CCO Problem Set #3. Inorganic and Coordination Chemistry. **Date: Dec 1, 2024**

Questions 1-3 should be solved together.

The bright blue mineral **A** is often found in the weathering zone of sulfide deposits, along with other secondary minerals. It has been used since ancient times as a blue mineral dye. When this mineral is ground into powder and heated above 300°C, it acquires a black color characteristic for **B**, losing 30.76% in mass. The gases released under these conditions had a density relative to hydrogen of 17.66. When cooled to room temperature, the gas density relative to hydrogen was measured to be 22, and the volume decreased approximately three times. If the resulting black powder **B** is heated in a stream of hydrogen, it acquires a pink-red color and loses 20.11% in mass forming **C**.

Both the original mineral **A** and the products of its decomposition **B** and **C** dissolve in sulfuric acid, but **C** dissolves only in concentrated sulfuric acid when heated above 200°C. The amounts of sulfuric acid required to dissolve equimolar quantities of **A** and **B** are equal and half of that amount is needed to dissolve **C**.

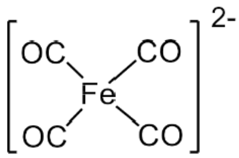
1. Write the chemical formula of the mineral **A**.

2. Write the chemical symbol of **B**.

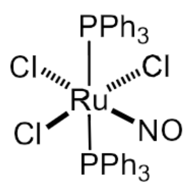
3. Write the chemical formula of **C**.

4. Calculate the crystal field stabilization energy for $[Co(H_2O)_6]^{2+}$. Δ_o = 13000 cm^{-1} and spin pairing energy is equal to 19000 cm^{-1}.

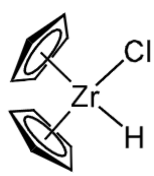
a. 4400 cm^{-1}
b. 10400 cm^{-1}
c. 14400 cm^{-1}
d. 23400 cm^{-1}
e. 29400 cm^{-1}



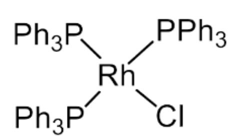
I



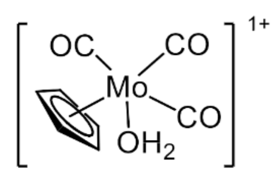
II



III



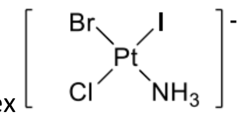
IV



V

5. Which of the above complexes do **not** follow the 18-electron rule?

a. **II** and **III**
b. only **IV**
c. **II**, **III**, and **IV**
d. **I** and **V**
e. **III**, **IV**, and **V**

6. Choose reactants suitable for the preparation of the complex 

. Note that generally Pt-N bonds are stronger than Pt-Hal, and consider the influence of the trans effect.

a. $K_2[PtCl_4]$ + *excess* KBr; then NH_3; then KI; then KCl
b. $K_2[PtCl_4]$ + KI; then KCl; then KBr; then NH_3
c. $K_2[PtCl_4]$ + NH_3; then *excess* KBr; then KI
d. $[Pt(NH_3)_4](ClO_4)_2$ + *excess* KI; then KBr; then KCl; then NH_3
e. $[Pt(NH_3)_4](ClO_4)_2$ + KCl; then KBr; then KI

Questions 7-8 should be solved together.

Two jars with worn labels were found on a shelf in the laboratory. Both jars contained black powders. When one of them was dissolved in concentrated hydrochloric acid, a yellow-green solution of coordination complex **A** was formed, which turned blue when diluted with water. When the other powder interacted with concentrated hydrochloric acid, a blue solution was formed, which turned pink when diluted with water due to the formation of coordination complex **B**.

7. Write the chemical formula of the complex **A**.

8. Write the chemical formula of the complex **B**.

Questions 9-12 should be solved together.

Chemists found three coins made of individual metals. The color of coin **X** was silvery, **Y** was light orange, and **Z** was black. The coins were dissolved in concentrated HNO_3 upon heating. As a result, solutions of different colors were obtained: **X1** - light green, **Y1** - blue, **Z1** - colorless. The solutions were diluted and divided into two parts.

A solution of NaOH was added to one part and three precipitates were obtained: **X2** - light green, **Y2** - blue, **Z2** - brown, all of which dissolved in a concentrated solution of NH_3. The following solutions were obtained after the treatment with ammonia: **X3** - violet, **Y3** - dark blue, **Z3** - colorless.

A solution of Na_2S was added to the other part and black precipitates fell out (**X4**, **Y4**, **Z4**).

Having done all these experiments, the chemists guessed the possible composition of the coins and carried out several more experiments to confirm it. When **X1** interacts with Br_2 in an alkaline medium, a black precipitate **X5** is formed. When a concentrated HCl solution is added to this precipitate, a yellow-green gas **A** is released.

When **Y1** interacts with a potassium iodide solution, a brown precipitate (**B**+**Y5**) is formed; and the subsequent addition of an excess of $Na_2S_2O_3$ turns the precipitate white.

When **Z1** interacts with $K_2S_2O_8$ in an alkaline medium, a black precipitate **Z5** is formed. Upon addition of a solution of $MnSO_4$ acidified with sulfuric acid to this precipitate, the solution acquires a light pink color characteristic of **C**.

9. Write the chemical symbol of the element **X**.

10. Write the chemical symbol of the element **Z**.

11. Write the chemical formula of **Y5**.

12. Write the chemical formula of **Z5**.

Questions 13-14 should be solved together.

Compounds **A**-**C** of a certain element contain 13.25% nitrogen and 33.55% chlorine. The pink-red compound **A** has low solubility at room temperature and turns into even less soluble yellow compound **B** when the solution is heated. The yellow compound **C** has slightly higher solubility in water (compared to **B**). The maximum molar conductivity of aqueous solutions of **A** is ≈ 110 $ohm^{-1}\cdot mol^{-1}\cdot cm^2$ for freshly prepared solutions but increases several times over a few minutes. For **B** and **C**, the initial value of conductivity is significantly lower, but increases by several orders of magnitude over 10-15 minutes.

13. Write the chemical formula of **A**.

14. Write the chemical formula of **B**.

15. Carbon monoxide was introduced into a 20.2-liter nickel vessel, the pressure of which at a temperature of 30 °C was equal to 2.0 bar. The vessel was heated to 105°C and then maintained at a constant temperature. The pressure began to fall and eventually dropped to 1.0 bar. The resulting gas mixture was transferred to another reactor, where it was heated to 250 °C. How many grams of ultrapure nickel were obtained?

a. 8.8 g
b. 12.3 g
c. 13.9 g
d. 15.7 g
e. 18.9 g

Questions 16-18 should be solved together.

Brown compound **A** of variable composition exists only in a nanosized state (particle diameter <10 nm), and is also necessarily present in living organisms in the form of protein complexes that ensure the storage and intercellular transport of the vital element **X**.

Substance **A** can be obtained in the laboratory by the action of excess aqueous ammonia on a solution of salt **B**. Freshly prepared substance **A** easily dissolves in sulfuric acid to form salt **B**. The interaction of **B** with SO_2 yields a water-soluble salt **C**, isolated from aqueous solutions in the form of a hydrate (mass fraction of **X**: 20.1%, mass fraction of water: 45.3%). In addition, aqueous solutions of **B** convert iodide and sulfide anions into free iodine and sulfur. Upon addition of a saturated solution of potassium sulfate to concentrated solutions of salt **B,** light-violet crystals of mixed sulfate **D** can be isolated in hydrate form (mass fraction of **X**: 11.1%, mass fraction of water: 42.9%).

Substance **A** in a concentrated alkali solution can be oxidized with chlorine to form a red-violet solution of compound **E**, which can be precipitated with barium hydroxide in the form of compound **F**. When 1.37 g of **F** is treated with excess hydrochloric acid, 179 mL of a suffocating yellow-green gas with a density of 3.17 g/L (at STP) is released.

16. Write the chemical formula of hydrate **C**.

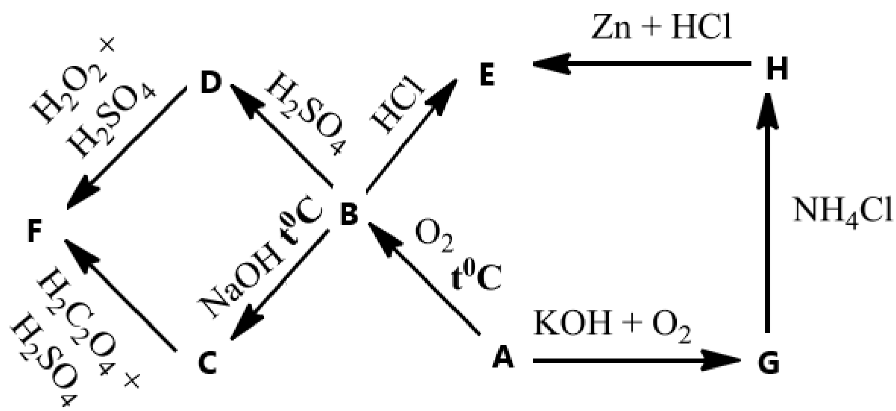
17. Write the chemical formula of hydrate **D**.

18. Write the chemical formula of **F**.

Questions 19-23 should be solved together.

Metal **A**, silver-gray in color, is a component of many highly durable alloys. Its most stable oxidation state is +5. The molar volume of metal **A** is 8.33×10^{-6} m^3/mol, and the density of the metal is 6.1 g/cm^3. When metal **A** is heated at temperatures above 500°C, red-colored substance **B** is formed, which is partially soluble in water.

Reactions of metal **A** are shown on the scheme. Additionally, it is known that ω_A=38.9 and ω_O=48.9 for **D,** ω_A=36.9 and ω_O=11.6 for **E,** ω_A=31.2 and ω_O=49.1 for **F**. **C**, **H** and **G** are white, whereas **E** and **F** are light-blue.



19. Write the chemical symbol of **A**.

20. Write the chemical formula of **D**.

21. Write the chemical formula of **E**.

22. Write the chemical formula of **F**.

23. Write the chemical formula of **H**.

Questions 24-28 should be solved together.

Complex mononuclear compound **A** can be obtained by the following procedure. Dark red oxide **B** is dissolved in water and an excess of 25% ammonia solution is added to the solution. Upon cooling, an excess of 30% hydrogen peroxide solution is added to the resulting mixture, then the reaction mixture is stirred at room temperature. After the release of oxygen is complete, the main reaction product, orange compound **C** is filtered off. Upon cooling the filtrate, brown crystals of the target product **A** precipitate.

Compound **A** consists of four elements and contains 30.54% ammonia and 38.32% oxygen by mass. It dissolves in water with decomposition and detonates with a flash when slightly heated. Upon decomposition of **A**, a dark green powder **D** and a mixture of three gaseous products are formed. By cooling this mixture to room temperature, a solution of one component in another can be prepared. This solution colors the litmus paper blue.

Compound **C** also decomposes violently on heating, yielding **D** and two gaseous products. This reaction is used in a well-known demonstration experiment.

It was experimentally shown that **A** has paramagnetic properties, and the central ion has two unpaired electrons. When exposed to hydrochloric acid, complex **A** releases oxygen and, depending on the conditions, can yield either compound **E** (24.82% metal by mass) or compound **F** (22.86% metal by mass). In these reactions, the central ion goes into its most stable oxidation state. An aqueous solution of **F** conducts electric current well, whereas a solution of **E** practically does not conduct it.

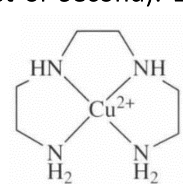
24. Write the chemical formula of **C**.

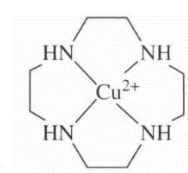
25. Write the chemical formula of complex **A**.

26. What is the oxidation state of the central ion in **A**? Write a sign and number, e.g. -2, +7, 0, etc.

27. Write the chemical formula of **E**.

28. How many geometric isomers does **F** have?

29. For each pair, choose the most stable complex (***f***irst or ***s***econd): 1) $[HgCl_4]^{2-}$ or $[HgI_4]^{2-}$; 2) $[Ni(NH_3)_6]^{2+}$ or $[Ni(en)_3]^{2+}$ (en = $NH_2CH_2CH_2NH_2$); 3)


or


; 4) $[Cr(SCN)_6]^{3-}$ or $[Cr(OH)_6]^{3-}$.
Your answer should look like a string of letters, e.g. fssf (first-second-second-first) or ffff (first in each case).

30. How many isomers does $[Ni(SCN)(en)Cl_3]^{2-}$ (en = $NH_2CH_2CH_2NH_2$) have?