Chapter 20

**PROPERTIES OF THE 3d TRANSITION METALS**

Exercises

20.1  
(a) \( \text{TiCl}_4(l) + \text{O}_2(g) \rightarrow \text{TiO}_2(s) + 2 \text{Cl}_2(g) \)  
(b) \( \text{Na}_2\text{Cr}_2\text{O}_7(s) + \text{S}(l) \rightarrow \text{Cr}_2\text{O}_3(s) + \text{Na}_2\text{SO}_4(s) \)  
(c) \( \text{Cu(OH)}_2(s) \rightarrow \text{CuO}(s) + \text{H}_2\text{O}(l) \)

20.3  
For the earlier part of the Period 4 transition metals, the maximum oxidation number is the same as the group number (that is, the sum of the 4s and 3d electrons). For the later members, the oxidation state of +2 predominates.

20.5  
Titanium(IV) chloride vaporizes readily, a characteristic of a covalent compound. Covalent behavior would be expected on the basis of the high charge density of the Ti\(^{4+}\) ion resulting in a strong attraction for the large, low charge density chloride ions (that is, covalent bond formation).

20.7  
(a) \( \text{MnO}_4^{-}(aq) + 8 \text{H}^{+}(aq) + 5 \text{e}^{-} \rightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l) \)  
(b) \( \text{MnO}_4^{-}(aq) + 2 \text{H}_2\text{O}(l) + 3 \text{e}^{-} \rightarrow \text{MnO}_2(s) + 4 \text{OH}^{-}(aq) \)

20.9  
Iron(II) chloride is prepared under comparatively reducing conditions as a result of the hydrogen gas production:  
\( \text{Fe}(s) + 2 \text{HCl}(g) \rightarrow \text{FeCl}_2(s) + \text{H}_2(g) \)  
Iron(III) chloride is prepared using highly oxidizing chlorine gas:  
\( 2 \text{Fe}(s) + 3 \text{Cl}_2(g) \rightarrow 2 \text{FeCl}_3(s) \)
20.11 (a) Cobalt:
\[
[\text{Co(OH}_2\text{)}_6]^{2+}(aq) + 4 \text{Cl}^−(aq) \rightarrow [\text{CoCl}_4]^{2−}(aq) + 6 \text{H}_2\text{O(l)}
\]
(b) Copper:
\[
2 \text{Cu(s)} + 2 \text{H}^+(aq) + 4 \text{Cl}^−(aq) \rightarrow 2[\text{CuCl}_2]^{−}(aq) + \text{H}_2\text{(g)}
\]
\[ [\text{CuCl}_2]^{−}(aq) \rightarrow \text{CuCl(s)} + \text{Cl}^−(aq) \]
(c) Chromium:
\[
2 \text{CrO}_4^{2−}(aq) + 2 \text{H}^+(aq) \rightarrow \text{Cr}_2\text{O}_7^{2−}(aq) + \text{H}_2\text{O(l)}
\]

20.13 The two reactants are the hexaaquairon(III) ion and thiosulfate ion:
\[
\text{Fe}^{3+}(aq) + 2 \text{S}_2\text{O}_3^{2−}(aq) \rightarrow [\text{Fe(S}_2\text{O}_3)_2]^{−}(aq)
\]
\[ [\text{Fe(S}_2\text{O}_3)_2]^{−}(aq) + \text{Fe}^{3+}(aq) \rightarrow 2 \text{Fe}^{2+}(aq) + \text{S}_4\text{O}_6^{2−}(aq) \]

20.15 (a) Fluoride stabilizes high oxidation states since it is a \(\pi\)-donor ligand. To maximize \(\pi\) interaction, the metal ion should have empty \(d\) orbitals and hence be in the highest possible oxidation state.
(b) The value of the crystal-field splitting, \(\Delta\), is very dependent upon oxidation state, so the nickel(IV) complex should have a very large \(\Delta\) value. Thus, even though fluoride is very low in the spectrochemical series, the complex is most likely to be low spin.

20.17 \[
\text{FeO}_4^{2−}(aq) + 8 \text{H}^+(aq) + 3 \text{e}− \rightarrow \text{Fe}^{3+}(aq) + 4 \text{H}_2\text{O(l)}
\]
\[
2 \text{NH}_3(aq) \rightarrow \text{N}_2\text{(g)} + 6 \text{H}^+(aq) + 6 \text{e}−
\]
\[
2 \text{FeO}_4^{2−}(aq) + 2 \text{NH}_3(aq) + 10 \text{H}^+(aq) \rightarrow 2 \text{Fe}^{3+}(aq) + \text{N}_2\text{(g)} + 8 \text{H}_2\text{O(l)}
\]

20.19 Chromium(VI) oxide. The very high charge density of the chromium metal ion will cause sufficient polarization of the electrons on the oxygens to result in covalent bond formation. Covalently bonded compounds have much lower melting points than ionic compounds (usually!).

20.21 Like aluminum and iron(III) ions, the chromium(III) ion will lose a hydrogen ion to a water molecule.
\[
[\text{Cr(OH}_2\text{)}_6]^{3+}(aq) + \text{H}_2\text{O(l)} \rightarrow [\text{Cr(OH)(OH}_2\text{)}_5]^{2+}(aq) + \text{H}_3\text{O}^+(aq)
\]

20.23 The insolubility of copper(I) chloride can be argued for reasons similar to those arguing why silver chloride is insoluble (Chapter 5). According to Fajan’s Rules, cations with non-noble-gas configurations are likely to have
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a more covalent character (in this case, the filled 3d orbitals can be polarized towards the anions). If the ionic charge in the crystal lattice is decreased by partial electron sharing, then the ion-water interaction will be less and the tendency to dissolve will, in turn, be less.

20.25 (a) In a well-aerated lake, the partial pressure of dioxygen would lead to a high positive potential, while the pH should be near neutral. FeO(OH) is the most likely species.
(b) In acid oxidizing conditions, Fe$^{3+}$ is the most probable species.
(c) Fe$^{2+}$ is most likely in these acid, reducing conditions.

20.27 They both form anhydrous chlorides that react with water to release hydrogen chloride gas while their hexahydrates are water soluble. The anhydrous chlorides both function as Friedel-Craft catalysts. In the gas phase, their chlorides exist as dimers, Al$_2$Cl$_6$ and Fe$_2$Cl$_6$, respectively. On the other hand, iron(III) oxide is basic, while the oxide of aluminum is amphoteric. Also, iron(III) compounds are colored, while those of aluminum are white.

20.29 Titanium:

\[
\text{TiO}_2(s) + 2 \text{C}(s) + 2 \text{Cl}_2(g) \xrightarrow{\Delta} \text{TiCl}_4(g) + 2 \text{CO}(g)
\]

\[
\text{TiCl}_4(g) + \text{O}_2(g) \xrightarrow{\Delta} \text{TiO}_2(s) + 2 \text{Cl}_2(g)
\]

\[
\text{TiCl}_4(g) + 2 \text{Mg}(l) \xrightarrow{\Delta} \text{Ti}(s) + 2 \text{MgCl}_2(l)
\]

Vanadium:

\[
[\text{H}_2\text{VO}_4]^{-}(aq) + 4 \text{H}^{+}(aq) + e^- \rightarrow \text{VO}^{2+}(aq) + 3 \text{H}_2\text{O}(l)
\]

\[
\text{VO}^{2+}(aq) + 2 \text{H}^{+}(aq) + e^- \rightarrow \text{V}^{3+}(aq) + \text{H}_2\text{O}(l)
\]

\[
[\text{V(OH}_2)_6]^{3+}(aq) + e^- \rightarrow [\text{V(OH}_2)_6]^{2+}(aq)
\]

Chromium:

\[
\text{CrO}_4^{2-}(aq) + 2 \text{Ag}^{+}(aq) \rightarrow \text{Ag}_2\text{CrO}_4(s)
\]

\[
\text{CrO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{HCrO}_4^{-}(aq) + \text{OH}^{-}(aq)
\]

\[
2 \text{CrO}_4^{2-}(aq) + 2 \text{H}^{+}(aq) \rightarrow \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l)
\]

\[
\text{Cr}_2\text{O}_7^{2-}(aq) + 2 \text{NH}_4^{+}(aq) \rightarrow (\text{NH}_4)_2\text{Cr}_2\text{O}_7(s)
\]

\[
(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \rightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + 4 \text{H}_2\text{O}(l)
\]

\[
\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^{+}(aq) + 6 e^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)
\]
Cr₂O₇²⁻(aq) + 2 K⁺(aq) → K₂Cr₂O₇(s)
K₂Cr₂O₇(s) + H₂SO₄(aq) → 2 CrO₃(s) + K₂SO₄(aq) + H₂O(l)
K₂Cr₂O₇(s) + 4 NaCl(s) + 6 H₂SO₄(l) → 2 CrO₂Cl₂(l) + 2 KHSO₄(s) + NaHSO₄(s) + 3 H₂O(l)
CrO₂Cl₂(l) + 4 OH⁻(aq) → CrO₄²⁻(aq) + 2 Cl⁻(aq) + 2 H₂O(l)
Cr₂O₇²⁻(aq) + 14 H⁺(aq) + 6 e⁻ → 2 Cr³⁺(aq) + 7 H₂O(l)
2 Cr³⁺(aq) + Zn(s) → 2 Cr²⁺(aq) + Zn²⁺(aq)
2 Cr²⁺(aq) + 4 CH₃COO⁻(aq) + 2 H₂O(l) → Cr₂(CH₃COO)₄(OH)₂(s)

Manganese:
MnO₄⁻(aq) + e⁻ → MnO₄²⁻(aq)
MnO₄²⁻(aq) + 2 H₂O(l) + 2 e⁻ → MnO₂(s) + 4 OH⁻(aq)
MnO₄⁻(aq) + 2 H₂O(l) + 3 e⁻ → MnO₂(s) + 4 OH⁻(aq)
MnO₄⁻(aq) + 8 H⁺(aq) + 5 e⁻ → Mn²⁺(aq) + 4 H₂O(l)
Mn²⁺(aq) + 2 OH⁻(aq) → Mn(OH)₂(s)
Mn(OH)₂(s) + OH⁻(aq) → MnO(OH)(s) + H₂O(l) + e⁻

Iron:
[Fe(OH₂)₆]³⁺(aq) + SCN⁻(aq) → [Fe(SCN)(OH₂)₅]²⁺(aq) + H₂O(l)
[Fe(OH₂)₆]³⁺(aq) + 4 Cl⁻(aq) ↔ [FeCl₄]⁻(aq) + 6 H₂O(l)
Fe³⁺(aq) + 3 OH⁻(aq) → FeO(OH)(s) + H₂O(l)
[Fe(OH₂)₆]³⁺(aq) + e⁻ → [Fe(OH₂)₅]²⁺(aq)
Fe³⁺(aq) + 2 S₂O₃²⁻(aq) → [Fe(S₂O₃)₂]⁻(aq)
[Fe(S₂O₃)₂]⁻(aq) + Fe³⁺(aq) → 2 Fe²⁺(aq) + S₄O₆²⁻(aq)
Fe²⁺(aq) + 2 OH⁻(aq) → Fe(OH)₂(s)
[Fe(OH₂)₆]²⁺(aq) + NO(aq) → [Fe(NO)(OH₂)₅]²⁺(aq) + H₂O(l)
Fe(OH)₂(s) + OH⁻(aq) → FeO(OH)(s) + H₂O(l) + e⁻
Fe²⁺(aq) + 2 e⁻ → Fe(s)
2 Fe(s) + 3 Cl₂(g) → 2 FeCl₃(s)
Fe(s) + 2 HCl(g) → FeCl₂(s) + H₂(g)

Cobalt:
[Co(OH₂)₆]³⁺(aq) + e⁻ → [Co(OH₂)₆]²⁺(aq)
[Co(OH₂)₆]²⁺(aq) + 4 Cl⁻(aq) → [CoCl₄]²⁻(aq) + 6 H₂O(l)
Co²⁺(aq) + 2 OH⁻(aq) → Co(OH)₂(s)
Co(OH)₂(s) + 2 OH⁻(aq) → Co(OH)₄²⁻(aq)
Beyond the Basics

20.31 Addition of an anhydrous calcium compound will result in formation of the hexaaquacalcium ion. This will reduce the available mole of ‘free’ water and hence ‘drive the reaction to the right’:

$$\text{CaX}_2(s) +aq \rightarrow [\text{Ca(OH)}_2]^{2+}(aq) + 2 \text{X}^{-}(aq)$$

Addition of an anhydrous zinc compound results in the formation of the competing complexation of the zinc ion to give the tetrachlorozincate ion and hence ‘drive the reaction to the left’:

$$\text{ZnX}_2(s) +aq + 4 \text{Cl}^{-}(aq) \rightarrow [\text{ZnCl}_4]^{2-}(aq) + 2 \text{X}^{-}(aq)$$

20.33 Dichromate is in equilibrium with the chromate ion:

$$\text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l) \rightarrow 2 \text{CrO}_4^{2-}(aq) + 2 \text{H}^{+}(aq)$$
The chromate then reacts with the lead ion to form insoluble lead(II) chromate (the dichromate being more soluble). As chromate ion is precipitated, more is produced, according to Le Châtelier’s principle.

\[ \text{Pb}^{2+}(aq) + \text{CrO}_4^{2-}(aq) \rightarrow \text{PbCrO}_4(s) \]

20.35 (a) A solution of cyanide ion will be basic:

\[ \text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HCN}(aq) + \text{OH}^-(aq) \]

Thus the precipitate will probably be nickel(II) hydroxide:

\[ \text{Ni}^{2+}(aq) + 2 \text{OH}^-(aq) \rightarrow \text{Ni(OH)}_2(s) \]

It is unlikely to be nickel(II) cyanide. Because nickel(II) chloride is soluble, nickel(II) cyanide also should be soluble (pseudohalide ion).

(b) This should be the square planar tetracyanonickelate(II) ion:

\[ \text{Ni(OH)}_2(s) + 4 \text{CN}^-(aq) \rightarrow [\text{Ni(CN)}_4]^{2-}(aq) + \text{OH}^-(aq) \]

(c) This must involve the addition of a fifth cyanide ion:

\[ [\text{Ni(CN)}_4]^{2-}(aq) + \text{CN}^-(aq) \rightarrow \text{Ni(CN)}_5^{3-}(aq) \]

20.37 (a) The high-charge cation (Fe\(^{3+}\)) will have a lowish lattice energy when combined with a low-charge anion (\(\text{ClO}_4^-\)). Solubility depends upon the competing factors of lattice energy and ion hydration enthalpies. The lowish lattice energy results in solubility. The high-charge cation (Fe\(^{3+}\)) will have a very high lattice energy when combined with a high-charge anion (\(\text{PO}_4^{3-}\)). This will be greater than the sum of the hydration enthalpies and the compound will be insoluble.

(b) Either: Ammonia and water are quite high in the spectrochemical series whereas phosphine and hydrogen sulfide are very low.

Or: Ammonia and water are hard bases, and the first row transition metals are mostly hard acids, while phosphine and hydrogen sulfide are soft bases.

(c) As Fe\(^{3+}\) high spin has one electron in each orbital, there is no strong color from \(d-d\) transitions. The color must result from
charge transfer. Bromide is more easily reduced than chloride; thus the transition
\[ \text{Fe}^{3+}\text{Br}^- \rightarrow \text{Fe}^{2+}\text{Br}_0 \]
takes place at a lower energy (more in the visible region) than in the chloride compound.

20.39 Like the equivalent iron compound, this is probably nickel(II) disulfide(2−)—the disulfide ion being analogous to the dioxide(2−) ion. The sulfur oxidation state would be −1.


\[
\begin{align*}
\text{NiS} + 2 \text{H}^+(aq) & \rightarrow \text{Ni}^{2+}(aq) + \text{H}_2\text{S}(g) \\
2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) & \rightarrow 2 \text{H}_2\text{O}(l) + 2 \text{SO}_2(g) \\
2 \text{H}_2\text{S}(g) + \text{SO}_2(g) & \rightarrow 2 \text{H}_2\text{O}(l) + 3 \text{S}(s) \\
2 \text{S}(s) + \text{Cl}_2(g) & \rightarrow \text{S}_2\text{Cl}_2(l) \\
\text{S}(s) + \text{Cl}_2(g) & \rightarrow \text{SCl}_2(l) \\
[\text{Ni(OH}_2)_6]^{2+}(aq) + 6 \text{NH}_3(aq) & \rightarrow [\text{Ni(NH}_3)_6]^{2+}(aq) + 6 \text{H}_2\text{O}(l) \\
\text{Ni}^{2+}(aq) + 2 \text{OH}^-(aq) & \rightarrow \text{Ni(OH)}_2(s) \\
\text{Ni}^{2+}(aq) + \text{Zn}(s) & \rightarrow \text{Ni}(s) + \text{Zn}^{2+}(aq) \\
\text{Ni}(s) + 4 \text{CO}(g) & \rightarrow \text{Ni(CO)}_4(l)
\end{align*}
\]

20.43 Vanadium is the only transition metal whose chemistry matches the information provided.

20.45 Chromium-52 has 28 neutrons corresponding to a full neutron shell.

20.47 3+, as the shared oxygen would have an oxidation state of −2 (−1 with each chromium). The linear shape suggests there is a π-bonding Cr–O–Cr system. This would use the filled p orbitals on oxygen together with the part-empty d_{xy}, d_{xz}, and d_{yz} orbitals. The equivalent cobalt compound would probably have a bent Co–O–Co bond, as those d orbitals on cobalt are fully occupied and thus cannot be used for π bonding.
20.49 Under normal conditions, the reduction would be:
\[ [\text{Fe(OH}_2]_6^{3+}(aq) + e^- \rightarrow [\text{Fe(OH}_2]_6^{2+}(aq) \]

In the presence of high concentrations of chloride ion, the reaction would become:
\[ [\text{FeCl}_4^-]^{-}(aq) + e^- \rightarrow [\text{FeCl}_4^2-](aq) \]

Presumably the chloride ligand has preferentially stabilized the 3+ oxidation state of the iron.

20.51 The charge transfer process can be represented as
\[ \text{Ag}^+ X^- \rightarrow \text{Ag}^0 X^0 \]
where \( X \) represents the halide ion. As the halide ion is more readily oxidized, the absorption of light will be of lower energy—more and more in the visible part of the spectrum. As iodide is the easiest oxidized and chloride the least, this represents the order of visible color intensity.

20.53 As calcium ion always has an oxidation state of 2+, it will replace the \( \text{Mn}^{3+} \) to give: \( 3\text{Mn}_2\text{O}_3 \cdot \text{CaSiO}_3 \). Iron would most likely be in the \( \text{Fe}^{3+} \) oxidation state, in which case it would replace the \( \text{Mn}^{3+} \) ion to give: \( 3\text{Fe}_2\text{O}_3 \cdot \text{MnSiO}_3 \). Titanium (as titanate) would replace the silicon in the silicate: \( 3\text{Mn}_2\text{O}_3 \cdot \text{MnTiO}_3 \). Aluminum as \( \text{Al}^{3+} \) could replace the \( \text{Mn}^{3+} \) to give: \( 3\text{Al}_2\text{O}_3 \cdot \text{MnSiO}_3 \), or as aluminate, it could replace silicon in silicate, though then the manganese would have to be \( \text{Mn}^{3+} \) to retain charge balance: \( 3\text{Mn}_2\text{O}_3 \cdot \text{MnAlO}_3 \).

20.55 The ring structure suggests that there could be some form of \( \pi \)-bonding of the multiple-bonded ligands through the \( d \) orbitals of the nickel ion.

20.57 (a) \( \text{Fe}(s) + \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s) \)
(b) The layer of unreactive sodium silicate will coat the iron and prevent the continuation of the oxidation.
(c) The red-hot iron would have reacted with water to give hydrogen gas.
\[ 2 \text{Fe}(s) + 3 \text{H}_2\text{O}(l) \xrightarrow{\Delta} \text{Fe}_2\text{O}_3(s) + 3 \text{H}_2(g) \]

The explosion would have resulted from the hydrogen/oxygen mixture:
\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) \]