CHAPTER 20
METALLURGY AND THE CHEMISTRY
OF METALS

20.11 For the given reaction we can calculate the standard free energy change from the standard free energies of formation. Then, we can calculate the equilibrium constant, $K_p$, from the standard free energy change.

$$
\Delta G^\circ = \Delta G^\circ_{f[Ni(CO)\text{]4}} - [4\Delta G^\circ_{f}(CO) + \Delta G^\circ_{f}(Ni)]
$$

$$
\Delta G^\circ = (1)(-587.4 \text{ kJ/mol}) - [(4)(-137.3 \text{ kJ/mol}) + (1)(0)] = -38.2 \text{ kJ/mol} = -3.82 \times 10^4 \text{ J/mol}
$$

Substitute $\Delta G^\circ$, $R$, and $T$ (in K) into the following equation to solve for $K_p$.

$$
\Delta G^\circ = -RT \ln K_p
$$

$$
\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-(3.82 \times 10^4 \text{ J/mol})}{(8.314 \text{ J/K mol})(353 \text{ K})}
$$

$$
K_p = 4.5 \times 10^5
$$

20.12 The cathode reaction is: $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu(s)}$

First, let’s calculate the number of moles of electrons needed to reduce 5.0 kg of Cu.

$$
5.00 \text{ kg Cu} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} = 1.57 \times 10^2 \text{ mol e}^-
$$

Next, let’s determine how long it will take for $1.57 \times 10^2$ moles of electrons to flow through the cell when the current is 37.8 C/s.

$$
(1.57 \times 10^2 \text{ mol e}^-) \times \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{37.8 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 111 \text{ h}
$$

20.13 Table 19.1 of the text shows that Pb, Fe, Co, Zn are more easily oxidized (stronger reducing agents) than copper. The Ag, Au, and Pt are harder to oxidize and will not dissolve.

Would you throw away the sludge if you were in charge of the copper refining plant? Why is it still profitable to manufacture copper even though the market price is very low?

20.14 The sulfide ore is first roasted in air:

$$
2\text{ZnS(s) + 3O}_2(g) \rightarrow 2\text{ZnO(s) + 2SO}_2(g)
$$

The zinc oxide is then mixed with coke and limestone in a blast furnace where the following reductions occur:

$$
\text{ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)}
$$

$$
\text{ZnO(s) + CO(g) \rightarrow Zn(g) + CO}_2(g)
$$

The zinc vapor formed distills from the furnace into an appropriate receiver.
20.15 The trick in this process centers on the fact that TiCl\textsubscript{4} is a liquid with a boiling point (136.4°C), a little higher than that of water. The tetrachloride can be formed by treating the oxide (rutile) with chlorine gas at high temperature. The balanced equation is:

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

The liquid tetrachloride can be isolated and purified by simple distillation. Purified TiCl\textsubscript{4} is then reduced with magnesium (a stronger reducing agent than Ti) at high temperature.

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

The other product, MgCl\textsubscript{2}, can be separated easily from titanium metal by dissolving in water.

20.16 (a) We first find the mass of ore containing \(2.0 \times 10^8\) kg of copper.

\[
(2.0 \times 10^8 \text{ kg Cu}) \times \frac{100\% \text{ ore}}{0.80\% \text{ Cu}} = 2.5 \times 10^{10} \text{ kg ore}
\]

We can then compute the volume from the density of the ore.

\[
(2.5 \times 10^{10} \text{ kg}) \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ cm}^3}{2.8 \text{ g}} = 8.9 \times 10^{12} \text{ cm}^3
\]

(b) From the formula of chalcopyrite it is clear that two moles of sulfur dioxide will be formed per mole of copper. The mass of sulfur dioxide formed will be:

\[
(2.0 \times 10^8 \text{ kg Cu}) \times \frac{1 \text{ mol Cu}}{0.06355 \text{ kg Cu}} \times \frac{2 \text{ mol SO}_2}{1 \text{ mol Cu}} \times \frac{0.06407 \text{ kg SO}_2}{1 \text{ mol SO}_2} = 4.0 \times 10^8 \text{ kg SO}_2
\]

20.17 Very electropositive metals (i.e., very strong reducing agents) can only be isolated from their compounds by electrolysis. No chemical reducing agent is strong enough. In the given list CaCl\textsubscript{2}, NaCl, and Al\textsubscript{2}O\textsubscript{3} would require electrolysis.

20.18 Iron can be produced by reduction with coke in a blast furnace; whereas, aluminum is usually produced electrolytically, which is a much more expensive process.

20.27 All of these reactions are discussed in Section 20.5 of the text.

(a) \(2\text{K}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{KOH}(aq) + \text{H}_2(g)\)

(b) \(\text{NaH}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NaOH}(aq) + \text{H}_2(g)\)

(c) \(2\text{Na}(s) + \text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s)\)

(d) \(\text{K}(s) + \text{O}_2(g) \rightarrow \text{KO}_2(s)\)

(e) \(2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)\)

(f) \(\text{Na}_2\text{CO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)\)

20.28 (a) \(2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g)\)

(b) \(2\text{NaOH}(aq) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)\)

(c) \(\text{Na}_2\text{CO}_3(s) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)\)

(d) \(\text{NaHCO}_3(aq) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)\)

(e) \(2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)\)

(f) \(\text{Na}_2\text{CO}_3(s) \rightarrow \text{no reaction. Unlike CaCO}_3(s), \text{Na}_2\text{CO}_3(s) \text{is not decomposed by moderate heating.}\)
20.29 \( \text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2 \)

20.30 The balanced equation is: \( \text{Na}_2\text{CO}_3(s) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \)

\[
\text{mol CO}_2 \text{ produced} = \frac{25.0 \text{ g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0 \text{ g Na}_2\text{CO}_3} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol Na}_2\text{CO}_3}} = 0.236 \text{ mol CO}_2
\]

\[
V_{\text{CO}_2} = \frac{nRT}{P} = \frac{(0.236 \text{ mol})(0.0821 \text{ L atm/K mol})(283 \text{ K})}{\left(\frac{746 \text{ mmHg}}{760 \text{ mmHg}}\right)} = 5.59 \text{ L}
\]

20.33 (a) \( \Delta H^o = \Delta H^o_{\text{f (MgO)}} + \Delta H^o_{\text{f (CO}_2)} - \Delta H^o_{\text{f (MgCO}_3)} \)

\[
\Delta H^o = (1)(-601.8 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol}) - (1)(-1112.9 \text{ kJ/mol}) = 117.6 \text{ kJ/mol}
\]

(b) \( \Delta H^o = \Delta H^o_{\text{f (CaO)}} + \Delta H^o_{\text{f (CO}_2)} - \Delta H^o_{\text{f (CaCO}_3)} \)

\[
\Delta H^o = (1)(-635.5 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol}) - (1)(-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}
\]

\( \Delta H^o \) is less for MgCO3; therefore, it is more easily decomposed by heat.

20.34 First magnesium is treated with concentrated nitric acid (redox reaction) to obtain magnesium nitrate.

\[
3\text{Mg}(s) + 8\text{HNO}_3(aq) \rightarrow 3\text{Mg(NO}_3)_2(aq) + 4\text{H}_2\text{O}(l) + 2\text{NO}(g)
\]

The magnesium nitrate is recovered from solution by evaporation, dried, and heated in air to obtain magnesium oxide:

\[
2\text{Mg(NO}_3)_2(s) \rightarrow 2\text{MgO}(s) + 4\text{NO}_2(g) + \text{O}_2(g)
\]

20.35 As described in Section 20.6 of the text, magnesium metal will combine with chlorine.

\[
\text{Mg}(s) + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s)
\]

Magnesium will also react with HCl.

\[
\text{Mg}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)
\]

Neither of the above methods are really practical because magnesium metal is expensive to produce (electrolysis of magnesium chloride!). Can you suggest a method starting with a magnesium compound like MgCO3?

20.36 The electron configuration of magnesium is [Ne]3s². The 3s electrons are outside the neon core (shielded), so they have relatively low ionization energies. Removing the third electron means separating an electron from the neon (closed shell) core, which requires a great deal more energy.

20.37 The water solubilities of the sulfates increase in the order Ra < Ba < Sr < Ca < Mg. The trend in this series is clearly in the sense of smaller ionic radius favoring greater solubility. Probably the smaller ion size results in much greater hydration energy (Section 6.7 of the text). Which sulfate in this series should have the largest lattice energy (Section 9.3 of the text)? Which is the more important factor in determining solubility in this series: hydration energy or lattice energy?
According to the *Handbook of Chemistry and Physics*, BeSO₄ reacts with water to form “BeSO₄•4H₂O”. In this sense it is not strictly comparable with the other sulfates of the Group 2A metals. However, this compound is really comprised of a sulfate ion and a Be(H₂O)₄²⁺ complex ion. The latter is just a very strongly hydrated Be²⁺ ion. The solubility of the “BeSO₄•4H₂O” is higher than any of other Group 2A sulfates, so it really does fit at the high solubility end of the series.

**20.38** Even though helium and the Group 2A metals have ns² outer electron configurations, helium has a closed shell noble gas configuration and the Group 2A metals do not. The electrons in He are much closer to and more strongly attracted by the nucleus. Hence, the electrons in He are not easily removed. Helium is inert.

**20.39** The formation of calcium oxide is:

\[
2\text{Ca(s)} + \text{O}_2(g) \rightarrow 2\text{CaO(s)}
\]

The conversion of calcium oxide to calcium hydroxide is:

\[
\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(s)
\]

The reaction of calcium hydroxide with carbon dioxide is:

\[
\text{Ca(OH)}_2(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O(l)}
\]

If calcium metal were exposed to extremely humid air, do you think that the oxide would still form?

**20.40** (a) quicklime: CaO(s) (b) slaked lime: Ca(OH)₂(s) (c) limewater: an aqueous suspension of Ca(OH)₂

**20.43** According to Table 19.1 of the text, the following metals can reduce aluminum ion to aluminum:

Be, Mg, Na, Ca, Sr, Ba, K, Li

In 2001, the cheapest of these metals (magnesium) costs about $12.00 per lb. The current cost of aluminum is $0.70 per lb. Is the Hall process an improvement?

**20.44** The reduction reaction is: \(\text{Al}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Al(s)}\)

First, we can calculate the amount of charge needed to deposit 664 g of Al.

\[
664 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \times \frac{96,500 \text{ C}}{1 \text{ mol e}^-} = 7.12 \times 10^6 \text{ C}
\]

Since a current of one ampere represents a flow of one coulomb per second, we can find the time it takes to pass this amount of charge.

\[
32.6 \text{ A} = 32.6 \text{ C/s}
\]

\[
(7.12 \times 10^6 \text{ C}) \times \frac{1 \text{ s}}{32.6 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 60.7 \text{ h}
\]

**20.45** The two complex ions can be classified as AB₄ and AB₆ structures (no unshared electron pairs on Al and 4 or 6 attached atoms, respectively). Their VSEPR geometries are tetrahedral and octahedral.
The accepted explanation for the nonexistence of $\text{AlCl}_6^{3-}$ is that the chloride ion is too big to form an octahedral cluster around a very small $\text{Al}^{3+}$ ion. What is your guess for the formulas of complex ions formed between $\text{Al}^{3+}$ and bromide or iodide ions? What about $\text{Ga}^{3+}$ and chloride ion?

20.46  (a) The relationship between cell voltage and free energy difference is:

$$\Delta G = -nFE$$

In the given reaction $n = 6$. We write:

$$E = \frac{-\Delta G}{nF} = \frac{-594 \times 10^3 \text{ J/mol}}{(6)(96500 \text{ J/V mol})} = -1.03 \text{ V}$$

The balanced equation shows two moles of aluminum. Is this the voltage required to produce one mole of aluminum? If we divide everything in the equation by two, we obtain:

$$\frac{1}{2}\text{Al}_2\text{O}_3(s) + \frac{3}{2}\text{C}(s) \rightarrow \text{Al}(l) + \frac{3}{2}\text{CO}(g)$$

For the new equation $n = 3$ and $\Delta G$ is $\left(\frac{1}{2}\right)(594 \text{ kJ/mol}) = 297 \text{ kJ/mol}$. We write:

$$E = \frac{-\Delta G}{nF} = \frac{-297 \times 10^3 \text{ J/mol}}{(3)(96500 \text{ J/V mol})} = -1.03 \text{ V}$$

The minimum voltage that must be applied is $1.03 \text{ V}$ (a negative sign in the answers above means that 1.03 V is required to produce the Al). The voltage required to produce one mole or one thousand moles of aluminum is the same; the amount of current will be different in each case.

(b) First we convert 1.00 kg (1000 g) of Al to moles.

$$(1.00 \times 10^3 \text{ g Al}) \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 37.1 \text{ mol Al}$$

The reaction in part (a) shows us that three moles of electrons are required to produce one mole of aluminum. The voltage is three times the minimum calculated above (namely, $-3.09 \text{ V}$ or $-3.09 \text{ J/C}$). We can find the electrical energy by using the same equation with the other voltage.

$$\Delta G = -nFE = -(37.1)\left(\frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \times \frac{96500 \text{ C}}{1 \text{ mol e}^-} \times \frac{-3.09 \text{ J}}{1 \text{ C}}\right) = 3.32 \times 10^7 \text{ J/mol} = 3.32 \times 10^4 \text{ kJ/mol}$$

This equation can be used because electrical work can be calculated by multiplying the voltage by the amount of charge transported through the circuit (joules = volts $\times$ coulombs). The $nF$ term in Equation (19.2) of the text used above represents the amount of charge.

What is the significance of the positive sign of the free energy change? Would the manufacturing of aluminum be a different process if the free energy difference were negative?

20.47 The half-reaction for the oxidation of Al to $\text{AlO}_2^-$ in basic solution is:

$$\text{Al}(s) + 4\text{OH}^-(aq) \rightarrow \text{AlO}_2^-(aq) + 2\text{H}_2\text{O}(l) + 3\text{e}^-$$
(a) The nitrate-ammonia half-reaction is:

\[
\text{NO}_3^- (aq) + 6\text{H}_2\text{O}(l) + 8e^- \rightarrow \text{NH}_3(aq) + 9\text{OH}^- (aq)
\]

Combining the equations:

\[
8\text{Al}(s) + 5\text{OH}^- (aq) + 3\text{NO}_3^- (aq) + 2\text{H}_2\text{O}(l) \rightarrow 9\text{AlO}_2^- (aq) + 3\text{NH}_3(aq)
\]

(b) The water-hydrogen half-reaction is:

\[
\text{H}_2\text{O}(l) + e^- \rightarrow \text{OH}^- (aq) + \frac{1}{2}\text{H}_2(g)
\]

Combining the equations:

\[
\text{Al}(s) + \text{OH}^- (aq) + \text{H}_2\text{O}(l) \rightarrow \text{AlO}_2^- (aq) + \frac{3}{2}\text{H}_2(g)
\]

(c) The \text{SnO}_3^{2-}-\text{Sn} half-reaction is:

\[
\text{SnO}_3^{2-} (aq) + 3\text{H}_2\text{O}(l) + 4e^- \rightarrow \text{Sn}(s) + 6\text{OH}^- (aq)
\]

Combining the equations:

\[
4\text{Al}(s) + 3\text{SnO}_3^{2-} (aq) + \text{H}_2\text{O}(l) \rightarrow 4\text{AlO}_2^- (aq) + 3\text{Sn}(s) + 2\text{OH}^- (aq)
\]

20.48 \quad 4\text{Al(NO}_3)_3(s) \longrightarrow 2\text{Al}_2\text{O}_3(s) + 12\text{NO}_2(g) + 3\text{O}_2(g)

20.49 Some of aluminum’s useful properties are: low density (light weight), high tensile strength, high electrical conductivity, high thermal conductivity, inert protective oxide surface coating.

20.50 The “bridge” bonds in \text{Al}_2\text{Cl}_6 break at high temperature: \text{Al}_2\text{Cl}_6(g) \rightleftharpoons 2\text{AlCl}_3(g).

This increases the number of molecules in the gas phase and causes the pressure to be higher than expected for pure \text{Al}_2\text{Cl}_6.

If you know the equilibrium constants for the above reaction at higher temperatures, could you calculate the expected pressure of the \text{AlCl}_3-\text{Al}_2\text{Cl}_6 mixture?

20.51 (a) \quad 2\text{Al}(s) + 3\text{Cl}_2(g) \rightarrow \text{Al}_2\text{Cl}_6(s)

(b) \quad 4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)

(c) \quad 2\text{Al}(s) + 3\text{H}_2\text{SO}_4(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\text{H}_2(g)

(d) \quad \text{Al}_2(\text{SO}_4)_3(aq) + (\text{NH}_4)_2\text{SO}_4(aq) \rightarrow 2\text{NH}_4\text{Al(\text{SO}_4)_2 \cdot 12H}_2\text{O}(s), \text{ followed by the evaporation of the solution.}

20.52 In \text{Al}_2\text{Cl}_6, each aluminum atom is surrounded by 4 bonding pairs of electrons (AB_4-type molecule), and therefore each aluminum atom is \textbf{sp}^3\textbf{ hybridized}. VSEPR analysis shows \text{AlCl}_3 to be an AB_3-type molecule (no lone pairs on the central atom). The geometry should be trigonal planar, and the aluminum atom should therefore be \textbf{sp}^2\textbf{ hybridized}.  

20.53 Both CaO and MgO are basic oxides; they react with the acidic oxides formed in the furnace as follows:

\[ 6\text{CaO(s)} + \text{P}_4\text{O}_{10(s)} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2(s) \quad \text{MgO(s)} + \text{SO}_2(g) \rightarrow \text{MgSO}_3(s) \]

20.54 The formulas of the metal oxide and sulfide are MO and MS (why?). The balanced equation must therefore be:

\[ 2\text{MS(s)} + 3\text{O}_2(g) \rightarrow 2\text{MO(s)} + 2\text{SO}_2(g) \]

The number of moles of MO and MS are equal. We let \( x \) be the molar mass of metal. The number of moles of metal oxide is:

\[ \frac{0.972 \text{ g}}{(x + 16.00) \text{ g}} \times 1 \text{ mol} \]

The number of moles of metal sulfide is:

\[ \frac{1.164 \text{ g}}{(x + 32.07) \text{ g}} \times 1 \text{ mol} \]

The moles of metal oxide equal the moles of metal sulfide.

\[ \frac{0.972}{(x + 16.00)} = \frac{1.164}{(x + 32.07)} \]

We solve for \( x \).

\[ 0.972(x + 32.07) = 1.164(x + 16.00) \]

\[ x = 65.4 \text{ g/mol} \]

20.55 Metals conduct electricity. If electrons were localized in pairs, they could not move through the metal.

20.56 Copper(II) ion is more easily reduced than either water or hydrogen ion (How can you tell? See Section 19.3 of the text.) Copper metal is more easily oxidized than water. Water should not be affected by the copper purification process.

20.57 The balanced equation for the permanganate/iron(II) reaction is:

\[ 5\text{Fe}^{2+}(aq) + \text{MnO}_4^-(aq) + 8\text{H}^+(aq) \rightarrow 5\text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l) \]

Thus one mole of permanganate is stoichiometrically equivalent to five moles of iron(II). The original amount of iron(II) is (Note: one mole of iron(II) is equivalent to one mole of iron(III)).

\[ \frac{50.0 \text{ mL} \times 0.0800 \text{ mol Fe}^{2+}}{1000 \text{ mL soln}} = 4.00 \times 10^{-3} \text{ mol Fe}^{2+} \]

The excess amount of iron(II) is determined by using the balanced equation:

\[ \text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6\text{Fe}^{2+}(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l) + 6\text{Fe}^{3+}(aq) \]

Thus one mole of dichromate is equivalent to six moles of iron(II). The excess iron(II) is:

\[ \frac{22.4 \text{ mL} \times 0.0100 \text{ mol Cr}_2\text{O}_7^{2-}}{1000 \text{ mL soln}} \times \frac{6 \text{ mol Fe}^{2+}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} = 1.34 \times 10^{-3} \text{ mol Fe}^{2+} \]
The amount of iron(II) consumed is \((4.00 \times 10^{-3} \text{ mol}) - (1.34 \times 10^{-3} \text{ mol}) = 2.66 \times 10^{-3} \text{ mol}\)

The mass of manganese is:

\[
(2.66 \times 10^{-3} \text{ mol Fe}^{2+}) \times \frac{1 \text{ mol MnO}_4}{5 \text{ mol Fe}^{2+}} \times \frac{1 \text{ mol Mn}}{1 \text{ mol MnO}_4} \times \frac{54.94 \text{ g Mn}}{1 \text{ mol Mn}} = 0.0292 \text{ g Mn}
\]

The percent by mass of Mn is:

\[
\frac{0.0292 \text{ g}}{0.450 \text{ g}} \times 100\% = 6.49\%
\]

**20.58** Using Equation (18.12) from the text:

(a) \[\Delta G_{\text{rxn}}^o = 4\Delta G_f^o(\text{Fe}) + 3\Delta G_f^o(\text{O}_2) - 2\Delta G_f^o(\text{Fe}_2\text{O}_3)\]

\[\Delta G_{\text{rxn}}^o = (4)(0) + (3)(0) - (2)(-741.0 \text{ kJ/mol}) = 1482 \text{ kJ/mol}\]

(b) \[\Delta G_{\text{rxn}}^o = 4\Delta G_f^o(\text{Al}) + 3\Delta G_f^o(\text{O}_2) - 2\Delta G_f^o(\text{Al}_2\text{O}_3)\]

\[\Delta G_{\text{rxn}}^o = (4)(0) + (3)(0) - (2)(-1576.4 \text{ kJ/mol}) = 3152.8 \text{ kJ/mol}\]

**20.59** Amphoterism means the ability to act both as an acid and as a base. Al(OH)₃ is amphoteric, as shown below:

**As an acid:**

\[\text{Al(OH)}_3(s) + \text{NaOH(aq)} \rightarrow \text{NaAl(OH)}_4(aq)\]

**As a base:**

\[\text{Al(OH)}_3(s) + 3\text{HCl(aq)} \rightarrow \text{AlCl}_3(aq) + 3\text{H}_2\text{O(l)}\]

**20.60** At high temperature, magnesium metal reacts with nitrogen gas to form magnesium nitride.

\[3\text{Mg(s)} + \text{N}_2(g) \rightarrow \text{Mg}_3\text{N}_2(s)\]

Can you think of any gas other than a noble gas that could provide an inert atmosphere for processes involving magnesium at high temperature?

**20.61** The sodium atom has an \(ns^1\) valence shell electron configuration. The molecular orbital diagram for the Na₂ molecule is exactly analogous to that of the Li₂ molecule that is discussed in Section 10.7 of the text. The \(ns^1\) valence electron from each sodium will occupy a bonding \(\sigma_3\) molecular orbital, giving Na₂ two more electrons in bonding molecular orbitals than in antibonding molecular orbitals. The bond order is one.

The alkaline earth metals all possess an \(ns^2\) valence shell electron configuration. As in the case of Be₂ that is discussed in Section 10.7 of the text, all dimers of the alkaline earth metals would have equal numbers of electrons in bonding and antibonding molecular orbitals: that is, \((\sigma_{ns})^2(\sigma_{ns}^*)^2\). The bond order is zero, and such dimers would not be expected to exist.

**20.62** (a) In water the aluminum(III) ion causes an increase in the concentration of hydrogen ion (lower pH). This results from the effect of the small diameter and high charge (3+) of the aluminum ion on surrounding water molecules. The aluminum ion draws electrons in the O–H bonds to itself, thus allowing easy formation of H⁺ ions.
(b) Al(OH)₃ is an amphoteric hydroxide. It will dissolve in strong base with the formation of a complex ion.

\[ \text{Al(OH)}_3(s) + \text{OH}^-(aq) \rightarrow \text{Al(OH)}_4^-(aq) \]

The concentration of OH⁻ in aqueous ammonia is too low for this reaction to occur.

20.63 The reactions are:

(a) \( \text{Al}_2(\text{CO}_3)_3(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{CO}_2(g) \)

(b) \( \text{AlCl}_3(s) + 3\text{K}(s) \rightarrow \text{Al}(s) + 3\text{KCl}(s) \)

(c) \( \text{Ca(OH)}_2(aq) + \text{Na}_2\text{CO}_3(aq) \rightarrow \text{CaCO}_3(s) + 2\text{NaOH}(aq) \)

20.64 Calcium oxide is a base. The reaction is a neutralization.

\[ \text{CaO}(s) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) \]

20.65 MgO + CO → Mg + CO₂

\[ \Delta G^\circ = \Delta G^\circ_1(\text{CO}_2) - \Delta G^\circ_1(\text{MgO}) - \Delta G^\circ_1(\text{CO}) \]

\[ = (1)(-394.4 \text{ kJ/mol}) - (1)(-569.6 \text{ kJ/mol}) - (1)(-137.3 \text{ kJ/mol}) = +312.5 \text{ kJ/mol} \]

\[ \Delta G^\circ = -RT\ln K_p \]

\[ 312.5 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol·K})(298 \text{ K})\ln K_p \]

\[ K_p = 1.7 \times 10^{-55} \]

\( K_p \) is much too small, even at high temperatures. No product will be formed.

20.66 Metals have closely spaced energy levels and (referring to Figure 20.10 of the text) a very small energy gap between filled and empty levels. Consequently, many electronic transitions can take place with absorption and subsequent emission continually occurring. Some of these transitions fall in the visible region of the spectrum and give rise to the flickering appearance.

20.67 Essentially the same as the other alkali metals, except that it is more reactive. Fr reacts with water.

\[ 2\text{Fr} + 2\text{H}_2\text{O} \rightarrow 2\text{FrOH} + \text{H}_2 \]

Like K, Rb, and Cs, Fr also forms superoxide (FrO₂), in addition to oxide and peroxide.

20.68 NaF is used in toothpaste to fight tooth decay.

Li₂CO₃ is used to treat mental illness.

Mg(OH)₂ is an antacid.

CaCO₃ is an antacid.

BaSO₄ is used to enhance X ray images of the digestive system.

Al(OH)₂NaCO₃ is an antacid.
20.69  

**Scheme I**

2\(\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}\)  

(a)  

\[
\text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}
\]  

(b)  

\[
\text{MgCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{MgCO}_3 + 2\text{NaCl}
\]  

(c)  

\[
\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2
\]  

(d)  

\[
\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]  

(e)  

\[
\text{MgO} + \text{2HCl} \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}
\]  

(f)  

\[
\text{MgCl}_2(aq) + \text{Na}_2\text{CO}_3 \rightarrow \text{MgCO}_3 + 2\text{NaCl}
\]  

(g)  

\[
\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2
\]  

(h)  

\[
\text{MgO} + \text{2HNO}_3 \rightarrow \text{Mg(NO}_3)_2 + 2\text{H}_2\text{O}
\]  

(i)  

\[
\text{2Mg(NO}_3)_2 \rightarrow \text{2MgO} + 4\text{NO}_2 + \text{O}_2
\]

\(\text{NO}_2\) is the brown gas.

20.70  Both Li and Mg form oxides (Li_2O and MgO). Other Group 1A metals (Na, K, etc.) also form peroxides and superoxides. In Group 1A, only Li forms nitride (Li_3N), like Mg (Mg_3N_2). Li resembles Mg in that its carbonate, fluoride, and phosphate have low solubilities.

20.71  N_2, because Li reacts with nitrogen to form lithium nitride.

20.72  You might know that Ag, Cu, Au, and Pt are found as free elements in nature, which leaves Zn by process of elimination. You could also look at Table 19.1 of the text to find the metal that is easily oxidized. Looking at the table, the standard oxidation potential of Zn is +0.76 V. The positive value indicates that Zn is easily oxidized to Zn^{2+} and will not exist as a free element in nature.

20.73  A thin metal oxide layer is formed when the metal surface is heated in air. This layer causes light interference to produce colors much like that observed when a thin film of oil is formed on water.

20.74  Because only B and C react with 0.5 \(M\) HCl, they are more electronegative than A and D. The fact that when B is added to a solution containing the ions of the other metals, metallic A, C, and D are formed indicates that B is the most electronegative metal. Because A reacts with 6 \(M\) HNO_3, A is more electronegative than D. The metals arranged in increasing order as reducing agents are:

\[
\text{D} < \text{A} < \text{C} < \text{B}
\]

Examples are: D = Au, A = Cu, C = Zn, B = Mg

20.75  Electrical conductance of metals is due to the electron delocalization in the conduction band. Heating leads to a greater degree of vibration of the lattice, which disrupts the extent of delocalization and the movement of electrons. Consequently, the metal’s electrical conductance decreases with increasing temperature. In an electrolyte solution, like CuSO_4(aq), the electrical conductance is the result of the movement of ions from the anode to the cathode (or vice versa). Heating increases the kinetic energy of the ions and hence the electrical conductance.
20.76 First, we calculate the density of O$_2$ in KO$_2$ using the mass percentage of O$_2$ in the compound.

\[
\frac{32.00 \text{ g O}_2}{71.10 \text{ g KO}_2} \times \frac{2.15 \text{ g}}{1 \text{ cm}^3} = 0.968 \text{ g/cm}^3
\]

Now, we can use Equation (5.11) of the text to calculate the pressure of oxygen gas that would have the same density as that provided by KO$_2$.

\[
\frac{0.968 \text{ g}}{1 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = 968 \text{ g/L}
\]

\[d = \frac{P \cdot M}{RT}\]

or

\[P = \frac{dRT}{M} = \left(\frac{968 \text{ g}}{1 \text{ L}}\right)\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(293 \text{ K})\]

\[= 727 \text{ atm}\]

Obviously, using O$_2$ instead of KO$_2$ is not practical.

20.77 There are 10.00 g of Na in 13.83 g of the mixture. This amount of Na is equal to the mass of Na in Na$_2$O plus the mass of Na in Na$_2$O$_2$.

\[10.00 \text{ g Na} = \text{mass of Na in Na}_2\text{O} + \text{mass of Na in Na}_2\text{O}_2\]

To calculate the mass of Na in each compound, grams of compound need to be converted to grams of Na using the mass percentage of Na in the compound. If \(x\) equals the mass of Na$_2$O, then the mass of Na$_2$O$_2$ is 13.83 – \(x\). We set up the following expression and solve for \(x\). We carry an additional significant figure throughout the calculation to minimize rounding errors.

\[
10.00 \text{ g Na} = \text{mass of Na in Na}_2\text{O} + \text{mass of Na in Na}_2\text{O}_2
\]

\[
10.00 \text{ g Na} = \left[ x \text{ g Na}_2\text{O} \times \left(\frac{22.99 \text{ g Na}}{61.98 \text{ g Na}_2\text{O}}\right)\right] + \left[ (13.83 - x) \text{ g Na}_2\text{O}_2 \times \left(\frac{22.99 \text{ g Na}}{77.98 \text{ g Na}_2\text{O}_2}\right)\right]
\]

\[10.00 = 0.74185x + 8.1547 - 0.58964x\]

\[0.15221x = 1.8453\]

\[x = 12.123 \text{ g}, \text{ which equals the mass of Na}_2\text{O}\]

The mass of Na$_2$O$_2$ is 13.83 – \(x\), which equals 1.707 g.

The mass percent of each compound in the mixture is:

\[
\% \text{ Na}_2\text{O} = \frac{12.123 \text{ g}}{13.83 \text{ g}} \times 100 = 87.66\%
\]

\[
\% \text{ Na}_2\text{O}_2 = 100\% - 87.66\% = 12.34\%
\]