

18.26 The splitting diagram to use in every case is the right-hand part of Figure 18.17.

(a) The Cr^{2+} ion is a d^4 case. In a strong octahedral field it has the ground-state configuration t_{2g}^4 for two unpaired electrons; in a weak octahedral field the configuration is $t_{2g}^3 e_g^1$ and all four electrons are unpaired.

(b) The V^{3+} ion is a d^2 case. It has two unpaired electrons (electron configuration t_{2g}^2) in both a strong and a weak octahedral field.

(c) The Ni^{2+} ion is a d^8 case. It has the configuration $t_{2g}^6 e_g^2$ for two unpaired electrons in both a strong and a weak octahedral field.

(d) The Pt^{4+} ion is a d^6 case. It has four unpaired electrons in a weak octahedral field ($t_{2g}^4 e_g^2$) and no unpaired electrons (t_{2g}^6) in a strong octahedral field.

(e) The Co^{2+} ion is a d^7 case. It has three unpaired electrons in a weak octahedral field ($t_{2g}^5 e_g^2$) and one unpaired electron ($t_{2g}^6 e_g^1$) in a strong octahedral field.

18.28 The Mn(III) ion in these two complexes has four d -electrons. When coordinated by Cl^- in the $[\text{MnCl}_6]^{3-}$ ion, the result is a high-spin complex—all four electrons are unpaired. With a stronger-field ligand in the $[\text{Mn}(\text{CN})_6]^{3-}$, there are no electrons in the higher-energy e_g -levels. Putting four electrons into the t_{2g} level requires pairing two. The other two are unpaired. In the first case, the CFSE is $-3/5\Delta_o$; in the second it is $-8/5\Delta_o$.

18.32 The ion $[\text{PtI}_6]^{2-}$ absorbs all across the visible spectrum.

18.34 A solution of hexaaquanickel(II) ion is green. It therefore absorbs the complementary color of green, which is red. We can estimate the wavelength of the absorption in the red as 700 nm (see text Figure 15.3). The corresponding energy is

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{700 \times 10^{-9} \text{ m}} = 2.8 \times 10^{-19} \text{ J}$$

The absorption occurs with the excitation of an electron from a t_{2g} to an e_g level so this energy is Δ_o . Multiplying Δ_o by Avogadro's number puts it on a molar basis. It is about 170 kJ mol^{-1} .

18.36 The CFSE for this d^8 complex is $-\frac{6}{5}\Delta_o$, or about -200 kJ mol^{-1} .

18.40 (a) The complex $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ results from the dissolution of $\text{Mn}(\text{NO}_3)_2$ in water. It is a high-spin d^5 complex. The excitation of an electron requires the reversal of a spin; such processes are fairly strictly forbidden. Their rarity makes the color of the ion faint. The $[\text{Mn}(\text{CN})_6]^{4-}$ ion on the other hand is a low-spin complex. The $t_{2g} \rightarrow e_g$ transitions are not spin-forbidden and are more intense.

(b) We expect $\text{Zn}(\text{NO}_3)_2$, CdSO_4 and AgClO_3 to be colorless in aqueous solution based on the full occupancy of the d -orbitals of the metal ion when coordinated by the solvent.

18.44 The mass of iron in one mole of hemoglobin is 0.33% of the mass of one mole of hemoglobin, which is given as $6.8 \times 10^4 \text{ g}$. This comes out to 224 g of iron. Dividing this mass of iron by the molar mass of iron establishes that there are four moles of iron in one mole of hemoglobin. Hence there are four atoms of iron per hemoglobin molecule.

- 18.52 (a) $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{CO}_3$ is most likely to have the same electrical conductivity per mole as MgSO_4 , which is also a 2 to 2 ionic compound.
- (b) $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_3$ matches best to GaCl_3 , which also has Cl^- as the anion, but also matches to Na_3PO_4 .
- (c) $[\text{Zn}(\text{H}_2\text{O})_3(\text{OH})]\text{Cl}$ matches best to NaCl .
- (d) $[\text{Fe}(\text{NH}_3)_6]_2(\text{CO}_3)_3$ matches best to $\text{Fe}_2(\text{SO}_4)_3$.
- (e) $[\text{Cr}(\text{NH}_3)_3\text{Br}_3]$ matches best to HCN ; both are nonelectrolytes.
- (f) $\text{K}_3[\text{Fe}(\text{CN})_6]$ matches well to both Na_3PO_4 , as well as to GaCl_3 .

18.62 The two compounds have the same number of unpaired electrons and both have Mn^{2+} , a d^5 -metal ion, as the central metal ion. The octahedral complex is a weak-field, high-spin complex and so is the tetrahedral complex.

18.76 The chemical amount of CO present is

$$n = \frac{PV}{RT} = \frac{(2.00 \text{ atm})(1.18 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 0.09646 \text{ mol CO}$$

The mass of CO in this is

$$(0.09646 \text{ mol CO})(28.01 \text{ g mol}^{-1}) = 2.70 \text{ g}$$

so the mass of the remaining osmium is

$$6.79 - 2.70 = 4.09 \text{ g Os}$$

The chemical amount of Os is

$$\frac{4.09 \text{ g Os}}{190.2 \text{ g mol}^{-1}} = 0.02149 \text{ mol Os}$$

The ratio is

$$\frac{0.09646}{0.02149} = 4.49 \approx 4.5 = \frac{9}{2}$$

so the probable empirical formula is $\text{Os}_2(\text{CO})_9$. This compound might have a single bridging CO ligand, with four other CO molecules attached separately to each Os atom.