CHAPTER 14

THE ELEMENTS: THE FIRST FOUR MAIN GROUPS

14.2 (a) thallium   (b) bismuth   (c) tin   (d) aluminum

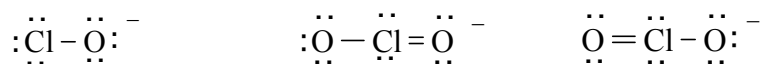**14.4** (a) rubidium   (b) germanium   (c) selenium   (d) aluminum

14.6 bismuth < arsenic < nitrogen

14.8 fluorine

14.10 tin

14.12 (a) $SnCl_2$. The radius of a metal atom with a higher oxidation number is smaller than that for the same metal ion with a lower oxidation number. (b) Here we should consider the Lewis structures:

$$:\ddot{C}l - \ddot{O}: ^{-} \qquad :\ddot{O} - \ddot{C}l = \ddot{O} \;^{-} \qquad \ddot{O} = \ddot{C}l - \ddot{O}: ^{-}$$

single bond   resonance structures give a bond order of 1.5

We expect the Cl–O bond in Cl– O^- to be longer because it is a single bond, whereas the Cl–O bond order in ClO_2^- is 1.5 and the bond should be shorter. One could also predict the Cl–O bond distance in ClO_2^- to be shorter because the Cl atom is in a higher oxidation state. (c) PH_3. The radius of phosphorus is larger than the radius of nitrogen.
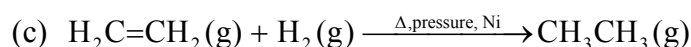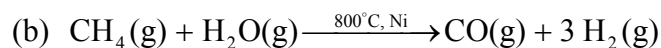
14.14 $Ca(s) + H_2(g) \rightarrow CaH_2(s)$

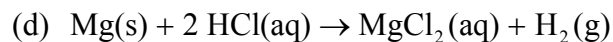**14.16** (a) molecular   (b) molecular   (c) saline   (d) metallic

14.18 (a) basic   (b) basic   (c) amphoteric   (d) acidic

14.20 (a) HNO_3 (c) H_3PO_4 (d) H_2SeO_4

14.22 (a) $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$

(b) $CH_4(g) + H_2O(g) \xrightarrow{\;800°C,\ Ni\;} CO(g) + 3\,H_2(g)$

(c) $H_2C{=}CH_2(g) + H_2(g) \xrightarrow{\;\Delta,pressure,\ Ni\;} CH_3CH_3(g)$

The oxidation number of C in $H_2C{=}CH_2$ is -2, and -3 in $H_3C{-}CH_3$. C has been reduced.

(d) $Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

14.24 (a) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

$\Delta H°_r = \Delta H°_f(CO_2, g) - [\Delta H°_f(CO, g) + \Delta H°_f(H_2O, g)]$

$= (-393.51\ kJ\cdot mol^{-1}) - [(-110.53\ kJ\cdot mol^{-1}) + (-241.82\ kJ\cdot mol^{-1})]$

$= -41.16\ kJ\cdot mol^{-1}$

(b) $\Delta S°_r = S°(CO_2, g) + S°(H_2, g)$

$\quad - [S°(CO, g) + S°(H_2O, g)]$

$\quad = 213.74\ J\cdot K^{-1}\cdot mol^{-1} + 130.68\ J\cdot K^{-1}\cdot mol^{-1} - [197.67\ J\cdot K^{-1}\cdot mol^{-1}$

$\quad + 188.83\ J\cdot K^{-1}\cdot mol^{-1}] = -42.08\ J\cdot K^{-1}\cdot mol^{-1}$

(c) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

$\Delta G°_r = \Delta G°_f(CO_2, g) - [\Delta G°_f(CO, g) + \Delta G°_f(H_2O, g)]$

$\quad = (-394.36\ kJ\cdot mol^{-1})$

$\quad\quad - [(-137\cdot17\ kJ\cdot mol^{-1}) + (-228.57\ kJ\cdot mol^{-1})]$

$\quad = -28.62\ kJ\cdot mol^{-1}$

$\Delta G°_r$ can also be calculated from $\Delta H°_r$ and $\Delta S°_r$:

$$\Delta G°_r = \Delta H°_r - T\Delta S°_r$$
$$= -41.16 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-42.08 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$
$$= -28.62 \text{ kJ} \cdot \text{mol}^{-1}$$

14.26 (a) $N_2(g) + 3 H_2(g) \xrightarrow{\text{400-600°C, Fe,150-160 atm}} 2 NH_3(g)$

(b) $H_2(g) + F_2(g) \rightarrow 2 HF(g)$

(c) $2 Cs(s) + H_2(g) \xrightarrow{\Delta} 2 CsH(s)$

(d) $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2 H^+(aq)$

14.28 (a) $Li \rightarrow Li^+ + e^-$ $\qquad\qquad E° = +3.05 \text{ V}$

$Cu^{2+} + 2 e^- \rightarrow Cu$ $\qquad E° = +0.34 \text{ V}$

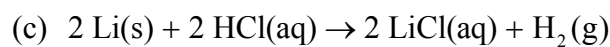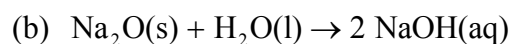$\underline{2 Li + Cu^{2+} \rightarrow Cu + 2 Li^+ \qquad E° = +3.39 \text{ V}}$
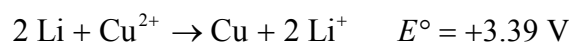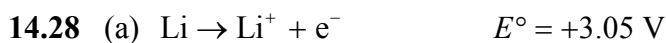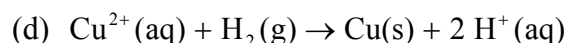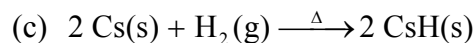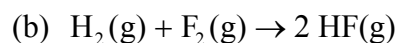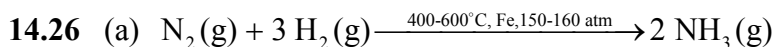
The maximum potential possible is + 3.39 V.

(b) The difficulty is isolating the two half cells but still maintaining electrical contact. Ions need to flow through the system to maintain charge balance in the reaction. In this case, a material that allows appropriate counter anions but not Cu^{2+} ions or water to pass through would be necessary. It is necessary to keep the Li compartment free of water because lithium and water react vigorously. Not only would this destroy the cell but it would circumvent the desired electrochemical process.

14.30 (a) ns^1
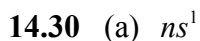
(b) It is relatively easy to remove the one valence electron of the alkali metals. All of them have a low first ionization energy.

14.32 (a) $K(s) + O_2(g) \rightarrow KO_2(s)$

(b) $Na_2O(s) + H_2O(l) \rightarrow 2 NaOH(aq)$

(c) $2 Li(s) + 2 HCl(aq) \rightarrow 2 LiCl(aq) + H_2(g)$

(d) $2\,Cs(l) + I_2(s) \rightarrow 2\,CsI(s)$
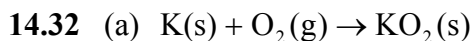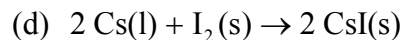
14.34 (a) $\Delta G°_r = -2\Delta G°_f (NaCl, s) = -2(-384.14\ kJ \cdot mol^{-1}) = 768.28\ kJ \cdot mol^{-1}$

(b) The reduction of sodium ions is a one-electron process,
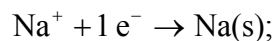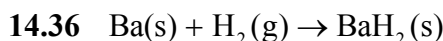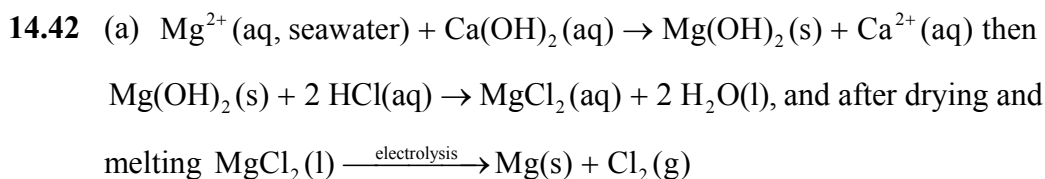
$Na^+ + 1\,e^- \rightarrow Na(s)$;

therefore, $1\ mol\ Na^+ = 1\ mol\ e^-$.

$$current = \left(\frac{400.\ g\ Na}{4.00\ h}\right)\left(\frac{1\ mol\ Na}{22.99\ g\ Na}\right)\left(\frac{96\ 485\ C}{1\ mol\ Na}\right)\left(\frac{1\ h}{3600\ s}\right)$$

$$= 117\ C \cdot s^{-1} = 117\ A$$

14.36 $Ba(s) + H_2(g) \rightarrow BaH_2(s)$

14.38 Due to the greater polarizing ability of the smaller Mg^{2+} ion on the carbonate ion, we expect $MgCO_3$ to be less stable than $CaCO_3$. Therefore, we expect that the oxide formed is MgO and that the carbonate is $CaCO_3$. Furthermore, for $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$, $\Delta G°_r$ is roughly +50 kJ, and for $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta G°_r$ is roughly +130 kJ (as calculated from the data in Appendix 2A). Thus, the formation of MgO versus that of CaO is thermodynamically favored.

14.40 The trend of decreasing lattice enthalpies down the group is related to the size of the ions (which increases down the group). Smaller ions have a greater concentration of charge than larger ions and can more strongly attract ions of opposite charge. Thus, the ions at the top of the group have larger lattice enthalpies than those at the bottom.

14.42 (a) $Mg^{2+}(aq, seawater) + Ca(OH)_2(aq) \rightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$ then

$Mg(OH)_2(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + 2\,H_2O(l)$, and after drying and melting $MgCl_2(l) \xrightarrow{\ electrolysis\ } Mg(s) + Cl_2(g)$

(b) $Ca(s) + 2\,H_2O(l) \rightarrow Ca(OH)_2\,(aq) + H_2\,(g)$

14.44 (a) $Mg(s) + Br_2\,(l) \rightarrow MgBr_2\,(s)$

(b) $3\,BaO(s) + 2\,Al(s) \xrightarrow{\Delta} Al_2O_3\,(s) + 3\,Ba(s)$

(c) $CaO(s) + SiO_2\,(s) \xrightarrow{\Delta} CaSiO_3\,(l)$

14.46

14.48 (a) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2\,(aq)$
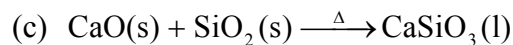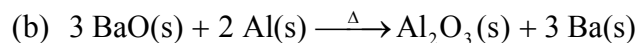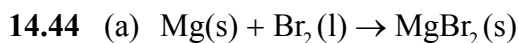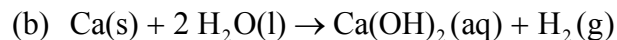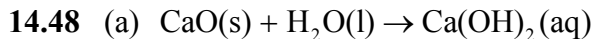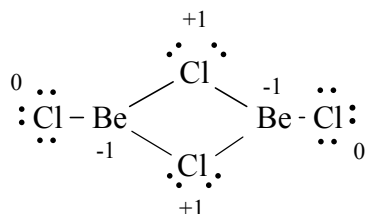
$\Delta H^\circ = -1002\cdot82\ \text{kJ}\cdot\text{mol}^{-1} - (-635.09\ \text{kJ}\cdot\text{mol}^{-1} - 285.83\ \text{kJ}\cdot\text{mol}^{-1})$

$\qquad = -81.9\ \text{kJ}\cdot\text{mol}^{-1}$

$q = 25\ \text{kg CaO}\left(\dfrac{1\ \text{mol CaO}}{56.08\times10^{-3}\ \text{kg CaO}}\right)\left(\dfrac{-81.9\ \text{kJ}}{1\ \text{mole}}\right)$

$\quad = -37\times10^3\ \text{kJ}$

(b) The $Ca(OH)_2\,(aq)$ is first treated with CO_2 to precipitate insoluble $CaCO_3$ from the solution. The $CaCO_3$ is then heated to produce CaO and CO_2.

14.50 $B_2O_3\,(s) + 3\,Mg(s) \xrightarrow{\Delta} 2\,B(s) + 3\,MgO(s)$

14.52 (a) $Al_2O_3\,(s) + 2\,OH^-\,(aq) + 3\,H_2O(l) \rightarrow 2[Al(OH)_4]^-\,(aq)$

(b) $Al_2O_3\,(s) + 6\,H_3O^+\,(aq) + 3\,H_2O(l) \rightarrow 2[Al(H_2O)_6]^{3+}\,(aq)$

(c) $2\,B(s) + 2\,NH_3\,(g) \xrightarrow{\Delta} 2\,BN(s) + 3\,H_2\,(g)$
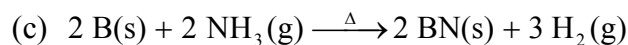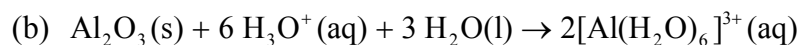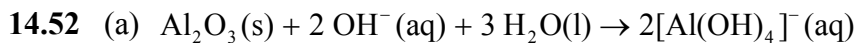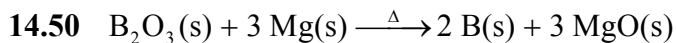
14.54 (a) BF_3: industrial catalyst used for its Lewis acidity

(b) $NaBH_4$: industrial reducing agent

(c) $Al_2(SO_4)_3$ is used in papermaking as a cellulose coagulant.

14.56 (a) Assuming that BF will display the same molecular orbital energy level order as N_2, the ground-state electron configuration will be

$$\sigma_{1s}{}^2\sigma_{1s}^{*}{}^2\sigma_{2s}{}^2\sigma_{2s}^{*}{}^2\pi_{2p}{}^4\sigma_{2p}{}^2 \; ;$$

$$BO = \tfrac{1}{2}(10-4) = 3$$

(b) The molecular orbitals in CO and BF differ in shape and energy since the atoms involved in bonding have different atomic orbital energies and sizes. The orbitals of BF will more closely resemble those of HF while those of CO will more closely resemble those of N_2 (see Chapter 3).

14.58 $2\,Al_2O_3(s) + 3\,C(gr) \rightarrow 4\,Al(s) + 3\,CO_2(g)$
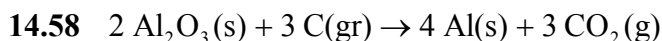
$$3.6\times10^6 \text{ tonnes} = 3.6\times10^9 \text{ kg} = 3.6\times10^{12} \text{ g}$$

mass of carbon lost $= (3.6\times10^{12} \text{ g})$

$$\times\left(\frac{1\text{ mol Al}}{26.98\text{ g Al}}\right)\left(\frac{3\text{ mol C}}{4\text{ mol Al}}\right)\left(\frac{12.01\text{ g C}}{1\text{ mol C}}\right)$$

$$= 1.2\times10^{12} \text{ g C}$$

14.60 $\Delta G°_r = -nFE°$, for $Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$

$$n = 3 = -3\times(9.65\times10^4 \text{ C}\cdot\text{mol}^{-1})(-1.66\text{ V})$$

$$= 4.80\times10^5 \text{ J}\cdot\text{mol}^{-1} = 480 \text{ kJ}\cdot\text{mol}^{-1}$$

The formation reaction for Al^{3+} (aq) is the reverse of the half-reaction above. Therefore, $\Delta G°_f(Al^{3+}, aq) = -480 \text{ kJ}\cdot\text{mol}^{-1}$. The standard free energy of formation of the ions in solution includes contributions from a number of sources, chief among them being the ionization energy of the metal and the hydration energy of the ion. The third ionization energy of Al is less than that of Tl, and its energy of hydration is much greater due

to its much smaller size. So Al^{3+} (aq) has a much greater tendency to form than Ti^{3+}; that is, its $\Delta G°_f$ would tend to be more negative.

14.62 Carbon occurs widely in the earth. Coal is largely carbon, though many other substances are present. Coal is converted into coke by distillation of its volatile components. Pure graphite is obtained from the coke by passing a large electric current through rods of the coke for several days. Carbon black, finely divided graphite, can be produced by the destructive distillation of gaseous hydrocarbons, which can be obtained from petroleum.

14.64 Carbon atoms have a special ability to form π-bonds; silicon atoms do not form them. This can be partly understood in terms of atomic size. In the larger silicon atoms, the sideways overlap of p-orbitals that results in π-bonds becomes much less effective. Because the distance between nuclei is greater in silicon than in carbon, the p-orbitals cannot overlap as strongly. Silicon occurs only in a diamond-like crystalline form; it does not form a graphite-like structure because of the weakness of π-bonding in silicon.
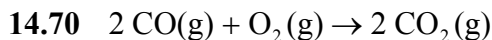
14.66 (a) $Sn(s) + 2\ OH^-(aq) + 2\ H_2O \rightarrow [Sn(OH)_4]^{2-} + H_2(g)$

(b) $C(s) + H_2O(g) \xrightarrow{\Delta} CO(g) + H_2(g)$

(c) $CH_4(g) + H_2O(g) \xrightarrow{800°C,\ Ni} CO(g) + 3\ H_2(g)$

(d) $Al_4C_3(s) + 12\ H_2O(l) \rightarrow 4\ Al(OH)_3(s) + 3\ CH_4(g)$
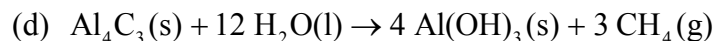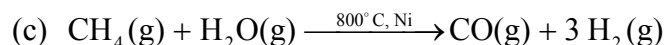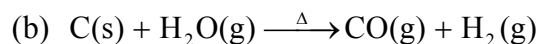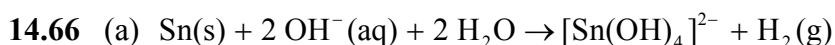
14.68 Refer to Fig. 14.43. Each Si atom is at the center of a tetrahedron formed from four O atoms at the corners. Each corner O atom is joined to another Si atom in a neighboring tetrahedron. The Si—O—Si bond angle should be about 109.5°.

14.70 $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$

$\Delta H°_r = \Delta H°_r(\text{products}) - \Delta H°_r(\text{reactants})$

$\Delta H°_r = (2)(-393.51\ kJ\cdot mol^{-1}) - [(2)(-110.53\ kJ\cdot mol^{-1})]$

$\qquad = -565.96\ kJ\cdot mol^{-1}$

$\Delta S°_r = S°(\text{products}) - S°(\text{reactants})$

$\Delta S°_r = (2)(213.74\ J\cdot K^{-1}\cdot mol^{-1})$

$\qquad - [(2)(+197.67\ J\cdot K^{-1}\cdot mol^{-1}) + 205.14\ J\cdot K^{-1}\cdot mol^{-1}]$

$\Delta S°_r = -173.00\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta G°_r = \Delta H°_r - T\Delta S°_r$

$\Delta G°_r = -565.96\ kJ\cdot mol^{-1}$

$\qquad - (298\ K)(-173.00\ J\cdot K^{-1}\cdot mol^{-1})/(1000\ J\cdot kJ^{-1})$

$\Delta G°_r = -5.144 \times 10^2\ kJ\cdot mol^{-1}$

$\Delta G°_r = -RT\ \ln K = \Delta H°_r - T\Delta S°_r$

when $K = 1$, $\ln K = 0$, $\Delta G°_r = 0$, and $T\Delta S°_r = \Delta H°_r$

$T = \dfrac{\Delta H°_r}{\Delta S°_r} = \dfrac{-565.96 \times 10^3\ J\cdot mol^{-1}}{-173.00\ J\cdot K^{-1}\cdot mol^{-1}} = 3271\ K$ (for $T < 3271\ K$, $K < 1$)

14.72 $SiCl_4$ can act as a Lewis acid, whereas CCl_4 cannot. The silicon atom is much bigger than the carbon atom and can expand its octet by using its *d*-orbitals, so it can accommodate the lone pair of an attacking Lewis base. A carbon atom is much smaller and has no low-lying *d*-orbitals, so it cannot act as a Lewis acid.

14.74 (a) If each silicon tetrahedron shares 2 O atoms, the empirical formula of the anion will be SiO_3^{2-}. This may exist either as rings (as in $Si_3O_9^{6-}$) or in chains. The formula is K_2SiO_3.

(b) If the tetrahedra share 3 O atoms, they will tend to form sheet-like layers of silicate anions. The simplest formula for such an arrangement is $[Si_4O_{10}]^{4-}$ giving a formula of $K_4Si_4O_{10}$ or $K_2Si_2O_4$.

14.76 Fluorite is CaF_2. It reacts with H_2SO_4 as follows:

$$CaF_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + 2\ HF(aq)$$
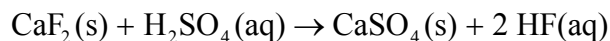
The HF produced in the reaction then etches the glass, forming SiF_6^{2-}.

14.78 $SiO_2 + 2\ OH^- \rightarrow SiO_2(OH)_2^{2-}$

$SiO_2 + 3\ OH^- \rightarrow SiO_3(OH)^{3-} + H_2O$

$SiO_2 + 4\ OH^- \rightarrow SiO_4^{4-} + 2\ H_2O$

$2\ SiO_2 + 6\ OH^- \rightarrow Si_2O_7^{6-} + 3\ H_2O$

$SiO_2 + 2\ OH^- \rightarrow SiO_3^{2-} + H_2O$
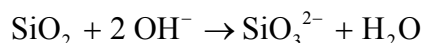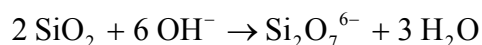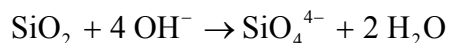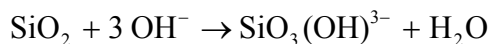
14.80 In the aluminosilicate before heating, the particles are held together by relatively weak forces, such as dipole-dipole interactions and hydrogen bonds. The particles have O—H groups covalently bonded to their surfaces. Heating causes these O—H groups to eliminate water in a procedure analogous to forming an anhydride. When the water is eliminated, the bonds holding the particles together are covalent and the rigidity of the structure is increased.

$-H_2O$

14.82 $Li^+ + e^- \rightarrow Li$ $\qquad\qquad\qquad E° = -3.05 \text{ V}$

$S + 2\,e^- \rightarrow S^{2-}$ $\qquad\qquad\qquad E° = -0.48 \text{ V}$
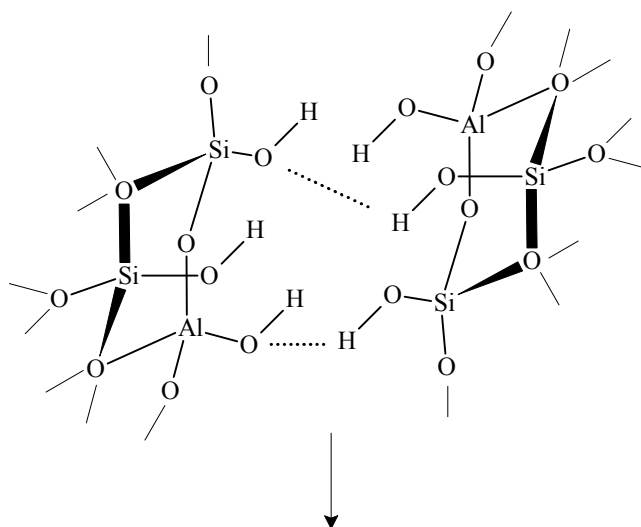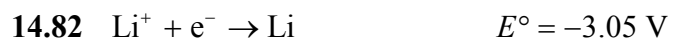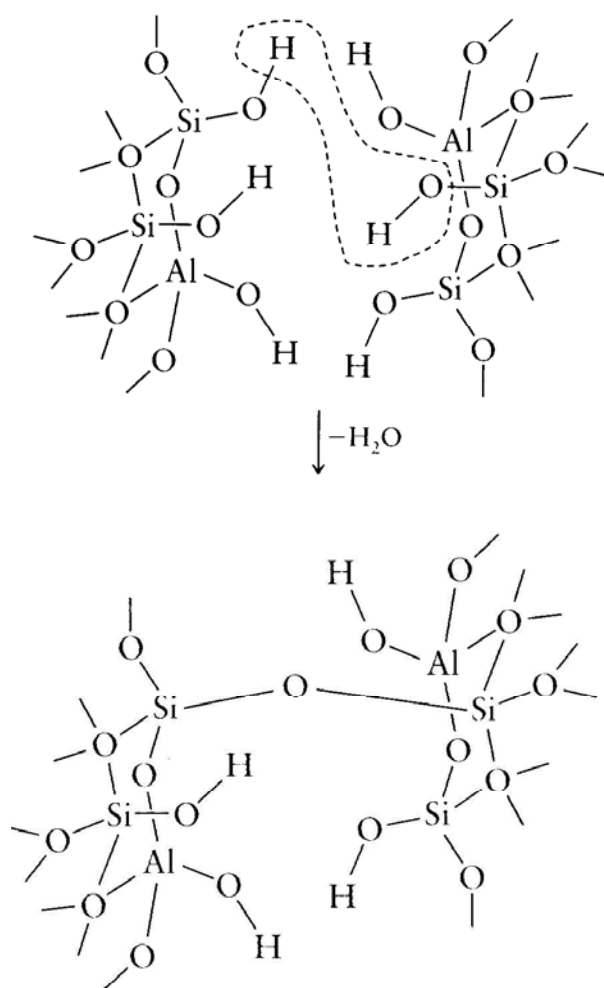
The potential for the overall reaction $2\,Li + S \rightarrow Li_2S$ will be

$E° = -0.48 \text{ V} - (-3.05 \text{ V}) = +2.57 \text{ V}.$

14.84
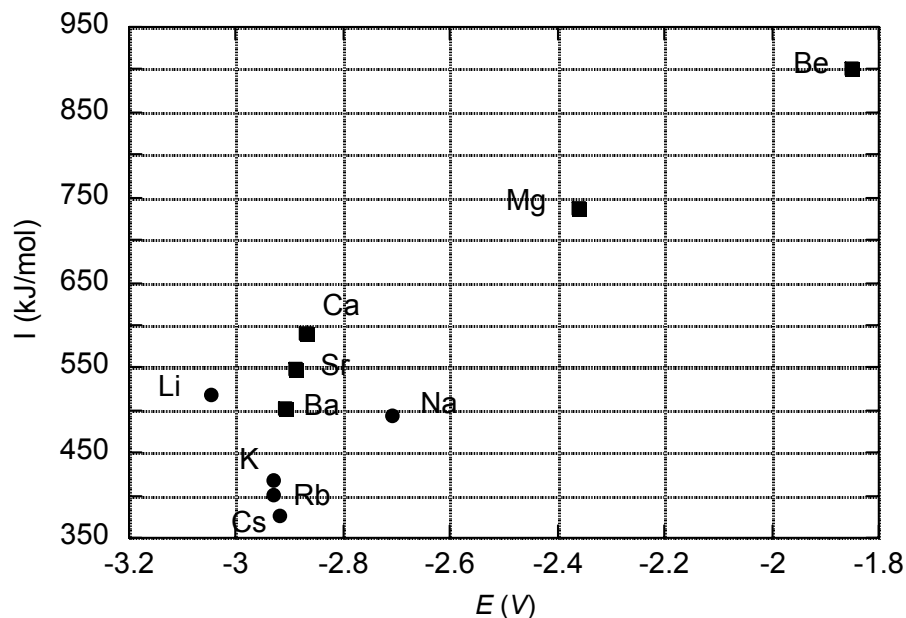
In general, as the atomic number increases down a Group (Group 1 Li to Na, Group 2 Be to Ba), both the first ionization energy and the standard reduction potential decrease (algebraically). This trend is seen more clearly in Group 2 than in Group 1. This correlation between ionization energy and standard reduction potential is not surprising, because both are measures of the ease of removal of electrons from atoms, though under different conditions. Discussion of the anomalous behavior of Li, due to the very small size of Li^+, is given in the solution to Exercise 14.83; this graph confirms the anomaly.

14.86 In aqueous solution, the Be^{2+} ion exists as $[Be(H_2O)_4]^{2+}$. It can react as an acid, with water acting as a base:

$$[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \rightleftharpoons [Be(H_2O)_3OH]^+(aq) + H_3O^+(aq)$$

$$[Be(H_2O)_3OH]^+(aq) + H_2O(l) \rightleftharpoons Be(H_2O)_2(OH)_2 + H_3O^+(aq)$$

$$Be(H_2O)_2(OH)_2(aq) + H_2O(l) \rightleftharpoons [Be(H_2O)(OH)_3]^- + H_3O^+(aq)$$

$$[Be(H_2O)(OH)_3]^- + H_2O(l) \rightleftharpoons [Be(OH)_4]^{2-} + H_3O^+(aq)$$
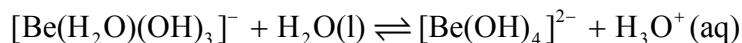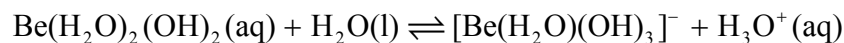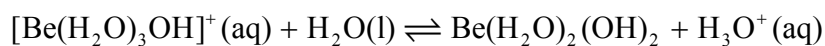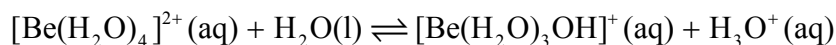
14.88

Element	Electronegativity
Ge	2.0
Sn	2.0
Tl	2.0
In	1.8
Ga	1.6
Al	1.6

		Element	$E°$(V)
Increasing		Al	−1.66
reducing	↑	Ga	−0.53
strength		Tl	−0.34
		Sn	−0.14
		In	−0.14

NOTE: The $E°$ value for Ge is not available in Appendix 2B.

14.90 (a) SiH_4, as opposed to CH_4, can function as a Lewis acid and can consequently accept the lone pair of an attacking Lewis base. This results from the larger size of the Si atom and the presence of low-lying empty d-orbitals, which are not present in carbon.

(b) $SiH_4(g) + 2\ H_2O(l) \xrightarrow{OH^-} SiO_2(s) + 4\ H_2(g)$
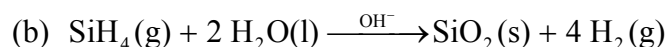
14.92 All ammonium salts are soluble in water, as are all Group 1 salts; all these ions have a $+1$ charge; the ionic radii of the Group 1 cations range from 58 pm for Li^+ to 170 pm for Cs^+, and the ammonium ion is in this range, ~149 pm. The ammonium ion forms ionic compounds analogous to the compounds of the Group 1 cations; for example, NH_4Cl is analogous to $NaCl$, $(NH_4)_2CO_3$ is analogous to Na_2CO_3, etc.

14.94
Mg   [Ne] $3s^2$
Ca   [Ar] $4s^2$
Sr   [Ar] $3d^{10}\ 4s^2\ 4p^6\ 5s^2$
Ba   [Kr] $4d^{10}\ 5s^2\ 5p^6\ 6s^2$
Ra   [Kr] $4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2$
Al   [Ne] $3s^2\ 3p^1$
Ga   [Ar] $3d^{10}\ 4s^2\ 4p^1$

In   [Ar] $3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^1$

Tl   [Kr] $4d^{10}\,4f^{14}\,5s^2\,5p^6\,5d^{10}\,6s^2\,6p^1$

In passing from Mg to Ca down Group 2, the outer electron configuration remains the same, ns^2, so the ionization energy is expected to decrease as electrons in the $4s^2$ sublevel are farther from the nucleus than those in the $3s^2$ sublevel and are well shiel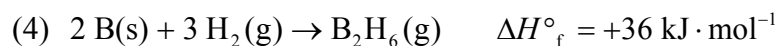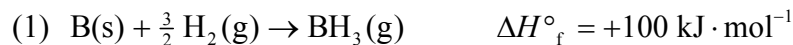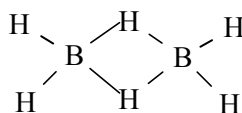ded. In passing from Al to Ga down Group 13, the nuclear charge increases by 18, but the shielding does not increase proportionately, because the electron configuration has changed from ns^2 np^1 to $(n-1)\,d^{10}\,ns^2\,np^1$, and d-electrons are not as effective at shielding outer electrons as s- or p-electrons.   Therefore, the outer electron in Ga "sees" a higher effective nuclear charge than the outer electron in aluminum, and its ionization energy increases rather than decreases. Similar arguments apply to the increase in ionization energy in passing from In to Tl down Group 13. The electron configuration changes by the addition of $(n-2)f^{14}$, and f-electrons do not shield outer electrons very efficiently.

14.96

(1) $B(s) + \frac{3}{2}\,H_2(g) \rightarrow BH_3(g)$ $\Delta H^{\circ}{}_f = +100\ \text{kJ}\cdot\text{mol}^{-1}$

(2) $B(s) \rightarrow B(g)$ $\Delta H^{\circ}{}_f = +563\ \text{kJ}\cdot\text{mol}^{-1}$

(3) $\frac{1}{2}\,H_2(g) \rightarrow H(g)$ $\Delta H^{\circ}{}_f = +218\ \text{kJ}\cdot\text{mol}^{-1}$

(4) $2\,B(s) + 3\,H_2(g) \rightarrow B_2H_6(g)$ $\Delta H^{\circ}{}_f = +36\ \text{kJ}\cdot\text{mol}^{-1}$
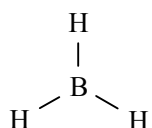
(a) Reverse equation 1, multiply equation 3 by 3, and add to equation 2:

$BH_3(g) \rightarrow B(s) + \frac{3}{2} H_2(g)$ $\Delta H° = -100 \text{ kJ} \cdot \text{mol}^{-1}$

$B(s) \rightarrow B(g)$ $\Delta H° = +563 \text{ kJ} \cdot \text{mol}^{-1}$

$\frac{3}{2} H_2(g) \rightarrow 3 H(g)$ $\Delta H° = 3(218) \text{ kJ} \cdot \text{mol}^{-1}$

$BH_3(g) \rightarrow B(g) + 3 H(g)$ $\Delta H° = +1117 \text{ kJ} \cdot \text{mol}^{-1}$
                             $= 3\Delta H(B - H)$
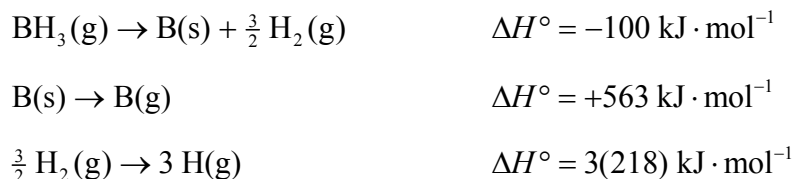
$\Delta H(B - H) = +372 \text{ kJ} \cdot \text{mol}^{-1}$

Assume terminal B—H bonds have the same bond enthalpy as B—H

bonds in BH_3, that is, $372 \text{ kJ} \cdot \text{mol}^{-1}$.

Reverse equation 4, multiply equation 2 by 2, and equation 3 by 6. Then

add.

$B_2H_6(g) \rightarrow 2 B(s) + 3 H_2(g)$ $\Delta H° = -36 \text{ kJ} \cdot \text{mol}^{-1}$

$2 B(s) \rightarrow 2 B(g)$ $\Delta H° = 2 \times 563 \text{ kJ} \cdot \text{mol}^{-1}$

$3 H_2(g) \rightarrow 6 H(g)$ $\Delta H° = 6 \times 218 \text{ kJ} \cdot \text{mol}^{-1}$

$B_2H_6(g) \rightarrow 2 B(g) + 6 H(g)$ $\Delta H° = 2398 \text{ kJ} \cdot \text{mol}^{-1}$
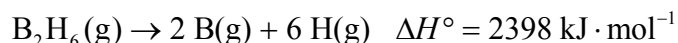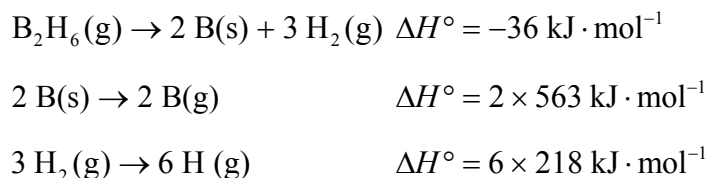
(b) $\Delta H° = 2398 \text{ kJ} \cdot \text{mol}^{-1} = 4 \times \Delta H \text{ (B—H)} + 4 \times \Delta H \text{ (B—H—B)}$

$\Delta H \text{ (B—H—B)} = \dfrac{2398 \text{ kJ} \cdot \text{mol}^{-1} - 4 \times 372 \text{ kJ} \cdot \text{mol}^{-1}}{4}$
                      $= 228 \text{ kJ} \cdot \text{mol}^{-1}$

As bond length and bond enthalpy are (very roughly) inversely related, the

stronger terminal B—H bonds are expected to be shorter.

14.98 (a) sp^2

(b) A tube with a diameter of about 1.3 nm will have a circumference of

$2\pi r$ or πd. Thus, the circumference of a 1.3×10^{-9} m diameter nanotube

will be $(1.3 \times 10^{-9} \text{ m})(\pi) = 4.1 \times 10^{-9}$ m.
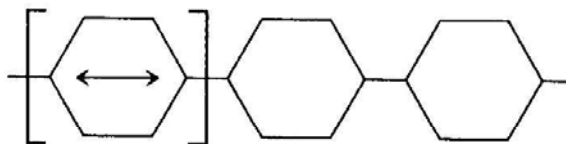
To calculate the number of C_6 rings that will be strung together, we need to calculate the distance across the C_6 ring as shown by the arrow.
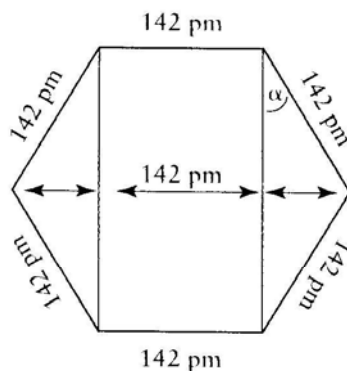

The total distance from one carbon to the opposite carbon on the ring will be given by

$d = 142 \text{ pm} + 2\,(142 \text{ pm} \times \sin 30°) = 284 \text{ pm}$

One repeat unit will be one benzene ring plus one C—C bond,

$284 \text{ pm} + 142 \text{ pm} = 426 \text{ pm or } 4.26 \times 10^{-10} \text{ m}$. There are thus about

$4.1 \times 10^{-9} \div 4.26 \times 10^{-10} = 10$ of units strung together around the smallest

nanotube known.

14.100 The relevant numbers from the Appendices are the atomic radii of Ca and

Sr, and their molar masses. The values are

Element	Atomic radius	Molar mass
Ca	197 pm	$40.08 \text{ g} \cdot \text{mol}^{-1}$
Sr	215 pm	$87.62 \text{ g} \cdot \text{mol}^{-1}$

For a metal that packs in a face-centered cubic lattice, there are a total of

four metal atoms in the unit cell. From Chapter 5 we learned that the edge

length, a, of the unit cell is related to the radius of the atom by the

relationship $4\,r = a\,\sqrt{2}$. Using the atomic radii given above, the unit cell

458

edge lengths for Ca and Sr will be 5.57×10^{-8} cm and 6.08×10^{-8} cm, respectively. The densities will be given by

$$d_{Ca} = \frac{4\left(\dfrac{40.08 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}\right)}{(5.57 \times 10^{-8} \text{ cm})^3} = 1.54 \text{ g} \cdot \text{cm}^{-3}$$

$$d_{Sr} = \frac{4\left(\dfrac{87.62 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}\right)}{(6.08 \times 10^{-8} \text{ cm})^3} = 2.59 \text{ g} \cdot \text{cm}^{-3}$$

Strontium is more dense than calcium.

14.102 In C_{60} the carbon atoms are sp^2 hybridized and are nearly planar. However, the curvature of the molecule introduces some strain at the carbon atoms so that there is some tendency for some of the carbon atoms to undergo conversion to sp^3 hybridization. However, to make every carbon sp^3 hybridized would introduce much more strain on the carbon cage and, after a certain point, further addition of hydrogen becomes unfavorable.

14.104 Both the antisymmetrical stretch (v_3) and the doubly degenerate bend (v_2) are vibrational modes that deform the molecule such that it is lop-sided in terms of its charge distribution and overall dipole moment, so these vibrations can absorb infrared radiation.

14.106 The equation for the process is

$$SiCl_4 + 2 \, H_2(g) \rightarrow Si(s) + 4 \, HCl(g)$$
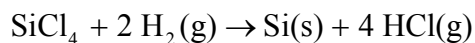
To determine the temperature range for the spontaneity of the reaction, we need to know ΔH°, and ΔS°, for the process. These are easily calculated from the data given and from data in Appendix 2A.

$$\Delta H^\circ_r = 4(\Delta H^\circ_{f,HCl}) - (\Delta H^\circ_{f,SiCl_4})$$
$$= 4(-92.31\ \text{kJ} \cdot \text{mol}^{-1}) - (-662.75\ \text{kJ} \cdot \text{mol}^{-1})$$
$$= +293.51\ \text{kJ} \cdot \text{mol}^{-1}$$
$$\Delta S^\circ_r = 4(S^\circ_{m,HCl}) + S^\circ_{m,Si} - [S^\circ_{m,SiCl_4} + 2S^\circ_{m,H_2}]$$
$$= 4(186.91\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 18.83\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$
$$- [330.86\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(130.68\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})]$$
$$= +174.25\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Because ΔH°_r and ΔS°_r are both positive, the reaction will be spontaneous at elevated temperatures. The temperature at which the process becomes spontaneous can be calculated by determining the temperature at which ΔG°_r is equal to 0.

$$\Delta G^\circ_r = (293.51 \times 10^3\ \text{J} \cdot \text{mol}^{-1}) - T(+174.25\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 0$$
$$T = 1684\ \text{K or } 1411°\text{C}$$

The reaction should be spontaneous approximately at temperatures above 1411°C.

14.108 (a) A reasonable, simple unit cell can be obtained by considering the nitrogen atoms to be at the corners of the unit cell.
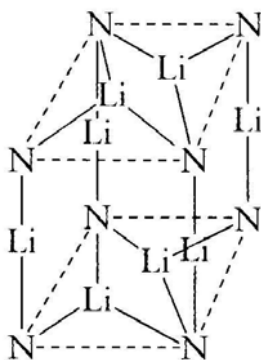
(b) The unit cell appears to be hexagonal.

(c) There is one nitrogen atom ($\frac{1}{8}$ of the eight corners) in the unit cell and three lithium atoms ($\frac{1}{4} \times 4$ atoms along edges plus $\frac{1}{2} \times 4$ atoms in the faces) in this unit cell, giving overall one formula unit per unit cell.

(d) The density is determined from the volume of the unit cell and the mass of the atoms that comprise it. The distances between planes containing the nitrogen atoms will be 2×194 pm $= 338$ pm. The dimensions of the unit cell that lie within the N-containing plane can be calculated using simple geometry, given that all the Li—N distances are 213 pm and all the angles are $60°$.

$$\tfrac{1}{2}d_{\text{N-N}} = 231 \text{ pm} \times \cos 30°$$
$$d_{\text{N-N}} = 2 \times 231 \text{ pm} \times \cos 30°$$
$$= 369 \text{ pm}$$
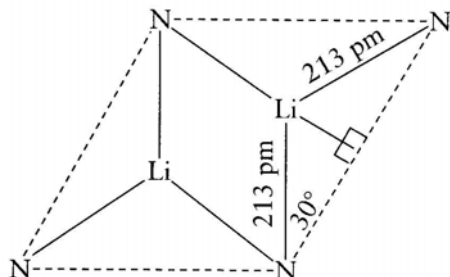
The area of the rhombohedron is given by $b \times h$. We know b, which we have just calculated to be 369 pm. The quantity h can be calculated from $\sin 60° = h/369$ pm or $h = 320$ pm. The area is

$369 \text{ pm} \times 320 \text{ pm} = 1.18 \times 10^5 \text{ pm}^2$. The volume is

$1.18 \times 10^5 \text{ pm}^2 \times 388 \text{ pm} = 4.58 \times 10^7 \text{ pm}^3$ per unit cell. Because one pm is equal to 1×10^{-10} cm, the volume of the unit cell is $4.58 \times 10^{-23} \text{ cm}^3$. There is only one Li_3N formula unit in the unit cell, which will give a mass of $34.83 \text{ g} \cdot \text{mol}^{-1} \div 6.02 \times 10^{23}$ formula

units $\cdot \text{mol}^{-1} = 5.78 \times 10^{-23} \text{ g} \cdot \text{unit cell}^{-1}$.

The density calculated is $5.78 \times 10^{-23} \text{ g} \div 4.58 \times 10^{-23} \text{ cm}^3 = 1.26 \text{ g} \cdot \text{cm}^{-3}$, which agrees with the experimental value.

14.110 (a) The dolomite and calcite structures are essentially identical. The cations and anions are located in the same positions in both structures.

(b) The structures differ in that in one the cations are all Ca^{2+} ions (calcite), and in the other the cations are a mix of Ca^{2+} and Mg^{2+}. (c) The Ca^{2+} ions and Mg^{2+} ions are randomly distributed over the cation positions in the unit cell.

14.112 $2\ CsO_2(s) + CO_2(g) \rightarrow Cs_2CO_3(s) + \frac{3}{2}\ O_2(g)$
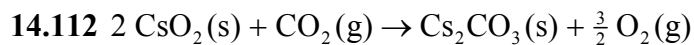
$$n_{O_2} = (30.0\ \text{g})\left(\frac{1\ \text{mol CsO}_2}{164.9\ \text{g CsO}_2}\right)\left(\frac{\frac{3}{2}\ \text{mol O}_2}{2\ \text{mol CsO}_2}\right) = 0.1364\ \text{mol}$$

$$V = \frac{nRT}{P} = (0.1364\ \text{mol})\frac{(0.08206\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})}{(1.00\ \text{atm})}$$

$$= 3.34\ \text{L}$$

14.114