH_3)_5Cl](NO_3)_2$?

pentaminechlorocobalt(III) nitrate

What is the formula for the coordination compound potassium diaquotetracyanochromate(II)?

$K_2[Cr(H_2O)_2(CN)_4]$

Problem 7. The table below contains data for a series of coordination compounds. For each empty box, enter the missing information. If you wish, use the space below the table to explain how you arrived at your answers; although not required of you, I will review any notes you leave there.

	empirical formula	free chlorides	ordinary valence	coordination valency	number of ions	chemical formula
(a)	$PtCl_4(NH_3)_6$	**4**	**+4**	6	5	$[Pt(NH_3)_6]Cl_4$
(b)	$PtCl_4(NH_3)_4$	2	**+4**	6	3	**$[Pt(NH_3)_4Cl_2]Cl_2$**
(c)	$PtCl_4(NH_3)_2$	**0**	+4	6	0	**$Pt(NH_3)_2Cl_4$**
(d)	K_2PtCl_6	**0**	**+4**	6	3	**$K_2[PtCl_6]$**
(e)	$KPtCl_3(NH_3)$	0	+2	4	**2**	**$K[Pt(NH_3)Cl_3]$**
(f)	$Pt_2Cl_4(NH_3)_4$	0	+2/+2	4/4	2	**$[Pt(NH_3)_4][PtCl_4]$**

The ordinary valency is the oxidation state of Pt, which we determine by noting that every chlorine carries a charge of –1 and every potassium carries a charge of +1. Using compound (d) as an example, the six chlorines have a combined charge of –6 and the two potassiums have a combined charge of +2; together, the net charge is –2, which leaves platinum with a +2 oxidation state.

If there are no ions, then there are no free chloride ions. If there are ions, then the number of free chlorides is equal to the number of ions minus the number of potassiums minus one for the metal-ligand complex. Using (d) as an example, the number of free chlorides is

$$3 - 2 - 1 = 0$$

The coordination valency is the number of bonds to Pt. Here we know that NH_3 is a ligand that bonds once to Pt, that Cl^- is either a ligand that binds once to Pt or is a free chloride ion present simply to balance charge, and that K^+ always is present as an ion to balance charge as it has no electrons with which to form a bond to Pt. The coordination valency, therefore, is the number of NH_3 ligands plus the difference between the number of chlorines and the number of free chlorides. Using (d) as an example, the coordination number is

$$0 + (6 - 0) = 6$$

The number of ions is zero if there are no potassiums and no free chloride ions, or equal to the number of potassiums and the number of free chloride ions plus one for the metal-ligand complex. Using (d) as an example, the number of ions is
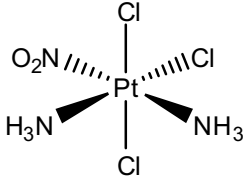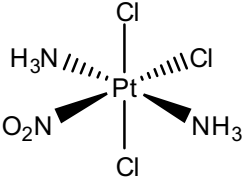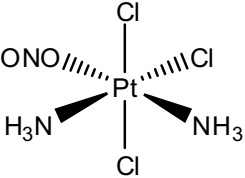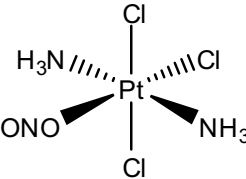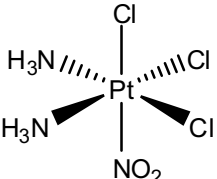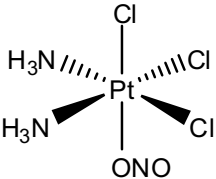
$$2 + 0 + 1 = 3$$

The lack of brackets for (c) indicates that this is a neutral compound; in all other cases, brackets are placed around the metal-ligand complex. Cations always are listed before anion.

Finally, another answer for (f) is $[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$; however $Pt(NH_3)_2Cl_2 \cdot Pt(NH_3)_2Cl_2$ is not an acceptable answer because in this case the two metal-ligand complexes are neutral and, therefore, does not include two ions.

Problem 8. As a ligand, the nitrite ion, NO_2^-, can bind to a metal ion through its nitrogen (—NO_2) or through its oxygen (—ONO). With this in mind, draw all possible geometric and linkage isomers for the octahedral coordination compound $Pt(NH_3)_2(NO_2)Cl_3$, placing each unique isomer in a separate cell in the table below. Be sure to draw each unique isomer only once. There are more spaces in the table than there are unique isomers. If you wish, use the space below the table and/or the reverse side of this page to sketch out your ideas and/or to explain your approach; although not required of you, I will review any notes and/or sketches that you leave there.

The best approach to this problem is to begin with the three chlorines and note that they may be arranged in a meridional geometry or a facial geometry. When the chlorines are in a meridional geometry, the two ammonia molecules have either a trans or a cis geometry; however, when the chlorines are in a facial geometry, the ammonia molecules have a cis geometry only. Finally, the single nitrite ion may bind to the last remaining site through its nitrogen or through its oxygen. This leaves us with six unique geometric isomers, as shown in the table below. To help you review cases where two or more of your structures are identical and to recognize structures that you overlooked, the shorthand notations of MCN, MTN, MCO, MTO, FCN, and FCO listed in the table are used to annotate your work.

meridional chlorine cis ammonia nitrite bonding through N identified as MCN	meridional chlorine trans ammonia nitrite bonding through N identified as MTN	meridional chlorine cis ammonia nitrite bonding through O identified as MCO
meridional chlorine trans ammonia nitrite bonding through O identified as MTO	facial chlorine cis ammonia nitrite bonding through N identified as FCN	facial chlorine cis ammonia nitrite bonding through O identified as FCO