CHAPTER 19

TRANSITION METALS AND COORDINATION CHEMISTRY

Transition Metals

6. Transition metal ions lose the s electrons before the d electrons.

a.	Ti: $[Ar]4s^23d^2$	b.	Re: $[Xe]6s^24f^{14}5d^5$	c.	Ir: $[Xe]6s^24f^{14}5d^7$
	$Ti^{2+}: [Ar]3d^2$		Re^{2+} : [Xe]4f ¹⁴ 5d ⁵		Ir^{2+} : [Xe]4f ¹⁴ 5d ⁷
	Ti ⁴⁺ : [Ar] or [Ne]3s ² 3p ⁶		Re^{3+} : [Xe]4f ¹⁴ 5d ⁴		$Ir^{3+}: [Xe]4f^{14}5d^{6}$

7. Cr and Cu are exceptions to the normal filling order of electrons.

a.	Cr: $[Ar]4s^{1}3d^{5}$	b.	Cu: $[Ar]4s^{1}3d^{10}$	c.	V: $[Ar]4s^{2}3d^{3}$
	$Cr^{2+}: [Ar]3d^{4}$		Cu ⁺ : [Ar] $3d^{10}$		$V^{2+}: [Ar]3d^{3}$
	Cr^{3+} : [Ar]3d ³		Cu^{2+} : [Ar]3d ⁹		$V^{3+}: [Ar]3d^2$

8. Chromium ([Ar]4s⁰3d⁵) and copper ([Ar]4s¹3d¹⁰) have electron configurations that are different from that predicted from the periodic table. Other exceptions to the predicted filling order are transition metal ions. These all lose the s electrons before they lose the d electrons. In neutral atoms, the *n*s and (n - 1)d orbitals are very close in energy, with the *n*s orbitals slightly lower in energy. However, for transition metal ions, there is an apparent shifting of energies between the *n*s and (n - 1)d orbitals. For transition metal ions, the energy of the (n - 1)d orbitals are significantly less than that of the *n*s electrons. So when transition metal ions form, the highest-energy electrons are removed, which are the *n*s electrons. For example, Mn²⁺ has the electron configuration [Ar]4s⁰3d⁵ and not [Ar]4s²3d³.

Most transition metals have unfilled d orbitals, which creates a large number of other electrons that can be removed. Stable ions of the representative metals are determined by how many s and p valence electrons can be removed. In general, representative metals lose all of the s and p valence electrons to form their stable ions. Transition metals generally lose the s electron(s) to form +1 and +2 ions, but they can also lose some (or all) of the d electrons to form other oxidation states as well.

9. The lanthanide elements are located just before the 5d transition metals. The lanthanide contraction is the steady decrease in the atomic radii of the lanthanide elements when going from left to right across the periodic table. As a result of the lanthanide contraction, the sizes of the 4d and 5d elements are very similar (see the following exercise). This leads to a greater similarity in the chemistry of the 4d and 5d elements in a given vertical group.

- 10. Size also decreases going across a period. Sc and Ti, and Y and Zr are adjacent elements. There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller.
- 11. a. molybdenum(IV) sulfide; molybdenum(VI) oxide

b. MoS_2 , +4; MoO_3 , +6; $(NH_4)_2Mo_2O_7$, +6; $(NH_4)_6Mo_7O_{24}$ •4 H_2O , +6

12. a. 4 O atoms on faces $\times 1/2$ O/face = 2 O atoms, 2 O atoms inside body; total: 4 O atoms

8 Ti atoms on corners \times 1/8 Ti/corner + 1 Ti atom/body center = 2 Ti atoms

Formula of the unit cell is Ti_2O_4 . The empirical formula is TiO_2 .

 $+4 -1 \quad 0 \quad +4 -2 \quad 0$ TiCl₄ + O₂ \rightarrow TiO₂ + 2 Cl₂; O is reduced, and Cl is oxidized. O₂ is the oxidizing agent, and TiCl₄ is the reducing agent.

- 13. TiF₄: ionic compound containing Ti^{4+} ions and F^- ions. TiCl₄, TiBr₄, and TiI₄: covalent compounds containing discrete, tetrahedral TiX₄ molecules. As these covalent molecules get larger, the boiling points and melting points increase because the London dispersion forces increase. TiF₄ has the highest boiling point because the interparticle forces are stronger in ionic compounds than in covalent compounds.
- 14. Fe_2O_3 : iron has a +3 oxidation state; Fe_3O_4 : iron has a +8/3 oxidation state. The three iron ions in Fe_3O_4 must have a total charge of +8. The only combination that works is to have two Fe^{3+} ions and one Fe^{2+} ion per formula unit. This makes sense from the other formula for magnetite, $FeO\bullet$ Fe_2O_3 . FeO has an Fe^{2+} ion, and Fe_2O_3 has two Fe^{3+} ions.
- 15. $H^+ + OH^- \rightarrow H_2O$; sodium hydroxide (NaOH) will react with the H^+ on the product side of the reaction. This effectively removes H^+ from the equilibrium, which will shift the reaction to the right to produce more H^+ and CrO_4^{2-} . As more CrO_4^{2-} is produced, the solution turns yellow.
- 16. a. Coordination compound: a compound composed of a complex ion (see b) and counter ions (see c) sufficient to give no net charge.
 - b. Complex ion: a charged species consisting of a metal ion surrounded by ligands (see e).
 - c. Counter ions: anions or cations that balance the charge on a complex ion in a coordination compound.
 - d. Coordination number: the number of bonds formed between the metal ion and the ligands (see e) in a complex ion.

- e. Ligand: species that donates a pair of electrons to form a covalent bond to a metal ion. Ligands act as Lewis bases (electron pair donors).
- f. Chelate: ligand that can form more than one bond to a metal ion.
- g. Bidentate: ligand that forms two bonds to a metal ion.
- 17. Because transition metals form bonds to species that donate lone pairs of electrons, transition metals are Lewis acids (electron pair acceptors). The Lewis bases in coordination compounds are the ligands, all of which have an unshared pair of electrons to donate. The coordinate covalent bond between the ligand and the transition metal just indicates that both electrons in the bond originally came from one of the atoms in the bond. Here, the electrons in the bond come from the ligand.
- Linear geometry $(180^{\circ} \text{ bond angles})$ is observed when the coordination number is 2. 18. Tetrahedral geometry (109.5° bond angles) or square planar geometry (90° bond angles) is observed when the coordination number is 4. Octahedral geometry (90 $^{\circ}$ bond angles) is observed when the coordination number is 6.

For the following complex ions, see Table 19.13 if you don't know the formula, the charge, or the number of bonds the ligands form.

- a. $Ag(CN)_2^-$ b. $Cu(H_2O)_4^+$ c. $Mn(C_2O_4)_2^{2-}$ d. $Pt(NH_3)_4^{2+}$
- e. Fe(EDTA)⁻; *note*: EDTA has an overall 4- charge and is a six coordinate ligand.
- f. $Co(Cl)_6^{4-}$
- g. $Cr(en)_3^{3+}$, where $en = ethylenediane (NH_2CH_2CH_2NH_2)$
- $Fe_2O_3(s) + 6 H_2C_2O_4(aq) \rightarrow 2 Fe(C_2O_4)_3^{3-}(aq) + 3 H_2O(1) + 6 H^+(aq);$ the oxalate anion 19. forms a soluble complex ion with iron in rust (Fe₂O₃), which allows rust stains to be removed.
- 20. a. With NH_4^+ ions, CI^- ions, and neutral H_2O molecules present, iron has a +2 charge. Fe^{2+} : [Ar]3d⁶
 - b. With I^- ions and neutral NH₃ and NH₂CH₂CH₂NH₂ molecules present, cobalt has a +2 charge. Co^{2+} : [Ar]3d⁷
 - c. With Na⁺ and F⁻ ions present, tantalum has a +5 charge. Ta⁵⁺: [Xe]4 f^{14} (expected)
 - d. Each platinum complex ion must have an overall charge if the two complex ions are counter ions to each other. Knowing that platinum forms +2 and +4 charged ions, we can deduce that the six coordinate complex ion has a +4 charged platinum ion and the four coordinate complex ion has a +2 charged ion. With I⁻ ions and neutral NH₃ molecules present, the two complex ions are $[Pt(NH_3)_4I_2]^{2+}$ and $[PtI_4]^{2-}$.

 Pt^{2+} : [Xe]4f¹⁴5d⁸; Pt^{4+} : [Xe]4f¹⁴5d⁶

- 21. See Section 19.3 for a good summary of the nomenclature rules.
 - a. The correct name is tetraamminecopper(II) chloride. The complex ion is named incorrectly in several ways.
 - b. The correct name is bis(ethylenediamine)nickel(II) sulfate. The ethylenediamine ligands are neutral, and sulfate has a 2- charge. Therefore, Ni²⁺ is present, not Ni⁴⁺.
 - c. The correct name is potassium diaquatetrachlorochromate(III). Because the complex ion is an anion, the –ate suffix ending is added to the name of the metal. Also, the ligands were not in alphabetical order (a in aqua comes before c in chloro).
 - d. The correct name is sodium tetracyanooxalatocobaltate(II). The only error is that tetra should be omitted in front of sodium. That four sodium ions are needed to balance charge is deduced from the name of the complex ion.
- 22. a. hexaamminecobalt(II) chloride b. hexaaquacobalt(III) iodide
 - c. potassium tetrachloroplatinate(II) d. potassium hexachloroplatinate(II)
 - e. pentaamminechlorocobalt(III) chloride f. triamminetrinitrocobalt(III)
- 23. To determine the oxidation state of the metal, you must know the charges of the various common ligands (see Tables 19.13 and 19.14 of the text).

a.	pentaamminechlororuthenium(III) ion	b.	hexacyanoferrate(II) ion
c.	tris(ethylenediamine)manganese(II) ion	d.	pentaamminenitrocobalt(III) ion
a.	pentaaquabromochromium(III) bromide	b.	sodium hexacyanocobaltate(III)
c.	bis(ethylenediamine)dinitroiron(III) chloride	d.	tetraamminediiodoplatinum(IV) tetraiodoplatinate(II)
a.	$K_2[CoCl_4]$	b.	[Pt(H ₂ O)(CO) ₃]Br ₂
c.	$Na_3[Fe(CN)_2(C_2O_4)_2]$	d.	[Cr(NH ₃) ₃ Cl(NH ₂ CH ₂ CH ₂ NH ₂)]I ₂
a.	FeCl ₄ ⁻	b.	$[Ru(NH_3)_5H_2O]^{3+}$

c. $[Cr(CO)_4(OH)_2]^+$ d. $[Pt(NH_3)Cl_3]^-$

24.

25.

26.

27. BaCl₂ gives no precipitate, so SO_4^{2-} must be in the coordination sphere (BaSO₄ is insoluble). A precipitate with AgNO₃ means the Cl⁻ is not in the coordination sphere, that is, Cl⁻ is a counter ion. Because there are only four ammonia molecules in the coordination sphere, SO_4^{2-} must be acting as a bidentate ligand. The structure is:



28. CN^- is a weak base, so OH^- ions are present. When the acid H_2S is added, OH^- and CN^- ions are removed as H_2O and HCN. The hydrated Ni^{2+} complex ion forms after the OH^- and CN^- ions are removed by addition of H_2S . The two reactions are:

Ni²⁺(aq) + 2 OH⁻(aq) → Ni(OH)₂(s); the precipitate is Ni(OH)₂(s). Ni(OH)₂(s) + 4 CN⁻(aq) → Ni(CN)₄²⁻(aq) + 2 OH⁻(aq); Ni(CN)₄²⁻ is a soluble species. Ni(CN)₄²⁻(aq) + 4 H₂S(aq) + 6 H₂O(l) → Ni(H₂O)₆²⁺(aq) + 4 HCN(aq) + 4 HS⁻(aq)

- 29. Because each compound contains an octahedral complex ion, the formulas for the compounds are [Co(NH₃)₆]I₃, [Pt(NH₃)₄I₂]I₂, Na₂[PtI₆], and [Cr(NH₃)₄I₂]I. Note that in some cases the I⁻ ions are ligands bound to the transition metal ion as required for a coordination number of 6, whereas in other cases the I⁻ ions are counter ions required to balance the charge of the complex ion. The AgNO₃ solution will only precipitate the I⁻ counter ions and will not precipitate the I⁻ ligands. Therefore, 3 mol AgI will precipitate per mole of [Co(NH₃)₆]I₃, 2 mol AgI will precipitate per mole of [Pt(NH₃)₄I₂]I₂, 0 mol AgI will precipitate per mole of Na₂[PtI₆], and 1 mol AgI will precipitate per mole of [Cr(NH₃)₄I₂]I.
- 30. Test tube 1: Added Cl⁻ reacts with Ag⁺ to form a silver chloride precipitate. The net ionic equation is Ag⁺(aq) + Cl⁻(aq) \rightarrow AgCl(s). Test tube 2: Added NH₃ reacts with Ag⁺ ions to form a soluble complex ion Ag(NH₃)₂⁺. As this complex ion forms, Ag⁺ is removed from solution, which causes the AgCl(s) to dissolve. When enough NH₃ is added, all the silver chloride precipitate will dissolve. The equation is AgCl(s) + 2 NH₃(aq) \rightarrow Ag(NH₃)₂⁺(aq) + Cl⁻(aq). Test tube 3: Added H⁺ reacts with the weak base NH₃ to form NH₄⁺. As NH₃ is removed from the Ag(NH₃)₂⁺ complex ion, Ag⁺ ions are released to solution and can then react with Cl⁻ to reform AgCl(s). The equations are Ag(NH₃)₂⁺(aq) + 2 H⁺(aq) \rightarrow Ag⁺(aq) + 2 NH₄⁺(aq) and Ag⁺(aq) + Cl⁻(aq) \rightarrow AgCl(s).
- 31. a. Isomers: species with the same formulas but different properties; they are different compounds. See the text for examples of the following types of isomers.
 - b. Structural isomers: isomers that have one or more bonds that are different.
 - c. Steroisomers: isomers that contain the same bonds but differ in how the atoms are arranged in space.
 - d. Coordination isomers: structural isomers that differ in the atoms that make up the complex ion.

- e. Linkage isomers: structural isomers that differ in how one or more ligands are attached to the transition metal.
- f. Geometric isomers: (cis-trans isomerism); steroisomers that differ in the positions of atoms with respect to a rigid ring, bond, or each other.
- g. Optical isomers: steroisomers that are nonsuperimposable mirror images of each other; that is, they are different in the same way that our left and right hands are different.
- 32. a. 2; forms bonds through the lone pairs on the two oxygen atoms.
 - b. 3; forms bonds through the lone pairs on the three nitrogen atoms.
 - c. 4; forms bonds through the two nitrogen atoms and the two oxygen atoms.
 - d. 4; forms bonds through the four nitrogen atoms.
- 33.



Note: $C_2O_4^{2-}$ is a bidentate ligand. Bidentate ligands bond to the metal at two positions that are 90° apart from each other in octahedral complexes. Bidentate ligands do not bond to the metal at positions 180° apart from each other.



c.





trans

cis

d.



Note: ŃŇ

is an abbreviation for the bidentate en ligand (ethylenediamine, NH₂CH₂CH₂NH₂).

34. a.





c.



d.

b.





No; both the trans and the cis forms of $Co(NH_3)_4Cl_2^+$ have mirror images that are superimposable. For the cis form, the mirror image only needs a 90° rotation to produce the original structure. Hence neither the trans nor cis form is optically active.

36.



To form the trans isomer, Cl^- would replace the NH₃ ligand that is bold in the structure above. If any of the other four NH₃ molecules are replaced by Cl^- , the cis isomer results. Therefore, the expected ratio of the cis:trans isomer in the product is 4:1.

37.

M = transition metal ion H_2N



39. Linkage isomers differ in the way that the ligand bonds to the metal. SCN⁻ can bond through the sulfur or through the nitrogen atom. NO_2^- can bond through the nitrogen or through the oxygen atom. OCN^- can bond through the oxygen or through the nitrogen atom. N_3^- , $NH_2CH_2CH_2NH_2$ and I^- are not capable of linkage isomerism.

40.



41. Similar to the molecules discussed in Figures 19.16 and 19.17 of the text, Cr(acac)₃ and cis-Cr(acac)₂(H₂O)₂ are optically active. The mirror images of these two complexes are nonsuperimposable. There is a plane of symmetry in trans-Cr(acac)₂(H₂O)₂, so it is not optically active. A molecule with a plane of symmetry is never optically active because the mirror images are always superimposable. A plane of symmetry is a plane through a molecule where one side exactly reflects the other side of the molecule. 42. There are five geometric isomers (labeled i-v). Only isomer v, where the CN^- , Br^- , and H_2O ligands are cis to each other, is optically active. The nonsuperimposable mirror image is shown for isomer v.



Bonding, Color, and Magnetism in Coordination Compounds

- 43. a. Ligand that will give complex ions with the maximum number of unpaired electrons.
 - b. Ligand that will give complex ions with the minimum number of unpaired electrons.
 - c. Complex with a minimum number of unpaired electrons (low spin = strong field).
 - d. Complex with a maximum number of unpaired electrons (high spin = weak field).
- 44. Cu^{2+} : [Ar]3d⁹; Cu^+ : [Ar]3d¹⁰; Cu(II) is d⁹ and Cu(I) is d¹⁰. Color is a result of the electron transfer between split d orbitals. This cannot occur for the filled d orbitals in Cu(I). Cd^{2+} , like Cu^+ , is also d¹⁰. We would not expect $Cd(NH_3)_4Cl_2$ to be colored since the d orbitals are filled in this Cd^{2+} complex.
- 45. Sc^{3+} has no electrons in d orbitals. Ti^{3+} and V^{3+} have d electrons present. The color of transition metal complexes results from electron transfer between split d orbitals. If no d electrons are present, no electron transfer can occur, and the compounds are not colored.
- 46. All these complex ions contain Co^{3^+} bound to different ligands, so the difference in d-orbital splitting for each complex ion is due to the difference in ligands. The spectrochemical series indicates that CN^- is a stronger field ligand than NH_3 , which is a stronger field ligand than F^- . Therefore, $\text{Co}(\text{CN})_6{}^{3^-}$ will have the largest d-orbital splitting and will absorb the lowest-wavelength electromagnetic radiation ($\lambda = 290 \text{ nm}$) because energy and wavelength are inversely related ($\lambda = \text{hc/E}$). $\text{Co}(\text{NH}_3)_6{}^{3^+}$ will absorb 440-nm electromagnetic radiation, whereas $\text{CoF}_6{}^{3^-}$ will absorb the longest-wavelength electromagnetic radiation ($\lambda = 770 \text{ nm}$) because F^- is the weakest field ligand present.



48. NH₃ and H₂O are neutral ligands, so the oxidation states of the metals are Co³⁺ and Fe²⁺. Both have six d electrons ([Ar]3d⁶). To explain the magnetic properties, we must have a strong field for Co(NH₃)₆³⁺ and a weak field for Fe(H₂O)₆²⁺.



Only this splitting of d orbitals gives a diamagnetic $\text{Co(NH}_{3})_{6}^{3+}$ complex ion (no unpaired electrons) and a paramagnetic $\text{Fe}(\text{H}_{2}\text{O})_{6}^{2+}$ complex ion (unpaired electrons present).

49. To determine the crystal field diagrams, you need to determine the oxidation state of the transition metal, which can only be determined if you know the charges of the ligands (see Table 19.13). The electron configurations and the crystal field diagrams follow.

a.	Ru^{2+} : [Kr]4d ⁶ , no unpaired e ⁻	b. Ni ²⁺ : $[Ar]3d^8$, 2 unpaired e ⁻
		<u>↑</u> <u>↑</u>
	$\underbrace{\uparrow\downarrow} \underline{\uparrow\downarrow} \underline{\uparrow\downarrow}$	$\underbrace{\uparrow\downarrow} \underbrace{\uparrow\downarrow} \underbrace{\uparrow\downarrow}$
	Low spin, large Δ	
c.	V^{3+} : [Ar]3d ² , 2 unpaired e ⁻	



Note: Ni^{2+} must have two unpaired electrons, whether high spin or low spin, and V^{3+} must have two unpaired electrons, whether high spin or low spin.

All have octahedral Co^{3+} ions, so the difference in d-orbital splitting and the wavelength of 50. light absorbed only depends on the ligands. From the spectrochemical series, the order of the ligands from strongest to weakest field is $CN^- > en > H_2O > I^-$. The strongest-field ligand produces the greatest d-orbital splitting (largest Δ) and will absorb light having the smallest wave-length. The weakest-field ligand produces the smallest Δ and absorbs light having the longest wavelength. The order is:

> $\text{Co(CN)}_{6}^{3-} < \text{Co(en)}_{3}^{3+} < \text{Co(H}_{2}\text{O)}_{6}^{3+} < \text{CoI}_{6}^{3-}$ shortest λ longest λ absorbed absorbed

- 51. Replacement of water ligands by ammonia ligands resulted in shorter wavelengths of light being absorbed. Energy and wavelength are inversely related, so the presence of the NH₃ ligands resulted in a larger d-orbital splitting (larger Δ). Therefore, NH₃ is a stronger-field ligand than H₂O.
- 52. In both compounds, iron is in the +3 oxidation state with an electron configuration of [Ar] $3d^5$. Fe³⁺ complexes have one unpaired electron when a strong-field case and five unpaired electrons when a weak-field case. $Fe(CN)_6^{2-}$ is a strong-field case, and $Fe(SCN)_6^{3-}$ is a weakfield case. Therefore, cyanide (CN⁻) is a stronger-field ligand than thiocyanate (SCN⁻).
- 53. From Table 19.16 of the text, the violet complex ion absorbs yellow-green light ($\lambda \approx 570$ nm), the yellow complex ion absorbs blue light ($\lambda \approx 450$ nm), and the green complex ion absorbs red light ($\lambda \approx 650$ nm). The spectrochemical series shows that NH₃ is a stronger-field ligand than H₂O, which is a stronger-field ligand than Cl⁻. Therefore, $Cr(NH_3)_6^{3+}$ will have

the largest d-orbital splitting and will absorb the lowest wavelength electromagnetic radiation ($\lambda \approx 450$ nm) because energy and wavelength are inversely related ($\lambda = hc/E$). Thus the yellow solution contains the Cr(NH₃)₆³⁺ complex ion. Similarly, we would expect the Cr(H₂O)₄Cl₂⁺ complex ion to have the smallest d-orbital splitting because it contains the weakest-field ligands. The green solution with the longest wavelength of absorbed light contains the Cr(H₂O)₄Cl₂⁺ complex ion. This leaves the violet solution, which contains the Cr(H₂O)₆³⁺ complex ion. This makes sense because we would expect Cr(H₂O)₆³⁺ to absorb light of a wavelength between that of Cr(NH₃)₆³⁺ and Cr(H₂O)₄Cl₂⁺.

- 54. Octahedral Cr^{2+} complexes should be used. Cr^{2+} : [Ar]3d⁴; High spin (weak field) Cr^{2+} complexes have four unpaired electrons, and low spin (strong field) Cr^{2+} complexes have two unpaired electrons. Ni²⁺: [Ar]3d⁸; octahedral Ni²⁺ complexes will always have two unpaired electrons, whether high or low spin. Therefore, Ni²⁺ complexes cannot be used to distinguish weak- from strong-field ligands by examining magnetic properties. Alternatively, the ligand field strengths can be measured using visible spectra. Either Cr^{2+} or Ni²⁺ complexes can be used for this method.
- 55. a. $Ru(phen)_3^{2+}$ exhibits optical isomerism [similar to Co(en)_3^{3+} in Figure 19.16 of the text].
 - b. Ru^{2+} : [Kr]4d⁶; because there are no unpaired electrons, Ru^{2+} is a strong-field (low-spin) case.

56. Co^{2+} : [Ar]3d⁷; the corresponding d-orbital splitting diagram for tetrahedral Co^{2+} complexes is:

 $\underbrace{\uparrow} \qquad \underbrace{\uparrow} \qquad \underbrace{\downarrow} \qquad \underbrace{\underbrace{\downarrow} \qquad \underbrace{\downarrow} \qquad \underbrace{\underbrace{\downarrow} \qquad \underbrace{\downarrow} \qquad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{\underbrace{\downarrow} \quad \underbrace{\underbrace{\underbrace{i} \quad i} \quad \underbrace{i} \quad \underbrace{i} \quad$

All tetrahedral complexes are high spin since the d-orbital splitting is small. Ions with two or seven d electrons should give the most stable tetrahedral complexes because they have the greatest number of electrons in the lower-energy orbitals as compared with the number of electrons in the higher-energy orbitals.

57. The crystal field diagrams are different because the geometries of where the ligands point are different. The tetrahedrally oriented ligands point differently in relationship to the d orbitals than do the octahedrally oriented ligands. Also, we have more ligands in an octahedral complex.

See Figure 19.28 for the tetrahedral crystal field diagram. Notice that the orbitals are reverse of that in the octahedral crystal field diagram. The degenerate d_{z^2} and $d_{x^2-y^2}$ are at a lower energy than the degenerate d_{xy} , d_{xz} , and d_{yz} orbitals. Again, the reason for this is that

tetrahedral ligands are oriented differently than octahedral field ligands, so the interactions with specifically oriented d orbitals are different. Also notice that the difference in magnitude of the d-orbital splitting for the two geometries. The d-orbital splitting in tetrahedral complexes is less than one-half the d-orbital splitting in octahedral complexes. There are no known ligands powerful enough to produce the strong-field case; hence all tetrahedral complexes are weak field or high spin.

- 58. From Table 19.16, the red octahedral $\text{Co}(\text{H}_2\text{O})_6^{2^+}$ complex ion absorbs blue-green light ($\lambda \approx 490 \text{ mm}$), whereas the blue tetrahedral $\text{Co}\text{Cl}_4^{2^-}$ complex ion absorbs orange light ($\lambda \approx 600 \text{ nm}$). Because tetrahedral complexes have a d-orbital splitting much less than octahedral complexes, one would expect the tetrahedral complex to have a smaller energy difference between split d orbitals. This translates into longer-wavelength light absorbed (E = hc/ λ) for tetrahedral complex ions compared to octahedral complex ions. Information from Table 19.16 confirms this.
- 59. $\operatorname{CoBr_6^{4-}}$ has an octahedral structure, and $\operatorname{CoBr_4^{2-}}$ has a tetrahedral structure (as do most Co^{2+} complexes with four ligands). Coordination complexes absorb electromagnetic radiation (EMR) of energy equal to the energy difference between the split d orbitals. Because the tetrahedral d-orbital splitting is less than one-half the octahedral d-orbital splitting, tetrahedral complexes will absorb lower-energy EMR, which corresponds to longer-wavelength EMR (E = hc/ λ). Therefore, $\operatorname{CoBr_6^{4-}}$ will absorb EMR having a wavelength shorter than 3.4 $\times 10^{-6}$ m.
- 60. Pd is in the +2 oxidation state in $PdCl_4^{2-}$; Pd^{2+} : $[Kr]4d^8$. If $PdCl_4^{2-}$ were a tetrahedral complex, then it would have two unpaired electrons and would be paramagnetic (see diagram below). Instead, $PdCl_4^{2-}$ has a square planar molecular structure with a d-orbital splitting diagram shown below. Note that all electrons are paired in the square planar diagram, which explains the diamagnetic properties of $PdCl_4^{2-}$.



Additional Exercises

61. $\operatorname{Hg}^{2+}(\operatorname{aq}) + 2 \operatorname{I}^{-}(\operatorname{aq}) \rightarrow \operatorname{HgI}_{2}(\operatorname{s})$, orange precipitate

 $HgI_2(s) + 2 I^{-}(aq) \rightarrow HgI_4^{2-}(aq)$, soluble complex ion

 Hg^{2+} is a d¹⁰ ion. Color is the result of electron transfer between split d orbitals. This cannot occur for the filled d orbitals in Hg^{2+} . Therefore, we would not expect Hg^{2+} complex ions to form colored solutions.

62. The transition metal ion must form octahedral complex ions; only with the octahedral geometry are two different arrangements of d electrons possible in the split d orbitals. These two arrangements depend on whether a weak field or a strong field is present. For four unpaired electrons in the first row, the two possible weak-field cases are for transition metal ions having either a $3d^4$ or a $3d^6$ electron configuration:



Of these two, only d⁶ ions have no unpaired electron in the strong-field case.



Therefore, the transition metal ion has a $3d^6$ valence electron configuration. Fe²⁺ and Co³⁺ are two possible metal ions that are $3d^6$. Thus one of these ions is probably present in the four coordination compounds, with each complex ion having a coordination number of 6 due to the octahedral geometry.

The colors of the compounds are related to the magnitude of Δ (the d-orbital splitting value). The weak-field compounds will have the smallest Δ , so the wavelength of light absorbed will be longest. Using Table 19.16, the green solution (absorbs 650-nm light) and the blue solution (absorbs 600-nm light) absorb the longest-wavelength light; these solutions contain the complex ions that are the weak-field cases with four unpaired electrons. The red solution (absorbs 490-nm light) and yellow solution (absorbs 450-nm light) contain the two strong-field case complex ions because they absorb the shortest-wavelength (highest-energy) light. These complex ions are diamagnetic.

- 63. Ni(CO)₄ is composed of 4 CO molecules and Ni. Thus nickel has an oxidation state of zero.
- 64. CN^{-} and CO form much stronger complexes with Fe^{2+} than O_2 . Thus O_2 cannot be transported by hemoglobin in the presence of CN^{-} or CO because the binding sites prefer the toxic CN^{-} and CO ligands.

65. i.
$$0.0203 \text{ g CrO}_3 \times \frac{52.00 \text{ g Cr}}{100.0 \text{ g CrO}_3} = 0.0106 \text{ g Cr}; \ \% \text{ Cr} = \frac{0.0106 \text{ g}}{0.105 \text{ g}} \times 100 = 10.1\% \text{ Cr}$$

ii. 32.93 mL HCl ×
$$\frac{0.100 \text{ mmol HCl}}{\text{mL}}$$
 × $\frac{1 \text{ mmol NH}_3}{\text{mmol HCl}}$ × $\frac{17.03 \text{ mg NH}_3}{\text{mmol}}$ = 56.1 mg NH₃

% NH₃ =
$$\frac{56.1 \text{ mg}}{341 \text{ mg}} \times 100 = 16.5\% \text{ NH}_3$$

iii. 73.53% + 16.5% + 10.1% = 100.1%; the compound must be composed of only Cr, NH₃, and I.

Out of 100.00 g of compound:

10.1 g Cr × $\frac{1 \text{ mol}}{52.00 \text{ g}}$ = 0.194 mol; $\frac{0.194}{0.194}$ = 1.00

16.5 g NH₃ ×
$$\frac{1 \text{ mol}}{17.03 \text{ g}}$$
 = 0.969 mol; $\frac{0.969}{0.194}$ = 4.99

73.53 g I × $\frac{1 \text{ mol}}{126.9 \text{ g}}$ = 0.5794 mol; $\frac{0.5794}{0.194}$ = 2.99

 $Cr(NH_3)_5I_3$ is the empirical formula. Cr^{3+} forms octahedral complexes. So compound A is made of the octahedral $[Cr(NH_3)_5I]^{2+}$ complex ion and two I⁻ ions as counter ions; the formula is $[Cr(NH_3)_5I]I_2$. Lets check this proposed formula using the freezing-point data.

iv. $\Delta T_f = iK_fm$; for [Cr(NH₃)₅I]I₂, i = 3.0 (assuming complete dissociation).

Molality =
$$m = \frac{0.601 \text{ g complex}}{1.000 \times 10^{-2} \text{ kg H}_2\text{O}} \times \frac{1 \text{ mol complex}}{517.9 \text{ g complex}} = 0.116 \text{ mol/kg}$$

$$\Delta T_f = 3.0 \times 1.86 \text{ }^{\circ}\text{C} \text{ kg/mol} \times 0.116 \text{ mol/kg} = 0.65 \text{ }^{\circ}\text{C}$$

Because ΔT_f is close to the measured value, this is consistent with the formula $[Cr(NH_3)_5I]I_2$.

- a. Copper is both oxidized and reduced in this reaction, so, yes, this reaction is an oxidation-reduction reaction. The oxidation state of copper in [Cu(NH₃)₄]Cl₂ is +2, the oxidation state of copper in Cu is zero, and the oxidation state of copper in [Cu(NH₃)₄]Cl is +1.
 - b. Total mass of copper used:

10,000 boards ×
$$\frac{(8.0 \text{ cm} \times 16.0 \text{ cm} \times 0.060 \text{ cm})}{\text{board}} \times \frac{8.96 \text{ g}}{\text{cm}^3} = 6.9 \times 10^5 \text{ g Cu}$$

Amount of Cu to be recovered = $0.80(6.9 \times 10^5 \text{ g}) = 5.5 \times 10^5 \text{ g}$ Cu

$$5.5 \times 10^{5} \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{1 \text{ mol } [\text{Cu}(\text{NH}_{3})_{4}]\text{Cl}_{2}}{\text{mol Cu}} \times \frac{202.59 \text{ g } [\text{Cu}(\text{NH}_{3})_{4}]\text{Cl}_{2}}{\text{mol } [\text{Cu}(\text{NH}_{3})_{4}]\text{Cl}_{2}}$$

= 1.8×10^6 g [Cu(NH₃)₄]Cl₂

 $5.5 \times 10^5 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{4 \text{ mol NH}_3}{\text{mol Cu}} \times \frac{17.03 \text{ g NH}_3}{\text{mol NH}_3} = 5.9 \times 10^5 \text{ g NH}_3$

67. M = metal ion



68. a. The optical isomers of this compound are similar to the ones discussed in Figure 19.16 of the text. In the following structures we omitted the 4 NH₃ ligands coordinated to the outside cobalt atoms.



mirror

b. All are Co(III). The three "ligands" each contain 2 OH⁻ and 4 NH₃ groups. If each cobalt is in the +3 oxidation state, then each ligand has a +1 overall charge. The +3 charge from the three ligands, along with the +3 charge of the central cobalt atom, gives the overall complex a +6 charge. This is balanced by the -6 charge of the six Cl⁻ ions.

c. Co³⁺: [Ar]3d⁶; There are zero unpaired electrons if a low-spin (strong-field) case.



- 69. No; in all three cases, six bonds are formed between Ni²⁺ and nitrogen, so Δ H values should be similar. Δ S° for formation of the complex ion is most negative for 6 NH₃ molecules reacting with a metal ion (seven independent species become one). For penten reacting with a metal ion, two independent species become one, so Δ S° is least negative for this reaction compared to the other reactions. Thus the chelate effect occurs because the more bonds a chelating agent can form to the metal, the more favorable Δ S° is for the formation of the complex ion, and the larger is the formation constant.
- 70. CrCl₃•6H₂O contains nine possible ligands, only six of which are used to form the octahedral complex ion. The three species not present in the complex ion will either be counter ions to balance the charge of the complex ion and/or waters of hydration. The number of counter ions for each compound can be determined from the silver chloride precipitate data, and the number of waters of hydration can be determined from the dehydration data. In all experiments, the ligands in the complex ion do not react.

Compound I:

mol CrCl₃•6H₂O = 0.27 g ×
$$\frac{1 \text{ mol}}{266.5 \text{ g}}$$
 = 1.0 × 10⁻³ mol CrCl₃•6H₂O

mol waters of hydration = 0.036 g H₂O ×
$$\frac{1 \text{ mol}}{18.02 \text{ g}}$$
 = 2.0 × 10⁻³ mol H₂O

$$\frac{\text{mol waters of hydration}}{\text{mol compound}} = \frac{2.0 \times 10^{-3} \text{ mol}}{1.0 \times 10^{-3} \text{ mol}} = 2.0$$

In compound I, two of the H_2O molecules are waters of hydration, so the other four water molecules are present in the complex ion. Therefore, the formula for compound I must be $[Cr(H_2O)_4Cl_2]Cl\bullet 2H_2O$. Two of the Cl⁻ ions are present as ligands in the octahedral complex ion, and one Cl⁻ ion is present as a counter ion. The AgCl precipitate data that refer to this compound are the one that produces 1430 mg AgCl:

mol Cl⁻ from compound I = 0.1000 L ×
$$\frac{0.100 \text{ mol} [Cr(H_2O)_4Cl_2]Cl \bullet 2H_2O}{L}$$
×
$$\frac{1 \text{ mol Cl}^-}{\text{mol} [Cr(H_2O)_4Cl_2]Cl \bullet 2H_2O} = 0.0100 \text{ mol Cl}^-$$

mass AgCl produced = 0.0100 mol Cl⁻ ×
$$\frac{1 \operatorname{mol} \operatorname{AgCl}}{\operatorname{mol} \operatorname{Cl}^{-}}$$
 × $\frac{143.4 \operatorname{g} \operatorname{AgCl}}{\operatorname{mol} \operatorname{AgCl}}$ = 1.43 g
= 1430 mg AgCl

Compound II:

$$\frac{\text{mol waters of hydration}}{\text{mol compound}} = \frac{0.018 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}}}{1.0 \times 10^{-3} \text{ mol compound}} = 1.0$$

The formula for compound II must be $[Cr(H_2O)_5Cl]Cl_2 \bullet H_2O$. The 2870-mg AgCl precipitate data refer to this compound. For 0.0100 mol of compound II, 0.0200 mol Cl⁻ is present as counter ions:

mass AgCl produced = 0.0200 mol Cl⁻ ×
$$\frac{1 \operatorname{mol} AgCl}{\operatorname{mol} Cl^{-}}$$
 × $\frac{143.4 \text{ g}}{\operatorname{mol}}$ = 2.87 g
= 2870 mg AgCl

Compound III:

This compound has no mass loss on dehydration, so there are no waters of hydration present. The formula for compound III must be $[Cr(H_2O)_6]Cl_3$. 0.0100 mol of this compound produces 4300 mg of AgCl(s) when treated with AgNO₃.

$$0.0300 \text{ mol } \text{Cl}^- \times \frac{1 \text{ mol } \text{AgCl}}{\text{mol } \text{Cl}^-} \times \frac{143.4 \text{ g } \text{AgCl}}{\text{mol } \text{AgCl}} = 4.30 \text{ g} = 4.30 \times 10^3 \text{ mg } \text{AgCl}$$

The structural formulas for the compounds are:

Compound I



Compound II

Compound III

$$\left[\begin{array}{c} H_{2}O \\ H_{2}O \\ H_{2}O \\ OH_{2}\end{array}\right]^{2+} Cl_{2} \bullet H_{2}O \qquad \left[\begin{array}{c} OH_{2} \\ H_{2}O \\ H_{2}O \\ OH_{2}\end{array}\right]^{3+} Cl_{3}$$

From Table 19.16 of the text, the violet compound will be the one that absorbs light with the shortest wavelength (highest energy). This should be compound III. H_2O is a stronger field ligand than Cl⁻; compound III with the most coordinated H_2O molecules will have the largest d-orbital splitting and will absorb the higher-energy light.

II III II II 71. $(H_2O)_5Cr-Cl-Co(NH_3)_5 \rightarrow (H_2O)_5Cr-Cl-Co(NH_3)_5 \rightarrow Cr(H_2O)_5Cl^{2+} + Co(II)$ complex

Yes; this is consistent. After the oxidation, the ligands on Cr(III) won't exchange. Because CI^{-} is in the coordination sphere, it must have formed a bond to Cr(II) before the electron transfer occurred (as proposed through the formation of the intermediate).

72. a. $Be(tfa)_2$ exhibits optical isomerism. Representations for the tetrahedral optical isomers are:



mirror

Note: The dotted line indicates a bond pointing into the plane of the paper, and the wedge indicates a bond pointing out of the plane of the paper. Also note that the placement of the double bonds in the tfa isomer is not important. The two double bonds can resonate between adjacent carbon or oxygen atoms. Therefore, multiple resonance structures can be drawn. Resonance structures are not different isomers.

b. Square planar $Cu(tfa)_2$ molecules exhibit geometric isomerism. In one geometric isomer, the CF_3 groups are cis to each other, and in the other isomer, the CF_3 groups are trans.



a. $Fe(H_2O)_6^{3+} + H_2O \implies Fe(H_2O)_5(OH)^{2+} + H_3O^+$

Initial 0.10 M 0 ~0
Equil. 0.10 - x x x x
$$K_{a} = \frac{[Fe(H_{2}O)_{5}(OH)^{2+}][H_{3}O^{+}]}{[Fe(H_{2}O)_{6}^{3+}]} = 6.0 \times 10^{-3} = \frac{x^{2}}{0.10 - x} \approx \frac{x^{2}}{0.10}$$

 $x = 2.4 \times 10^{-2}$; assumption is poor (x is 24% of 0.10). Using successive approximations:

$$\frac{x^2}{0.10 - 0.024} = 6.0 \times 10^{-3}, \ x = 0.021$$
$$\frac{x^2}{0.10 - 0.021} = 6.0 \times 10^{-3}, \ x = 0.022; \ \frac{x^2}{0.10 - 0.022} = 6.0 \times 10^{-3}, \ x = 0.022$$

$$x = [H^+] = 0.022 M; \text{ pH} = 1.66$$

73.

- b. Because of the lower charge, $Fe^{2+}(aq)$ will not be as strong an acid as $Fe^{3+}(aq)$. A solution of iron(II) nitrate will be less acidic (have a higher pH) than a solution with the same concentration of iron(III) nitrate.
- 74. We need to calculate the Pb^{2+} concentration in equilibrium with EDTA⁴⁻. Because K is large for the formation of PbEDTA²⁻, let the reaction go to completion; then solve an equilibrium problem to get the Pb^{2+} concentration.

 Pb^{2+} + $EDTA^{4-}$ \Rightarrow $PbEDTA^{2-}$ $K = 1.1 \times 10^{18}$

$D_{1010} = 0.010 M = 0.030 M = 0$	
0.010 mol/L Pb ²⁺ reacts completely (large K)	
Change -0.010 -0.010 \rightarrow $+0.010$ Reacts	s completely
After 0 0.040 0.010 New in	initial condition
x mol/L PbEDTA ²⁻ dissociates to reach equilibrium	
Equil. $x = 0.040 + x = 0.010 - x$	

$$1.1 \times 10^{18} = \frac{(0.010 - x)}{(x)(0.040 + x)} \approx \frac{(0.010)}{x(0.040)}, \ x = [Pb^{2+}] = 2.3 \times 10^{-19} M;$$
 assumptions good.

Now calculate the solubility quotient for $Pb(OH)_2$ to see if precipitation occurs. The concentration of OH⁻ is 0.10 *M* because we have a solution buffered at pH = 13.00.

$$Q = [Pb^{2+}]_0 [OH^-]_0^2 = (2.3 \times 10^{-19})(0.10)^2 = 2.3 \times 10^{-21} < K_{sp} (1.2 \times 10^{-15})$$

Pb(OH)₂(s) will not form because Q is less than K_{sp}.

75. a. In the lungs, there is a lot of O_2 , and the equilibrium favors $Hb(O_2)_4$. In the cells, there is a deficiency of O_2 , and the equilibrium favors HbH_4^{4+} .

- b. CO_2 is a weak acid in water; $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$. Removing CO_2 essentially decreases H^+ . $Hb(O_2)_4$ is then favored, and O_2 is not released by hemoglobin in the cells. Breathing into a paper bag increases $[CO_2]$ in the blood, thus increasing $[H^+]$, which shifts the reaction left.
- c. CO_2 builds up in the blood, and it becomes too acidic, driving the equilibrium to the left. Hemoglobin can't bind O_2 as strongly in the lungs. Bicarbonate ion acts as a base in water and neutralizes the excess acidity.

$$HbO_{2} \rightarrow Hb + O_{2} \qquad \Delta G^{\circ} = -(-70 \text{ kJ})$$

$$Hb + CO \rightarrow HbCO \qquad \Delta G^{\circ} = -80 \text{ kJ}$$

$$HbO_{2} + CO \rightarrow HbCO + O_{2} \qquad \Delta G^{\circ} = -10 \text{ kJ}$$

$$\Delta G^{\circ} = -RT \ln K, \quad K = \left(\frac{-\Delta G^{\circ}}{RT}\right) = \exp\left[\frac{-(-10 \times 10^{3} \text{ J})}{(8.3145 \text{ J K}^{-1} \text{mol}^{-1})(298 \text{ kJ})}\right] = 60$$

Challenge Problems

77.

76.

The $d_{x^2 - y^2}$ and d_{xy} orbitals are in the plane of the three ligands and should be destabilized the most. The amount of destabilization should be about equal when all the possible interactions are considered. The d_{z^2} orbital has some electron density in the xy plane (the doughnut) and should be destabilized a lesser amount than the $d_{x^2 - y^2}$ and d_{xy} orbitals. The d_{xz} and d_{yz} orbitals have no electron density in the plane and should be lowest in energy.

78. $Ni^{2+} = d^8$; if ligands A and B produced very similar crystal fields, the trans- $[NiA_2B_4]^{2+}$ complex ion would give the following octahedral crystal field diagram for a d^8 ion:

$$\frac{1}{1} \frac{1}{1}$$
 This is paramagnetic.

Because it is given that the complex ion is diamagnetic, the A and B ligands must produce different crystal fields, giving a unique d-orbital splitting diagram that would result in a diamagnetic species.

79.



The d_{z^2} orbital will be destabilized much more than in the trigonal planar case (see Exercise 19.77). The d_{z^2} orbital has electron density on the z axis directed at the two axial ligands. The $d_{x^2-y^2}$ and d_{xy} orbitals are in the plane of the three trigonal planar ligands and should be destabilized a lesser amount than the d_{z^2} orbital; only a portion of the electron density in the $d_{x^2-y^2}$ and d_{xy} orbitals is directed at the ligands. The d_{xz} and d_{yz} orbitals will be destabilized the least since the electron density is directed between the ligands.

80. Ni^{2+} : [Ar]3d⁸; the coordinate system for trans-[Ni(NH₃)₂(CN)₄]²⁻ is shown below. Because CN⁻ produces a much stronger crystal field, it will dominate the d-orbital splitting. From the coordinate system, the CN⁻ ligands are in a square planar arrangement. Therefore, the diagram will most resemble the square planar diagram given in Figure 19.29. Note that the relative position of d_{r^2} orbital is hard to predict; it could switch positions with the d_{xy} orbital.





$$\begin{array}{ccc} Co^{3^{+}} + e^{-} \rightarrow Co^{2^{+}} & E_{c}^{o} = 1.82 \text{ V} \\ Co(en)_{3}^{2^{+}} \rightarrow Co(en)_{3}^{3^{+}} + e^{-} & -E_{a}^{o} = ? \end{array}$$

$$\hline Co^{3^{+}} + Co(en)_{3}^{2^{+}} \rightarrow Co^{2^{+}} + Co(en)_{3}^{3^{+}} & E_{cell}^{o} = 1.82 - E_{a}^{o} \end{array}$$

The equilibrium constant for this overall reaction is:

$$Co^{3^{+}} + 3 \text{ en} \rightarrow Co(\text{en})_{3}^{3^{+}} \qquad K_{1} = 2.0 \times 10^{47}$$

$$Co(\text{en})_{3}^{2^{+}} \rightarrow Co^{2^{+}} + 3 \text{ en} \qquad K_{2} = 1/1.5 \times 10^{12}$$

$$Co^{3^{+}} + Co(\text{en})_{3}^{2^{+}} \rightarrow Co(\text{en})_{3}^{3^{+}} + Co^{2^{+}} \qquad K = K_{1}K_{2} = \frac{2.0 \times 10^{47}}{1.5 \times 10^{12}} = 1.3 \times 10^{35}$$

From the Nernst equation for the overall reaction:

$$E_{cell}^{o} = \frac{0.0591}{n} \log K = \frac{0.0591}{1} \log(1.3 \times 10^{35}), \quad E_{cell}^{o} = 2.08 \text{ V}$$
$$E_{cell}^{o} = 1.82 - E_{a}^{o} = 2.08 \text{ V}, \quad -E_{a}^{o} = 2.08 \text{ V} - 1.82 \text{ V} = 0.26 \text{ V}, \text{ so } E_{c}^{o} = -0.26 \text{ V}$$

- b. The stronger oxidizing agent will be the more easily reduced species and will have the more positive standard reduction potential. From the reduction potentials, Co^{3+} (E° = 1.82 V) is a much stronger oxidizing agent than Co(en)₃³⁺ (E° = -0.26 V).
- c. In aqueous solution, Co^{3+} forms the hydrated transition metal complex $\text{Co}(\text{H}_2\text{O})_6^{3+}$. In both complexes, $\text{Co}(\text{H}_2\text{O})_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$, cobalt exists as Co^{3+} , which has six d electrons. Assuming a strong-field case for each complex ion, the d-orbital splitting diagram for each is:

$$\underbrace{ \uparrow \downarrow } \underbrace{ \uparrow \downarrow } \underbrace{ \uparrow \downarrow } \underbrace{ \uparrow \downarrow } t_{2g}$$

When each complex gains an electron, the electron enters a higher-energy e_g orbital. Because en is a stronger-field ligand than H₂O, the d-orbital splitting is larger for $Co(en)_3^{3^+}$, and it takes more energy to add an electron to $Co(en)_3^{3^+}$ than to $Co(H_2O)_6^{3^+}$. Therefore, it is more favorable for $Co(H_2O)_6^{3^+}$ to gain an electron than for $Co(en)_3^{3^+}$ to gain an electron.

82. a. Cr^{3+} : [Ar]3d³; we will assume the A ligands lie on the z axis.



b.



c. The major difference in the two diagrams involves the d_{xy} , d_{xz} , and d_{yz} orbitals. These are degenerate in the MO diagram (only σ bonding assumed) but are not degenerate in the crystal field diagram. If the d orbitals were involved in π bonding, this might reconcile the differences between the two diagrams. One expects involvement of d_{xy} to be different from d_{xz} and d_{yz} because of the symmetry of the complex. This would remove the degeneracy of these orbitals in the MO picture.

83. a.
$$AgBr(s) \rightleftharpoons Ag^{+} + Br^{-} K_{sp} = [Ag^{+}][Br^{-}] = 5.0 \times 10^{-13}$$

Initial $s = solubility (mol/L)$ 0 0
Equil. s s
 $K_{sp} = 5.0 \times 10^{-13} = s^{2}, s = 7.1 \times 10^{-7} mol/L$
b. $AgBr(s) \rightleftharpoons Ag^{+} + Br^{-} K_{sp} = 5.0 \times 10^{-13}$
 $Ag^{+} + 2 NH_{3} \rightleftharpoons Ag(NH_{3})_{2}^{+} K_{f} = 1.7 \times 10^{7}$
 $AgBr(s) + 2 NH_{3}(aq) \rightleftharpoons Ag(NH_{3})_{2}^{+}(aq) + Br^{-}(aq) K = K_{sp} \times K_{f} = 8.5 \times 10^{-6}$
 $AgBr(s) + 2 NH_{3}(aq) \rightleftharpoons Ag(NH_{3})_{2}^{+}(aq) + Br^{-}(aq) K = K_{sp} \times K_{f} = 8.5 \times 10^{-6}$
 $AgBr(s) + 2 NH_{3} \rightleftharpoons Ag(NH_{3})_{2}^{+} + Br^{-}$
Initial $3.0 M$ 0 0
 $s mol/L \text{ of } AgBr(s) \text{ dissolves to reach equilibrium = molar solubility}$
Equil. $3.0 - 2s$ s s

$$K = \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2} = \frac{s^2}{(3.0 - 2s)^2}, \ 8.5 \times 10^{-6} \approx \frac{s^2}{(3.0)^2}, \ s = 8.7 \times 10^{-3} \text{ mol/L}$$

Assumption good.

c. The presence of NH₃ increases the solubility of AgBr. Added NH₃ removes Ag^+ from solution by forming the complex ion $Ag(NH_3)_2^+$. As Ag^+ is removed, more AgBr(s) will dissolve to replenish the Ag^+ concentration.

d. Mass AgBr = 0.2500 L ×
$$\frac{8.7 \times 10^{-3} \text{ mol AgBr}}{\text{L}}$$
 × $\frac{187.8 \text{ g AgBr}}{\text{mol AgBr}}$ = 0.41 g AgBr

- e. Added HNO₃ will have no effect on the AgBr(s) solubility in pure water. Neither H⁺ nor NO₃⁻ reacts with Ag⁺ or Br⁻ ions. Br⁻ is the conjugate base of the strong acid HBr, so it is a terrible base. Added H⁺ will not react with Br⁻ to any great extent. However, added HNO₃ will reduce the solubility of AgBr(s) in the ammonia solution. NH₃ is a weak base (K_b = 1.8×10^{-5}). Added H⁺ will react with NH₃ to form NH₄⁺. As NH₃ is removed, a smaller amount of the Ag(NH₃)₂⁺ complex ion will form, resulting in a smaller amount of AgBr(s) that will dissolve.
- 84. For a linear complex ion with ligands on the x axis, the $d_{x^2-y^2}$ will be destabilized the most, with the lobes pointing directly at the ligands. The d_{yz} orbital has the fewest interactions with x-axis ligands, so it is destabilized the least. The d_{xy} and d_{xz} orbitals will have similar destabilization but will have more interactions with x-axis ligands than the d_{yz} orbital. Finally, the d_{z^2} orbital with the doughnut of electron density in the xy plane will probably be destabilized more than the d_{xy} and d_{xz} orbitals but will have nowhere near the amount of destabilization that occurs with the $d_{x^2-y^2}$ orbital. The only difference that would occur in the diagram if the ligands were on the y axis is the relative positions of the d_{xy} , d_{xz} , and d_{yz} orbitals. The d_{xz} will have the smallest destabilization of all these orbitals, whereas the d_{xy} and d_{yz} orbitals will be degenerate since we expect both to be destabilized equivalently from y-axis ligands. The d-orbital splitting diagrams are:



linear y-axis ligands

linear x-axis ligands