

Chem 130 – Third Exam Key

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 ____/15

Question 5 ____/15

Question 2 ____/17

Question 6 ____/8

Question 3 ____/15

Question 7 ____/15

Question 4 ____/15

Total ____/100

Potentially useful equations and constants:

$$c = \lambda\nu$$

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

$$KE = h\nu - W$$

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

$$FC_a = V_a - N_a - \frac{B_a}{2}$$

$$V \propto \frac{Q_+ Q_-}{d}$$

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

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

$$c = 2.998 \times 10^8 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

Other potentially useful information is available as separate handouts.

Problem 1. For each pair of acids, circle the one that is the stronger acid and, in no more than 2–3 sentences each, explain the reason(s) for your choice. For the compounds in (b) and in (c), the acidic hydrogen is attached to oxygen.

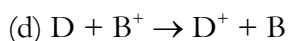
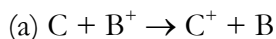
For all three pairs, the stronger acid is the compound with the weakest X–H bond, where X is the element to which the acidic hydrogen is bound.

(a) NH_4^+ vs. PH_4^+ : In this case we are comparing a N–H bond to a P–H bond and the length of the bond is the important consideration. Because P has a larger radius than N, the P–H bond is longer and weaker, making PH_4^+ the stronger of the two acids.

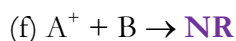
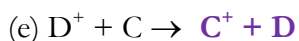
(b) HOBr vs. HOI : In this case this acidic hydrogen is bound to an oxygen for both molecules. Here the important consideration is the electronegative element to which oxygen is bound and its effect on the strength of the O–H bond as it pulls electron density away from this bond, weakening the bond. The more electronegative Br has a greater effect than the less electronegative I, making HOBr the stronger of the two acids.

(c) H_2CO_3 vs. HCO_3^- : In this case the acidic hydrogen is bound to an oxygen that is, in turn, bound to a carbon. There are no differences in the electronegativities of the elements in the two compounds, nor are there any differences in oxidation states that might explain a difference in acidity. Here, the important consideration is charge; it is more difficult to remove a positive charge (a proton, H^+) from an anion than it is from a neutral molecule; thus, H_2CO_3 is the stronger acid.

Problem 2. The following information is known for reactions between the elements A, B, C, and D, and their +1 cations, A^+ , B^+ , C^+ , and D^+ ; note that NR means there is no reaction:



Predict the products of the following two reactions, writing NR if there is no reaction.



In the space below, present a convincing argument that your responses are correct by arranging the cation/element pairs into a reactivity series ordered from the strongest oxidizing agent to the weakest oxidizing agent **and** explaining how you arrived at this order; in addition, explain why your reactivity series supports your predictions. Limit the written portion of your response to 3–6 sentences.

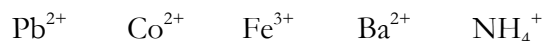
strongest oxidizing agent



weakest oxidizing agent

From reactions (a) and (d) we know that B^+ is a stronger oxidizing agent than D^+ and C^+ , which places B^+/B above D^+/D and C^+/C . From reaction (b) we know that C^+ is a weaker oxidizing agent than A^+ , which places C^+/C below A^+/A . From reaction (c) we know that D^+ is a stronger oxidizing agent than A^+ , which places D^+/D above A^+/A , giving the final order shown on the left. The predictions above for the reactions recognize that a stronger oxidizing agent (upper left) will react with a stronger reducing agent (lower right).

Problem 3. Suppose you have a solution that might contain one or more of the following cations:



To identify the ions in the solution you add HCl to the solution and observe a precipitate. After centrifuging, you remove the supernatant solution from the precipitate, add H_2SO_4 to this solution, and observe a precipitate. After centrifuging, you remove the supernatant from this second precipitate, add NaOH to this solution, and observe that no precipitate forms. In the table below, place each of the five cations in the cell that matches your prediction that it must be present, that it must be absent, or that you do not have sufficient information to determine if it is present or if it is absent.

cation must be present	cation must be absent	insufficient information
Pb^{2+} and Ba^{2+}	Co^{2+} and Fe^{3+}	NH_4^+

In the space below and in a short paragraph of 3–5 sentences, present a convincing argument that your assignments for all five cations are correct. Note: to receive full credit your explanation here must support your predictions.

The solution to this problem requires three things: solubility rules, recognizing that a positive test for an ion requires that you have an opportunity to see it precipitate or not precipitate, and recognizing that once an ion is precipitated the supernatant no longer contains that ion. With these in mind, we note that adding HCl produces a precipitate of $\text{PbCl}_2(s)$ as this is the only cation here that forms a precipitate with Cl⁻. Adding H_2SO_4 to the supernatant produces a precipitate of $\text{BaSO}_4(s)$ as this is the only remaining cation that forms a precipitate with SO_4^{2-} . Adding NaOH to the supernatant does not produce a precipitate, which means neither Co^{2+} nor Fe^{3+} are present because they would form $\text{Co}(\text{OH})_2(s)$ and $\text{Fe}(\text{OH})_3(s)$. Finally, none of the reagents can react with NH_4^+ , so we have insufficient information to determine if it is or is not present.

Problem 4. The drug Nipride, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, is a metal-ligand complex that is used as a source of molecular NO during surgery where it helps moderate blood pressure. Although the compound releases molecular NO into the blood stream, it is present in the metal-ligand complex as the cation NO^+ . When we first described a metal-ligand complex we characterized the metal in terms of its coordination valency and its ordinary valency. Using Nipride as an example, in 2-4 sentences, clearly explain the difference between these two types of valencies and report their values for the metal-ligand complex in Nipride.

The ordinary valency is the metal's oxidation state. In this case, the two Na^+ ions tell us that the metal-ligand complex carries a charge of -2. Each of the five cyanide ligands has a charge of -1 (CN^-) and the nitrosyl ligand has a charge of +1 (NO^+); thus, the ligands combine for a charge of -4, which means the iron is present with a charge of +2.

The coordination valency is the number of electron pairs donated to the metal to form metal-ligand bonds. Each of the six ligands donates an electron pair, so the coordination number is 6.

The iron in this metal-ligand complex is expected to be low-spin due to the presence of the cyano and the nitrosyl ligands. How many unpaired electrons are in iron's *d*-orbitals? Explain how you arrived at your response in 2-3 sentences.

Iron(II) has a valence shell electron configuration of $3d^6$. For a low spin complex, the three lower energy *d*-orbitals fill completely before electrons enter the two higher energy *d*-orbitals. With six electrons, this means that each of the three lower energy *d*-orbitals has two paired electrons and there are not unpaired electrons.

Problem 5. Octahedral metal-ligand complexes of chromium (III) are quite colorful. For example, the following is a list of several such metal-ligand complexes and their colors.

$\text{Cr}(\text{acac})_3$: red — absorbs a wavelength of approximately 525 nm

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$: violet — absorbs a wavelength of approximately 575 nm

$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$: green — absorbs a wavelength of approximately 665 nm

$[\text{Cr}(\text{urea})_6]^{3+}$: green — absorbs a wavelength of approximately 665 nm

$[\text{Cr}(\text{NH}_3)_6]^{3+}$: yellow — absorbs a wavelength of approximately 415 nm

$\text{Cr}(\text{CH}_3\text{CO}_2)_3(\text{H}_2\text{O})_3$: blue-violet — absorbs a wavelength of approximately 590 nm

where the ligands are acetylacetonate (written here in shorthand notation as acac), water, chloride, urea, ammonia, and acetate (which is CH_3CO_2^-). Arrange the ligands in order of increasing values for the octahedral field splitting, Δ_o . Explain how you arrived at your ordering in a paragraph of 4–6 sentences. Note: to receive full credit your explanation here must support your predictions.

The color we see is the opposite of the color of light absorbed. Using a color wheel, therefore, gives the wavelengths absorbed by the compounds that are listed above. Because there is an inverse relationship between energy and wavelength and a direct relationship between energy and Δ_o , a shorter wavelength means a larger Δ_o . This is sufficient to put the compounds in order of smallest Δ_o to largest Δ_o , but the problem asks us **to order the ligands, not the compounds**. The largest Δ_o belongs to $[\text{Cr}(\text{NH}_3)_6]^{3+}$, so NH_3 has the largest Δ_o . The next largest Δ_o is for $\text{Cr}(\text{acac})_3$, so acac has the second largest Δ_o . The ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ comes next, so H_2O has the third largest Δ_o . The compound $\text{Cr}(\text{CH}_3\text{CO}_2)_3(\text{H}_2\text{O})_3$ comes next and, as we know that H_2O favors a higher Δ_o , then acetate must have a smaller Δ_o . Finally, both $[\text{Cr}(\text{urea})_6]^{3+}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ have the same color, but Cl^- must have the smaller Δ_o given that the compound also includes H_2O , which favors a higher Δ_o . The order, therefore, is, from smallest-to-largest Δ_o : $\text{Cl}^- < \text{urea} < \text{acetate} < \text{H}_2\text{O} < \text{acac} < \text{NH}_3$.

Problem 6. Provide the chemical formula for the coordination compound that has the following name: hexamminecobalt(III) pentachlorocuprate(II).

The formula is $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$. As a check, note that the cation has a charge of +3 and the anion has a charge of -3.

Provide the name for the coordination compound that has the following formula: $(\text{NH}_4)_4[\text{Fe}(\text{ox})_3]$ where “ox” is short for the oxalate anion, $\text{C}_2\text{O}_4^{2-}$.

The name is ammonium trioxalatoferrate(II). Note that the number of ammoniums is implied by the formula of the anion, that the name of the oxalate anion is changed to oxalato, and that the metal's name takes on a suffix of -ate and gives the oxidation state. Iron is named as ferrate (for ferrum), but ironate is accepted here as well.

Problem 7. Consider the hypothetical octahedral metal-ligand complex $MABC_2D_2$, which consists of the ligands A, B, C, and D. Draw all possible geometric isomers for this metal-ligand complex. Do not consider optical isomers. Be careful to draw only once each unique geometric isomer. There are more cells available to you in the table below than there are unique isomers.

You may use the space at the bottom of the page or on the back of this page to consider possibilities, but only those structures placed in the table will be evaluated. Be sure your structures are clear and easy to understand. If making a change to a structure makes it too messy, then place a large X through the structure and redraw it in a new cell.

To draw all of the isomers it helps to note that the two Cs can only be cis or trans to each other, that the two Ds can only be cis or trans to each other, and the A and B can only be cis or trans to each other. This leads us to six unique isomers that appear below and that are represented as well using the shorthand notation

geometry for A & B / geometry for C & C / geometry for D & D

Note that the C/C/C arrangement appears twice because A can be either trans to C or trans to D (as noted by the symbols AC_T and AD_T).

