

## Chem 130 – Third Exam Key

Name \_\_\_\_\_

On the following pages you will find eight questions covering various 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 a question, move to another; 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.

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

Question 1 \_\_\_\_/16      Question 5 \_\_\_\_/12

Question 2 \_\_\_\_/14      Question 6 \_\_\_\_/12

Question 3 \_\_\_\_/16      Question 7 \_\_\_\_/8

Question 4 \_\_\_\_/6      Question 8 \_\_\_\_/16

Total \_\_\_\_/100

Potentially useful equations and constants:

$$c = \lambda\nu$$

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

$$KE = h\nu - W$$

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

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

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

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

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

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

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

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

Other potentially useful information is available as separate handouts.

**Problem 1.** For each pair of acids, circle the one that is stronger and in no more than two sentences explain your reason for this choice. The acidic proton in each compound is underlined.

- (a)  $\underline{\text{H}}_2\text{S}$  vs.  $\underline{\text{H}}_2\text{Te}$  In this case strength depends on the relative ease of breaking the H–X bond, where X is sulfur or tellurium. Because tellurium is larger than sulfur, the H–Te bond is longer and weaker, making  $\text{H}_2\text{Te}$  the stronger acid.
- (b)  $\text{ClH}_2\text{CCOO}\underline{\text{H}}$  vs.  $\underline{\text{F}}\text{H}_2\text{CCOO}\underline{\text{H}}$  In this case strength depends on the relative ease of breaking the O–H bond. Because fluorine is more electronegative than chlorine, it pulls more electron density away from the O–H bond, weakening the bond and making  $\text{FH}_2\text{CCOOH}$  the stronger acid.
- (c)  $\underline{\text{H}}\text{ClO}$  vs.  $\underline{\text{H}}\text{ClO}_2$  In this case strength depends on the relative ease of breaking the O–H bond. Because chlorine's oxidation state is greater in  $\text{HClO}_2$  (+3) than it is in  $\text{HClO}$  (+1), it pulls more electron density away from the O–H bond, weakening the bond and making  $\text{HClO}_2$  the stronger acid.
- (d)  $\underline{\text{H}}_2\text{SO}_3$  vs.  $\text{HSO}_3^-$  In this case strength depends on the relative ease of breaking the O–H bond. Because  $\text{HSO}_3^-$  carries a negative charge, it is harder to remove a positively charged  $\text{H}^+$ , strengthening the bond and making  $\text{H}_2\text{SO}_3$  the stronger acid.

**Problem 2.** The metals A, B, C, and D have the following properties:

- (a) all four metals dissolve in  $\text{HNO}_3$ , forming +2 cations and releasing  $\text{NO}(g)$
- (b) A and C, but not B and D, dissolve in  $\text{HCl}$ , releasing  $\text{H}_2(g)$
- (c) adding C to an aqueous solution containing  $\text{A}^{2+}$ ,  $\text{B}^{2+}$ , or  $\text{D}^{2+}$  results in the formation of  $\text{A}(s)$ ,  $\text{B}(s)$ , or  $\text{D}(s)$
- (d) D undergoes oxidation in the presence of  $\text{B}^{2+}$

Based on these observations, rank the redox couples



from the strongest oxidizing agent to the weakest oxidizing agent. Explain the reason for your rankings in no more than five sentences.

strongest oxidizing agent

1.  $\text{NO}_3^-/\text{NO}$
2.  $\text{B}^{2+}/\text{B}$
3.  $\text{D}^{2+}/\text{D}$
4.  $\text{H}^+/\text{H}_2$
5.  $\text{A}^{2+}/\text{A}$
6.  $\text{C}^{2+}/\text{C}$

weakest oxidizing agent

From (a), we know that  $\text{NO}_3^-$  is the strongest oxidizing agent because it can oxidize all four metals. From (b), we know that  $\text{H}^+$  is a stronger oxidizing agent than  $\text{A}^{2+}$  or  $\text{B}^{2+}$  because it will dissolve A and C; we also know that  $\text{H}^+$  is a weaker oxidizing agent than  $\text{B}^{2+}$  and  $\text{D}^{2+}$  because it will not dissolve B or D. From (c) we know that  $\text{C}^{2+}$  is the weakest oxidizing agent because  $\text{A}^{2+}$ ,  $\text{B}^{2+}$ , and  $\text{D}^{2+}$  can oxidize C. Finally, from (d) we know  $\text{B}^{2+}$  is a stronger oxidizing agent than  $\text{D}^{2+}$  because  $\text{B}^{2+}$  oxidizes D.

**Problem 3.** The table below has rows containing cations and columns containing anions. For each possible combination of cation and anion, determine if a precipitate will form when a solution of the anion is added to a solution of the cation. If a precipitate forms, then enter the precipitate's chemical formula. If a precipitate does not form, then write no reaction (NR) in the corresponding cell.

Answers here follow from general solubility rules: all  $K^+$  salts are soluble; all  $NO_3^-$  salts are soluble; all  $Cl^-$  salts are soluble except for  $Ag^+$ ,  $Hg_2^{2+}$ , and  $Pb^{2+}$ ; all  $OH^-$  salts are insoluble and all  $PO_4^{3-}$  salts are insoluble (except for cases where cation is always soluble).

	$Cl^-$	$OH^-$	$NO_3^-$	$PO_4^{3-}$
$K^+$	NR	NR	NR	NR
$Fe^{3+}$	NR	$Fe(OH)_3$	NR	$FePO_4$
$Ca^{2+}$	NR	$Ca(OH)_2$	NR	$Ca_3(PO_4)_2$
$Ag^+$	$AgCl$	$AgOH$	NR	$Ag_3PO_4$

**Problem 4.** Moving between a coordination compound's name and its formula is an important skill. With that in mind, what is the name for  $Na_3[AlF_6]$ ?

sodium hexafluoroaluminate(III)

What is the formula for diamminetriaquahydroxochromium(III) nitrate?

$[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$

**Problem 5.** When discussing coordination compounds we describe the metal in terms of its ordinary valency and its coordination valency. Using  $[Cr(en)_3]Cl_3$  and  $K_4[CrF_6]$  as examples, and in no more than six sentences, explain the difference between these two valencies. As part of your answer, be sure to clearly state the values for chromium's two valencies in each compound and how you determined their values. Note that "en" is the bidentate ligand ethylenediamine, which has the structure  $H_2NCH_2CH_2NH_2$ .

A metal's ordinary valency is the same as its oxidation state. For  $[Cr(en)_3]Cl_3$ , the three chloride ions provide a net charge of  $-3$  and the ethylenediamines do not carry a charge, leaving a net charge of  $+3$  for chromium and an ordinary valency of 3. For  $K_4[CrF_6]$ , the six fluoride ions provide a net charge of  $-6$  and the four potassium ions provide a net charge of  $+4$ , leaving a net charge of  $+2$  for chromium, which makes chromium's ordinary valence 2.

A metal's coordination valency is the number of electron-pairs it accepts in forming a metal-ligand complex. Each fluoride ion provides a single electron-pair, which means the chromium in  $K_4[CrF_6]$  accepts six electron-pairs and has a coordination valency of 6. For  $[Cr(en)_3]Cl_3$ , each ethylenediamine provides two electron-pairs for a total of six electron-pairs, which means chromium's coordination valency is 6.

**Problem 6.** Of the two complex ions  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{CoF}_6]^{3-}$ , one is paramagnetic and one is diamagnetic. In 4–6 sentences, explain why this is possible.

In the presence of an octahedral field, cobalt's five  $d$  orbitals split into a group of three  $d$  orbitals that are lower in energy than the other two  $d$  orbitals. The difference between the energies of these orbitals is  $\Delta_o$ . In both compounds cobalt has a +3 oxidation state and a  $3d^6$  valence shell electron configuration. If  $\Delta_o$  is greater than the energy for pairing electrons, then the three lower energy orbitals fill before the higher energy orbitals, giving the energy diagram on the left; as all electrons are paired, the compound is diamagnetic. If  $\Delta_o$  is smaller than the energy for pairing electrons, then each orbital accepts an electron before a second electron enters any orbital, giving the energy diagram on the right; as there are unpaired electrons, the compound is paramagnetic.



Of the two complexes,  $[\text{CoF}_6]^{3-}$  is green and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is yellow-orange. Identify the complex that is paramagnetic (circle your choice) and, in 2–4 sentences, explain your reasoning.



The paramagnetic compound is the one with the smaller value for  $\Delta_o$ , which we can determine by examining the color of the compounds. The compound  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is yellow-orange, which means it absorbs light with a wavelength of 430 nm; the compound  $[\text{CoF}_6]^{3-}$  is green, which means it absorbs light with a wavelength between 630–700 nm. The longer the wavelength, the smaller the energy ( $E = hc/\lambda$ ), which means that  $\Delta_o$  is smaller for  $[\text{Co}(\text{F})_6]^{3-}$ , making it the paramagnetic compound.

**Problem 7.** There are two isomers of the compound having an empirical formula of  $\text{Co}(\text{NH}_3)_5\text{SO}_4\text{Br}$ . When dissolved in water, one isomer forms a white precipitate upon adding  $\text{BaCl}_2$  or  $\text{AgNO}_3$ ; the other isomer forms a white precipitate upon adding  $\text{AgNO}_3$ , but does not form a precipitate with  $\text{BaCl}_2$ . In 2–4 sentences, provide an explanation for these observations. As part of your answer, provide the structural formulas for each compound.

In a coordination compound it is the “free” anions—those not present as ligands—that can form a precipitate with  $\text{BaCl}_2$  or  $\text{AgNO}_3$ . We know that sulfate ion,  $\text{SO}_4^{2-}$ , forms a precipitate with both  $\text{Ag}^+$  and  $\text{Ba}^{2+}$ , and we know that bromide ion,  $\text{Br}^-$ , forms a precipitate with  $\text{Ag}^+$  but not with  $\text{Ba}^{2+}$ . Only anions can precipitate with  $\text{Ba}^{2+}$  or with  $\text{Ag}^+$ ; thus, in one isomer  $\text{SO}_4^{2-}$  is present as an anion and  $\text{Br}^-$  is present as a ligand, and in the other isomer,  $\text{SO}_4^{2-}$  is bound to cobalt as a ligand and  $\text{Br}^-$  is present as an anion. The two isomers are  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .

**Problem 8.** Consider the hypothetical metal-ligand complex  $MABC_3D$ , where M is a metal ion and A, B, C, and D are ligands. Draw all possible geometric isomers for this octahedral metal-ligand complex. Do not consider optical isomers. Be careful to draw only once each unique geometric isomer. There are more spaces than unique geometric isomers!

The three Cs have two possible arrangements: meridional and facial. For the meridional structure, we can place one of A, B, or D in the same plane as the three Cs (or, if you wish, you can see this as placing one of AB, AD, or BD *trans* to each other); thus, there are three possible meridional isomers. For the facial structure, there is just one possible isomer as A, B, and D are all *cis* to each other and all *trans* to one C and *cis* to the other two Cs; all other facial isomers that we might draw are either the same structure rotated, or an optical isomer. Together, there are four unique geometric isomers.

		
		