

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 ____/12

Question 5 ____/12

Question 2 ____/16

Question 6 ____/12

Question 3 ____/12

Question 7 ____/8

Question 4 ____/12

Question 8 ____/16

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. Suppose you have a mixture that might contain any of the following cations as nitrate salts: Co^{2+} , Pb^{2+} , Ba^{2+} , K^{+} , and NH_4^{+} . To identify which cations are present, you run through the three tests described below.

- (a) Placing a 1-mL portion of your mixture in a test tube, you add 10 drops of NaCl and observe that no precipitate forms.
- (b) You add 10 drops of Na_2SO_4 to the contents of the test tube from (a) and observe that a precipitate forms.
- (c) After centrifuging the contents of the test tube from (b), you transfer the supernatant to a clean test tube, add 10 drops of NaOH to the supernatant, and observe that a precipitate forms.

Based on these three tests, identify which of the five cations **must** be present in your mixture, which of the five cations **cannot** be present in your mixture, and for which of the five cations you **have insufficient** information to determine its presence or absence.

From (a), we know that Pb^{2+} forms a precipitate with Cl^{-} ; thus, the absence of a precipitate tells us that **Pb^{2+} cannot be present in the mixture**. From (b), we know that Pb^{2+} and Ba^{2+} will precipitate with SO_4^{2-} ; we know from (a) that Pb^{2+} is absent, so the precipitate here means that **Ba^{2+} must be in the mixture**. Finally, from (c) we know that Co^{2+} and Pb^{2+} will precipitate with OH^{-} ; we know from (a) that Pb^{2+} is absent, so the precipitate here means that **Co^{2+} must be in the mixture**. We have **insufficient information to determine if K^{+} and NH_4^{+} are present in the mixture** because they do not form precipitates with Cl^{-} , SO_4^{2-} , or OH^{-} .

Problem 2. For each of the following pairs of compounds or ions, circle the one that is the stronger acid and explain the reason for your choice in 1-2 sentences each.

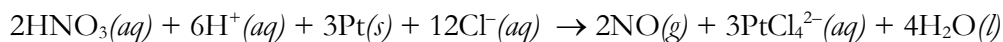
H_2Se or **H_2Te** : For this pair, the important factor is the $X\text{--H}$ bond length, where X is Se or Te. Longer bonds are weaker and thus easier to break. Because Te has a greater radius than Se, the Te--H bond is longer and weaker, making H_2Te the stronger acid.

H_3PO_4 or H_3AsO_4 : For this pair, the important factor is the EN of the central atom, which is P and As. The more electronegative the central atom, the more it pulls electron density toward it, weakening the O--H bonds and increasing the acid's strength. Phosphorous is more EN than arsenic, so H_3PO_4 is the stronger acid.

HBrO_4 or HBrO_3 : For this pair, the important factor is the oxidation state of the central atom, which is Br. For HBrO_4 , bromine has an oxidation state of +7 and for HBrO_3 it has an oxidation state of +5. The more positive the oxidation state, the more the central atom pulls electron density toward it, weakening the O--H bonds and increasing the acid's strength; thus HBrO_4 is the stronger acid.

CH_4 or **NH_4^{+}** : For this pair, the important factor is the charge on the species as it is easier to remove a H^{+} from a species that carries a positive charge; thus NH_4^{+} is the stronger acid.

Problem 3. Platinum, Pt, is valuable because it is rare and because it is very unreactive and, therefore, very stable. In 800 A.D. the Islamic alchemist Jabir Ibn Hayyan discovered that although Pt will not dissolve in HCl or in HNO₃, it does dissolve in a mixture of the two acids as shown by the following oxidation-reduction reaction



In the space below, identify all elements that change oxidation states and report their specific changes in oxidation state. What reactant is the oxidizing agent?

The elements that change oxidation states are platinum, which has an oxidation state of 0 as the reactant Pt(s) and an oxidation state of +2 as the product PtCl₄²⁻(aq), and nitrogen, which has an oxidation state of +5 as the reactant HNO₃(aq) and an oxidation state of +2 as the product NO(g). All other elements maintain their oxidation states. The oxidizing agent is the reactant that has the element that, itself, undergoes reduction, which makes HNO₃ the oxidizing agent.

Problem 4. Quite a few years ago there was a local discharge of potassium permanganate, KMnO₄, a hazardous material that must be neutralized. Dave Roberts, storeroom manager and hazardous waste expert, treated the spill using sodium bisulfate, NaHSO₃. Knowing that K_a for HMnO₄ is 0.5 and that K_a for HSO₃⁻ is 6.4 × 10⁻⁸, and using the handout on redox reactivity, which of the following reactions (unbalanced) was responsible for cleaning up the spill? Circle the correct reaction and explain the reason for your choice in 2-3 sentences.



The chart of oxidizing and reducing strengths shows that the redox reaction is possible as a stronger oxidizing agent reacts with a stronger reducing agent to produce a weaker oxidizing agent and a weaker reducing agent. A complete answer would also show that the acid–base reaction is not possible. To show this, we note that the K_a for HSO₃⁻ is smaller than the K_a for HMnO₄, which means that the proposed acid–base reaction converts a weaker acid to a stronger acid, which is not possible as acid–base reactions always turn stronger acids and stronger bases into weaker acids and weaker bases.

Problem 5. The drug Nipride, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, is a coordination compound used to reduce blood pressure during surgery. The compound's anion is a metal-ligand complex where the ligands are the cyanide anion, CN^- , and the nitrosyl cation, NO^+ . Using the iron in Nipride as an example, explain the difference between a metal's **ordinary (or primary) valency** and its **coordination (or secondary) valency**, limiting your response to 3-5 sentences. Be sure your reply includes the specific values for iron's ordinary valency and coordination valency.

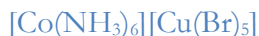
A metal's ordinary valency is the same as its oxidation state. To determine iron's ordinary valency we note that the metal-ligand complex must have a charge of -2 to balance the two Na^+ ions. The five cyanide ligands have a total charge of -5 and the single nitrosyl ligand has a charge of $+1$, for a total charge of $+4$; this leaves iron with a charge and oxidation state of $+2$.

A metal's coordination valency is the number of bonds it forms with ligands, which in this case is six, one for each of the cyanide ligands and one for the nitrosyl ligand.

Problem 6. As we saw during class, there are two coordination compounds with an empirical formula of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ because the nitrite anion, NO_2^- , can bind to cobalt through either its nitrogen or through one of its oxygens. The nitro complex is yellow in color and the nitrito complex is reddish-orange in color. In 3-4 sentences explain why the two compounds have different colors.

In an octahedral metal-ligand complex, the d -orbitals split into two groups, three at a lower energy and two at a higher energy with the difference in the energy identified as Δ_{oct} . As long as the two upper d -orbitals are not filled—which is true for Co(III) as it has just six valence electrons and it takes 10 electrons to completely fill the five d orbitals—then the compound can absorb visible light and move an electron from the lower set of orbitals to the upper set of orbitals. The magnitude of Δ_{oct} depends on the ligand, which explains why it is possible for the two complexes to have different colors. In this case, the yellow nitro complex absorbs light with a wavelength of approximately 415 nm and the red-orange nitrito complex absorbs light with a wavelength of approximately 490 nm; thus Δ_{oct} is greater for the nitro complex.

Problem 7. Provide the chemical formula for the coordination compound hexaminecobalt(III) pentabromocuprate(II).

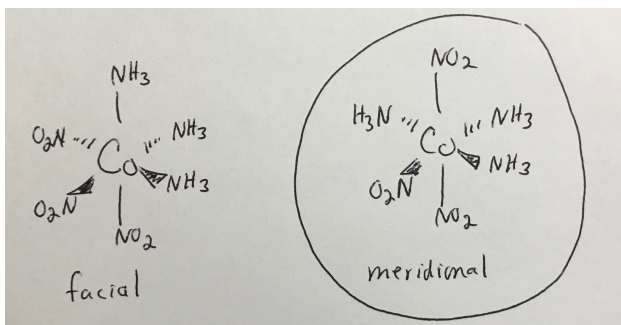


Provide the name for the coordination compound $(\text{NH}_4)_4[\text{Fe}(\text{ox})_3]$ where **ox** is a shorthand notation for the oxalate anion, $\text{C}_2\text{O}_4^{2-}$.

ammonium trioxalatoferrate(II)

Problem 8. Draw all possible geometric isomers of the metal-ligand complex, $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$, in which the nitrite ligands, NO_2^- , bind through their nitrogen only. Be careful to draw each possible geometric isomer just once.

As shown below, there are just two possible geometric isomers for $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$, one in which the three NH_3 ligands and the three NO_2^- ligands each show a facial arrangement and one in which they each show a meridional arrangement.



The reaction of $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ with HCl yields the coordination compound $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$ in which the two chlorides in the cation's metal-ligand complex are **trans** to each other. Assuming the NH_3 groups remain in place when $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ reacts with HCl , which of the geometric isomers for $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ that you drew above must react to form $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$? Circle your choice and explain the reason for your choice in 1-3 sentences.

The correct choice is the meridional arrangement circled above as this is the only structure in which the two chlorides in the cation's metal-ligand can be trans to each other. In a facial arrangement of three ligands, each ligand is at 90° from the other two ligands and, therefore, only a cis arrangement of the two chlorides would be possible; see the images below.

