Exercises

Stoichiometry

1. A student was given 1.00 g of ammonium dichromate for the preparation of a coordination compound. The sample was ignited, thereby producing chromium(III) oxide, water, and nitrogen gas. The chromium(III) oxide was allowed to react at 600°C with carbon tetrachloride to yield chromium(III) chloride and phosgene (COCl₂). Upon treatment with excess liquid ammonia, the chromium(III) chloride reacted to produce hexaamminechromium(III) chloride. Calculate the maximum amount of hexaamminechromium(III) chloride that the student could prepare from the 1.00-g sample of ammonium dichromate.

2. When silver nitrate is added to a solution of a substance with the empirical formula CoCl₃ · 5NH₃, how many moles of AgCl will be precipitated per mole of cobalt present? Why?

3. Co(III) occurs in octahedral complexes with the general empirical formula CoClₘ · nNH₃. What values of n and m are possible? What are the values of n and m for the complex that precipitates 1 mole of AgCl for every mole of Co present?

4. How many ions per mole will you expect to find in solution when a compound with the empirical formula PtCl₄⁻ · 3NH₃ is dissolved in water? What about PtCl₂ · 3NH₃? Draw diagrams of each of the complex cations.

5. Each of the following is dissolved in water to make a 0.001 M solution. Rank the compounds in order of decreasing conductivity of their solutions; K₂PtCl₆, Co(NH₃)₆Cl₃, Cr(NH₃)₄Cl₃, Pt(NH₃)₆Cl₄. Rewrite each compound by using brackets to distinguish the complex ion present in aqueous solution.

Formulas and nomenclature

6. Give the systematic names of [Co(NH₃)₄Cl₂]Br, K₃Cr(CN)₅, and Na₂CoCl₄.

7. Write the formulas for each of the following compounds by using brackets to distinguish the complex ion from the other ions: (}
   1. hexaaquonickel(II) perchlorate
   2. trichlorotriammineplatinum(IV) bromide
   3. dichlorotetraammineplatinum(IV) sulfate
   4. potassium monochloropentacyanoferrate (III)
8. Write the formula for each of the following by using brackets to distinguish the complex ion:

1. hydroxopentaaquoaluminum(III) chloride
2. sodium tricarbonatocobaltate(III)
3. sodium hexacyanoferrate(II)
4. ammonium hexanitrocobaltate(III)

**Isomers**

9. How many isomers are there of the compound \([\text{Cr(NH}_3\text{)}_4\text{Cl}_2\text{]}\text{Cl}\)? Sketch them.

10. Sketch all the geometrical and optical isomers of \(\text{PtCl}_2\text{[NH}_3\text{]}_2\).

11. How many geometrical and optical isomers are there of the complex ion \(\text{Co(en)}_2\text{Cl}_4\)? Of these, how many pairs of isomers are there differing only by a mirror reflection? How many isomers have a plane of symmetry and hence do not exist in pairs of optical isomers?

12. Repeat Problem 11 with propylenediamine substituted for ethylenediamine. Ignore optical isomers from the propylene carbon.

13. How many different structural isomers are there of a substance with the empirical formula \(\text{FeBrCl} \cdot 3\text{NH}_3 \cdot 2\text{H}_2\text{O}\)? For each different structural isomer, how many different geometrical isomers exist? How many of these can be grouped into right-handed and left-handed pairs of optical isomers?

**Electronic structure**

14. The \(\text{Co}^{2+}\) ion in aqueous solution is octahedrally coordinated and paramagnetic, with three unpaired electrons. Which one or ones of the following statements follow from this observation:

1. \(\text{Co(H}_2\text{O})_4^{2+}\) is square planar
2. \(\text{Co(H}_2\text{O})_4^{2+}\) is tetrahedral
3. \(\text{Co(H}_2\text{O})_4^{2+}\) has a \(\Delta_0\) that is larger than the electron—pairing energy;
4. the \(d\) levels are split in energy and filled as follows: \((t_{2g})^5(e_g)^2\)
5. the \(d\) levels are split in energy and filled as follows: \((t_{2g})^6(e_g)^1\)

15. The coordination compound potassium hexafluorochromate(III) is paramagnetic. What is the formula for this compound? What is the configuration of the \(\text{Cr}\) \(d\) electrons?

16. How many unpaired electrons are there in \(\text{Cr}^{3+}, \text{Cr}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{3+}, \text{Co}^{2+}\) in

1. a strong octahedral ligand Held and
2. a very weak octahedral field?
17. A low-spin tetrahedral complex has never been reported, although numerous high-spin complexes of this geometry have been prepared. What conclusion may be drawn regarding the magnitude of $\Delta_t$ from this fact?

18. Certain platinum complexes have been found to be active antitumor agents. Among these are cis-Pt(NH$_3$)$_2$Cl$_4$, cis-Pt(NH$_3$)$_2$Cl$_2$, and cis-Pt(en)Cl$_2$ (none of the trans isomers are effective). Use valence bond theory to account for the diamagnetism of these complexes. Are these inner or outer complexes? What kinds of hybrid orbitals are used in bonding?

19. What is the $d$-orbital electronic configuration of Cr(NH$_3$)$_6^{3+}$? How many unpaired electrons are present? If six Br$^-$ groups were substituted for the six NH$_3$ groups to give CrBr$_6^{3-}$, would you expect $\Delta_0$ to increase or decrease?

20. Diagram the electronic arrangements in Fe(H$_2$O)$_6^{2+}$ and Fe(CN)$_6^{4-}$ for both the valence bond and crystal field models. Briefly compare these models.

21. For each of the following, sketch the $d$-orbital energy levels and the distribution of $d$ electrons among them:

   1. Ni(CN)$_4^{2-}$ (square planar)
   2. Ti(H$_2$O)$_6^{2+}$ (octahedral)
   3. NiCl$_4^{2-}$ (tetrahedral)
   4. CoF$_6^{3-}$ (high-spin complex)
   5. Co(NH$_3$)$_6^{3+}$ (low—spin complex)

22. Co(III) can occur in the complex ion Co(NH$_3$)$_6^{3+}$.

   1. What is the geometry of this ion? In the valence bond theory, what Co orbitals are used in making bonds to the ligands?
   2. What is the systematic name for the chloride salt of this ion?
   3. Using crystal Field theory, draw two possible $d$—electron configurations for this ion. Assign to them the labels *high spin, low spin, paramagnetic, diamagnetic*. Which two labels are correct for the ammine complex?
   4. Co(NH$_3$)$_6^{3+}$ can be reduced to Co(NH$_3$)$_6^{2+}$ by adding an electron. Draw the preferred $d$-electron configuration for this reduced ion. Why is it preferred?

23. Pt(II) can occur in the complex ion PtCl$_4^{2-}$.

   1. What is the geometry of this ion? In the valence bond theory, what Pt orbitals are used in making bonds to the Cl$^-$ ions?
   2. What is the systematic name for the sodium salt of this ion?
   3. Using crystal field theory, draw the $d$-electron configuration for this ion. Is the ion paramagnetic or diamagnetic?
   4. Pt(II) can be oxidized to Pt(IV). Draw the $d$-electron configuration for the chloride complex ion of Pt(IV). Explain the difference between this configuration and that of Pt(II). Is the Pt(IV) chloride complex ion paramagnetic or diamagnetic?
Formation constants

24. A solution is prepared that is 0.025M in tetraamminecopper(III), Cu(NH$_3$)$_4^{4+}$. What will be the concentration of Cu$^{2+}$ hydrated copper ion if the ammonia concentration is 0.10, 0.50, 1.00, and 3.00 M respectively? What ammonia concentration is needed to keep the Cu$^{2+}$ concentration less than $10^{-15}$ M?

25. From the data in Table 20-8, calculate the pH of a 0.10M solution of Cr$^{3+}$ ion. Hint: Consider the reactions

\[
\text{Cr}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Cr(OH)}^{2+} + \text{H}^+ \quad \text{K} = \ ?
\]

\[
\text{Cr}^{3+} + \text{OH}^- \leftrightarrow \text{Cr(OH)}^{2+} \quad \text{K}_f = 1 \times 10^{10}
\]

\[
\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} \quad \text{K}_w = \ ?
\]

26. From the data in Table 20-8, calculate the pH of 0.10M solutions of Mn$^{2+}$, Fe$^{2+}$, and Ag$^+$. See Problem 25 if you need help. From the results of these two problems, can you correlate the “acidity” of positive ions with their charge?

27. The ion Co(NH$_3$)$_6^{3+}$ is very stable, with $K_f = 2.3 \times 10^{34}$. If the hydrolysis constant for the ammonium ion, $K_b$, is $5 \times 10^{-10}$, show that the equilibrium in the reaction

\[
\text{Co(NH}_3\text{)}_{6}^{3+} + 6\text{H}^+ \leftrightarrow \text{Co}^{3+} + 6\text{NH}_4^+
\]

lies far to the right. Then why does Co(NH$_3$)$_6^{3+}$ remain intact in hot concentrated sulfuric acid?

28. What is the concentration of chromate ion, CrO$_4^{2-}$ when solid BaCrO$_4$ is placed in contact with water? What is the chromate ion concentration when solid BaCrO$_4$ is placed in contact with a solution of 0.2M Ba$^{2+}$? BaCrO$_4$ can be dissolved in a solution of pyridine (py), producing the complex Ba(py)$_2^{2+}$, with a formation constant of $4 \times 10^{-12}$. If 0.10M BaCrO$_4$ is dissolved in a solution with a constant pyridine concentration of 1.0 mole liter$^{-1}$, what is the concentration of Ba$^{2+}$ ion?

29. What is the solubility of Cu(OH)$_2$ in pure water? In buffer at pH 6? Copper(II) forms a complex with NH$_3$, Cu(NH$_3$)$_4^{2+}$, with $K_f = 1.0 \times 10^{12}$. What concentration of ammonia must be maintained in a solution to dissolve 0.10 mole of Cu(OH)$_2$ per liter of solution?

30. Calculate the silver ion concentration in a saturated solution of AgCl in water. Silver ions react with an excess of Cl$^-$ as follows:

\[
\text{Ag}^+ + 2\text{Cl}^- \leftrightarrow \text{AgCl}_2 \quad \text{K}_f : 1 \times 10^{2}
\]

Calculate the concentration of AgCl; and show that you were justified in ignoring the complex ion formation in calculating the silver ion concentration at the beginning of the problem.

31. The formation constant for the pyridine complex of silver
Ag$^+ + 2\text{py} \leftrightarrow 2\text{Ag(py)}^+$

is $K_f : 1 \times 10^{10}$. If a solution is initially 0.10M in AgNO$_3$ and 1.0M in pyridine, what are the equilibrium concentrations of silver ion, pyridine, and the complex ion?

32. In 0.10M NaCl, the concentration of silver ions cannot exceed $10^{-9}$ mole liter$^{-1}$ because AgCl is so slightly soluble. What concentration of pyridine must be added to dissolve 0.10 mole of AgCl per liter of solution?