

CHAPTER 14

THE ELEMENTS: THE FIRST FOUR MAIN GROUPS

14.1 (a) carbon (b) lithium (c) indium (d) iodine

14.3 (a) sulfur (b) selenium (c) sodium (d) oxygen

14.5 iodine < bromine < chlorine

14.7 chlorine

14.9 antimony

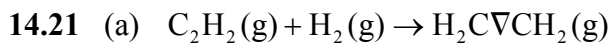
14.11 (a) KCl because the ionic radius of K^+ is larger than that of Na^+
(b) Na—O. The higher charge on Mg^{2+} makes its ionic radius much smaller than that of Na^+ . (c) Thallium(I) chloride because the Tl(I) ion is larger.

14.13 $2 K(s) + H_2(g) \rightarrow 2 KH(s)$

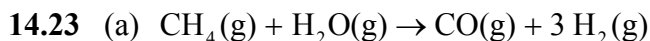
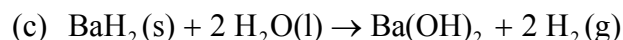
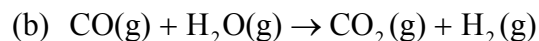
14.15 (a) saline (b) molecular (c) molecular (d) metallic

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

14.19 (a) CO_2 (b) SO_3



Oxidation number of C in $\text{C}_2\text{H}_2 = -1$; of C in $\text{H}_2\text{C}\nabla\text{CH}_2 = -2$, carbon has been reduced.



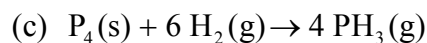
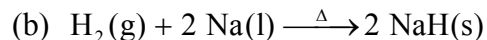
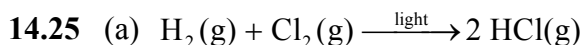
$$\begin{aligned}\Delta H^\circ_{\text{r}} &= \Delta H^\circ_{\text{f}}(\text{CO}, \text{g}) - [\Delta H^\circ_{\text{f}}(\text{CH}_4, \text{g}) + \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}, \text{g})] \\ &= (-110.53 \text{ kJ} \cdot \text{mol}^{-1}) - [(-74.81 \text{ kJ} \cdot \text{mol}^{-1}) + (-241.82 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= +206.10 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

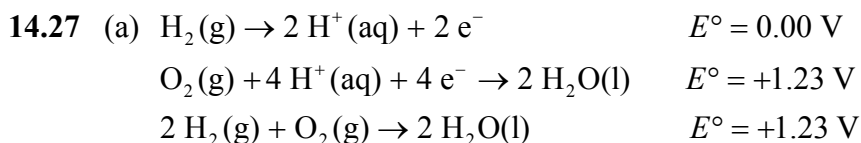
$$\begin{aligned}\text{(b)} \quad \Delta S^\circ_{\text{r}} &= S^\circ(\text{CO}, \text{g}) + 3S^\circ(\text{H}_2, \text{g}) - [S^\circ(\text{CH}_4, \text{g}) + S^\circ(\text{H}_2\text{O}, \text{g})] \\ &= 197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 3(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad - [186.26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= +214.62 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{(c)} \quad \Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{f}}(\text{CO}, \text{g}) - [\Delta G^\circ_{\text{f}}(\text{CH}_4, \text{g}) + \Delta G^\circ_{\text{f}}(\text{H}_2\text{O}, \text{g})] \\ &= (-137.17 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - [(-50.72 \text{ kJ} \cdot \text{mol}^{-1}) + (-228.57 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= +142.12 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$\Delta G^\circ_{\text{r}}$ can also be calculated from $\Delta H^\circ_{\text{r}}$ and $\Delta S^\circ_{\text{r}}$:

$$\begin{aligned}\Delta G^\circ_{\text{r}} &= \Delta H^\circ_{\text{r}} - T\Delta S^\circ_{\text{r}} \\ &= +206.10 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(+214.62 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= +142.14 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

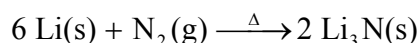




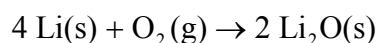
The maximum potential possible is 1.23 V.

(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 hydrogen ions but not hydrogen gas or oxygen gas to pass through would be necessary.

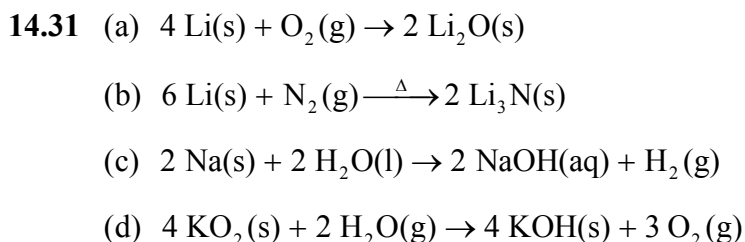
14.29 Lithium is the only Group 1 element that reacts directly with nitrogen to form lithium nitride:



Lithium reacts with oxygen to form mainly the oxide:

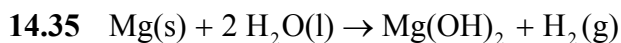


The other members of the group form mainly the peroxide or superoxide. Lithium exhibits the diagonal relationship that is common to many first members of a group. Li is similar in many of its compounds to the compounds of Mg. This behavior is related to the small ionic radius of Li^+ , 58 pm, which is closer to the ionic radius of Mg^{2+} , 72 pm, but substantially less than that of Na^+ , 102 pm.



14.33 1 mol $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ yields 1 mol Na_2CO_3 in water.

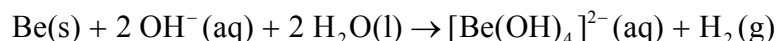
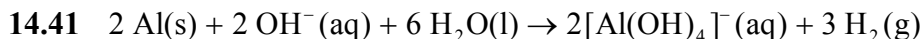
$$\begin{aligned}
 \text{mass of Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O} &= 0.500 \text{ L} \times 0.135 \text{ mol} \cdot \text{L}^{-1} \\
 &\quad \times 286.15 \text{ g Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O} \cdot \text{mol}^{-1} \\
 &= 19.3 \text{ g Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}
 \end{aligned}$$



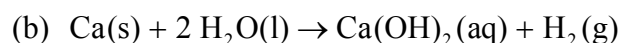
(b)

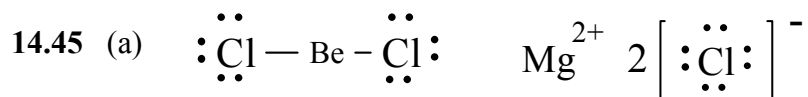
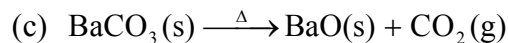
$$\begin{aligned}
 \Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{f}}(\text{Ca(OH)}_2, \text{s}) - [\Delta G^\circ_{\text{f}}(\text{CaO}, \text{s}) + \Delta G^\circ_{\text{f}}(\text{H}_2\text{O}, \text{l})] \\
 &= -898.49 \text{ kJ} \cdot \text{mol}^{-1} - [(-604.03 \text{ kJ} \cdot \text{mol}^{-1}) + (-237.13 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -57.33 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

14.39 Be is the weakest reducing agent; Mg is stronger, but weaker than the remaining members of the group, all of which have approximately the same reducing strength. This effect is related to the very small radius of the Be^{2+} ion, 27 pm; its strong polarizing power introduces much covalent character into its compounds. Thus, Be attracts electrons more strongly and does not release them as readily as other members of the group. Mg^{2+} is also a small ion, 58 pm, so the same reasoning applies to it as well, but to a lesser extent. The remaining ions of the group are considerably larger, release electrons more readily, and are better reducing agents.

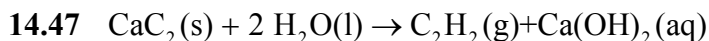


Be and Al are diagonal neighbors in the periodic table and exhibit similar chemical behavior.





MgCl_2 is ionic; BeCl_2 is a molecular compound. (b) 180° (c) *sp*



$$25.0 \text{ g CaC}_2 \times \frac{1 \text{ mole}}{64.10 \text{ g}} = 0.3900 \text{ mol CaC}_2$$

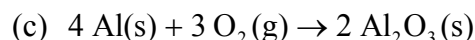
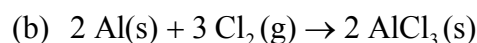
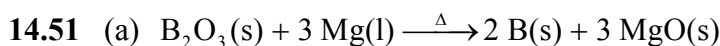
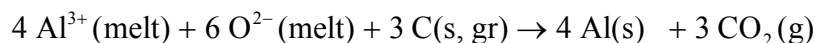
$$25.0 \text{ mL H}_2\text{O} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mole}}{18.02 \text{ g}} = 13.87 \text{ mol H}_2\text{O}$$

Since the reaction is 1:2, only 0.780 mol of water would be needed to completely react with all of the calcium carbide. Calcium carbide is the limiting reagent while water is present in excess.

mass ethyne =

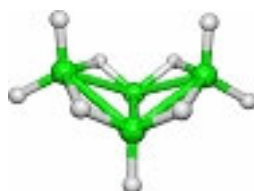
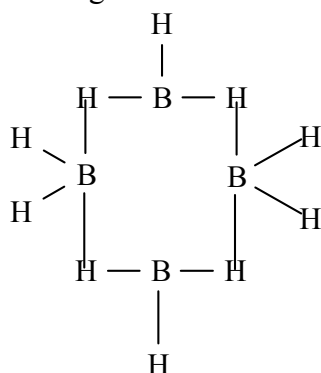
$$0.3900 \text{ mol CaC}_2 \left(\frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol CaC}_2} \right) \left(\frac{26.04 \text{ g C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} \right) = 10.2 \text{ g C}_2\text{H}_2$$

14.49 The overall equation for the electrolytic reduction in the Hall process is



14.53 (a) The hydrate of AlCl_3 , that is, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, functions as a deodorant and antiperspirant. (b) α -Alumina is corundum. It is used as an abrasive in sandpaper. (c) $\text{B}(\text{OH})_3$ is an antiseptic and insecticide.

14.55 Since there are only 22 valence electrons, or 11 electron pairs, it is not possible to draw a good conventional Lewis structure for tetraborane, B_4H_{10} , that includes four B-H-B bridges. For the suggested structure given below, each bridging H and each four-coordinate B would have a formal charge of 1- while each of the six terminal H atoms and each three-coordinate B would have a formal charge of 0. The total formal charge adds up to 6- in this case even though the molecule is neutral. However, if the bridges are viewed as 3-center 2-electron bonds, then every atom can be assigned a formal charge of 0.



This drawing shows the structure of tetraborane

See:

www.chem.leeds.ac.uk/boronweb/articles/incredible_boron/incredible.htm

14.57 The cathode reaction is $Al^{3+}(\text{melt}) + 3 e^{-} \rightarrow Al(l)$

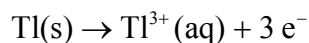
$$\text{charge consumed} = (12.0 \text{ h}) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) (3.0 \times 10^6 \text{ C} \cdot \text{s}^{-1}) = 1.3 \times 10^{11} \text{ C}$$

mass of Al produced

$$\begin{aligned} &= (1.3 \times 10^{11} \text{ C}) \left(\frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \right) \left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \right) \left(\frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \right) \\ &= 1.2 \times 10^7 \text{ g Al} \end{aligned}$$

14.59 (a) We want E° for $\text{Tl}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Tl}(\text{s})$, $n = 3$.

This reaction is the reverse of the formation reaction:



Therefore, for the Tl^{3+}/Tl couple, $\Delta G^\circ_{\text{r}} = -215 \text{ kJ} \cdot \text{mol}^{-1}$

$$\Delta G^\circ_{\text{r}} = -nFE^\circ = -215 \text{ kJ} \cdot \text{mol}^{-1}$$

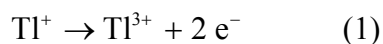
$$E^\circ = \frac{\Delta G^\circ_{\text{r}}}{-nF} = \frac{-2.15 \times 10^5 \text{ J} \cdot \text{mol}^{-1}}{-3 \times 9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}} = +0.743 \text{ V}$$

(b) Using the potential from part (a) and the potential from Appendix 2B

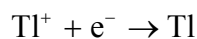
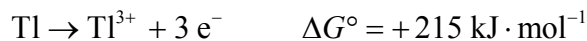
for the reduction of Tl^+ , we can decide whether or not Tl^+ will disproportionate in solution. The equation of interest is



The half-reactions to combine are



The potential for reaction (1) must be obtained using the ΔG° values of the two known half-reactions:



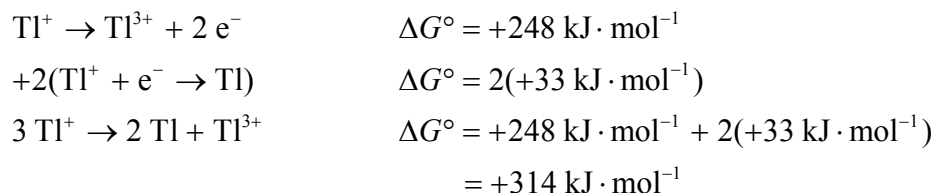
$$\Delta G^\circ = -nFE^\circ$$

$$\begin{aligned} &= -1(9.65 \times 10^4 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})(-0.34 \text{ V})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= +33 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

ΔG° for the combined half-reaction $\text{Tl}^+ \rightarrow \text{Tl}^{3+} + 2 \text{e}^-$ is the sum of these two numbers:

$$+215 \text{ kJ} \cdot \text{mol}^{-1} + 33 \text{ kJ} \cdot \text{mol}^{-1} = +248 \text{ kJ} \cdot \text{mol}^{-1}$$

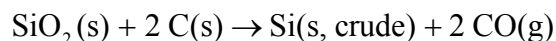
We can now combine this with the reduction process for Tl^+ to get the desired equation:



Since ΔG° is large and positive, $K \ll 1$. This disproportionation reaction does not favor products.

14.61 Silicon occurs widely in the Earth's crust in the form of silicates in rocks and as silicon dioxide in sand. It is obtained from quartzite, a form of quartz (SiO_2), by the following processes:

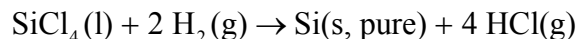
(1) reduction in an electric arc furnace



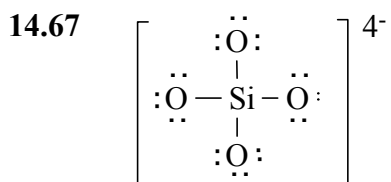
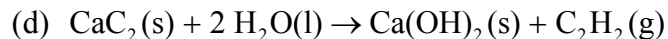
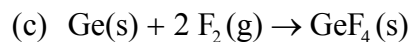
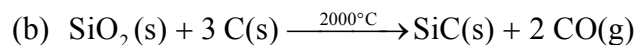
(2) purification of the crude product in two steps



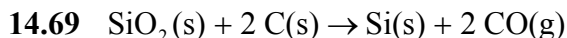
followed by reduction with hydrogen to the pure element



14.63 In diamond, carbon is sp^3 hybridized and forms a tetrahedral, three-dimensional network structure, which is extremely rigid. Graphite carbon is sp^2 hybridized and planar. Its application as a lubricant results from the fact that the two-dimensional sheets can “slide” across one another, thereby reducing friction. In graphite, the unhybridized p -electrons are free to move from one carbon atom to another, which results in its high electrical conductivity. In diamond, all electrons are localized in sp^3 hybridized C—C σ -bonds, so diamond is a poor conductor of electricity.



formal charges: Si = 0, O = -1; oxidation numbers: Si = +4, O = -2; This is an AX₄ VSEPR structure; therefore, the shape is tetrahedral.



$$\begin{aligned} \Delta H^\circ_r &= \Delta H^\circ_f(\text{products}) - \Delta H^\circ_f(\text{reactants}) \\ &= [(2)(-110.53 \text{ kJ} \cdot \text{mol}^{-1})] - [-910.94 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= +689.88 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_r &= S^\circ(\text{products}) - S^\circ(\text{reactants}) \\ &= [18.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + (2)(197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &\quad - [41.84 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + (2)(5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= +360.85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\ &= 689.88 \text{ kJ} \cdot \text{mol}^{-1} - (298.15 \text{ K})(360.85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/1000 \text{ J} \cdot \text{kJ}^{-1} \\ &= +582.29 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The temperature at which the equilibrium constant becomes greater than 1 is the temperature at which $\Delta G^\circ_r = -RT \ln K = 0$, because $\ln 1 = 0$.

Above this temperature, the equilibrium constant is greater than 1. $\Delta G^\circ_r = 0$ when $T\Delta S^\circ_r = \Delta H^\circ_r$, or

$$T = \frac{\Delta H^\circ_r}{\Delta S^\circ_r} = \frac{+689.88 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{+360.85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 1912 \text{ K}$$

$$\begin{aligned}
 \text{14.71 mass of HF} &= (3.00 \times 10^{-3} \text{ g}) \left(\frac{1 \text{ mol SiO}_2}{60.09 \text{ g SiO}_2} \right) \left(\frac{6 \text{ mol HF}}{1 \text{ mol SiO}_2} \right) \left(\frac{20.01 \text{ g HF}}{1 \text{ mol HF}} \right) \\
 &= 5.99 \times 10^{-3} \text{ g HF} = 5.99 \text{ mg HF}
 \end{aligned}$$

14.73 (a) The $\text{Si}_2\text{O}_7^{6-}$ ion is built from two SiO_4^{4-} tetrahedral ions in which the silicate tetrahedra share one O atom. This is the only case in which one O is shared. (b) The pyroxenes, for example, jade, $\text{NaAl}(\text{SiO}_3)_2$, consist of chains of SiO_4 units in which two O atoms are shared by neighboring units. The repeating unit has the formula SiO_3^{2-} . See Fig. 14.39.

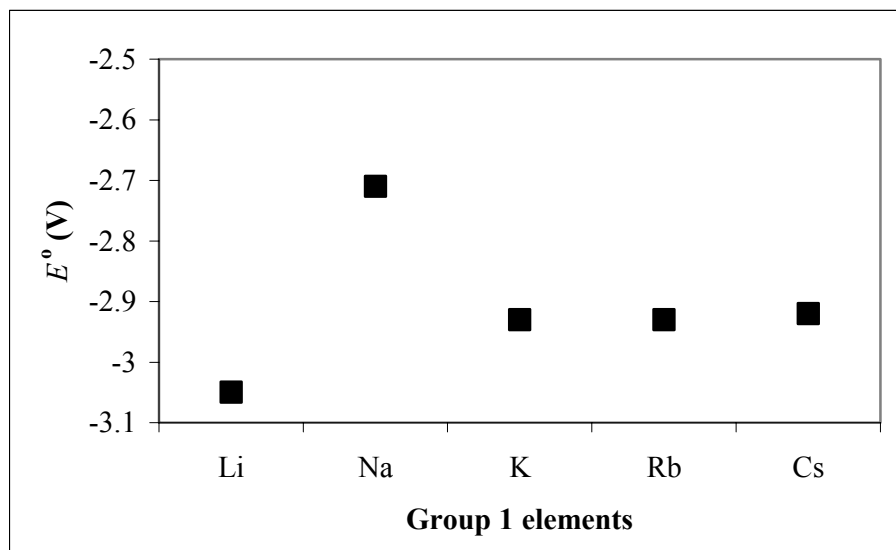
14.75 SiF_6^{2-}

14.77 Ionic fluorides react with water to liberate HF, which then reacts with the glass. Glass bottles used to store metal fluorides become brittle and may disintegrate upon standing on the shelf.

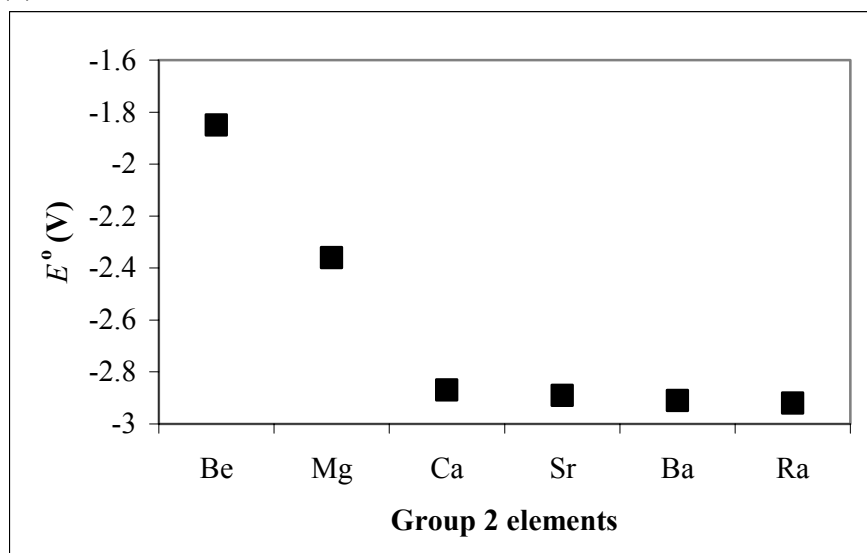
14.79 The iron ions impart a deep red color to the clay, which is not desirable for the manufacture of fine china; a white base is aesthetically more pleasing.

14.81 In the majority of its reactions, hydrogen acts as a reducing agent. Examples are $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$ and various ore reduction processes, such as $\text{NiO}(\text{s}) + \text{H}_2(\text{g}) \xrightarrow{\Delta} \text{Ni}(\text{s}) + \text{H}_2\text{O}(\text{g})$. With highly electropositive elements, such as the alkali metals, $\text{H}_2(\text{g})$ acts as an oxidizing agent and forms metal hydrides, for example, $2 \text{K}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2 \text{KH}(\text{s})$.

14.83 (a)



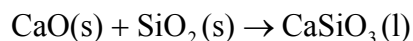
(b)



(b) For both groups, the trend in standard potentials with increasing atomic number is overall downward (they become more negative), but lithium is anomalous. This overall downward trend makes sense, because we expect that it is easier to remove electrons that are farther away from the nuclei. However, because there are several factors that influence ease of removal, the trend is not smooth. The potentials are a net composite of the free energies of sublimation of solids, dissociation of gaseous molecules, ionization enthalpies, and enthalpies of hydration of gaseous

ions. The origin of the anomalously strong reducing power of Li is the strongly exothermic energy of hydration of the very small Li^+ ion, which favors the ionization of the element in aqueous solution.

- 14.85** (a) The oxide ion, O^{2-} , in CaO acts as a Lewis base and reacts with the Lewis acid, SiO_2 , in a Lewis acid-base reaction:

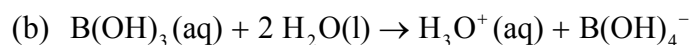


SiO_2 , which is an impurity in iron ore, is removed by this reaction. The calcium oxide in this reaction can be obtained from limestone

$[\text{CaCO}_3\text{(s)} \xrightarrow{\Delta} \text{CaO(s)} + \text{CO}_2\text{(g)}]$. This is the reason that limestone is important in the iron industry.

- (b) $\text{CaO(s)} + \text{CO}_2\text{(g)} \rightarrow \text{CaCO}_3\text{(s)}$ (not an efficient preparation of CaCO_3 , because of the weak Lewis acidity of CO_2).

- 14.87** (a) H_3BO_3 , acid; B(OH)_4^- , conjugate base



- 14.89** (a) The ionization energies decrease down Groups 13/III and 14/IV.

		Ionization energy,	Atomic radius,
Element		$\text{kJ} \cdot \text{mol}^{-1}$	pm
Group 13	B	799	88
	Al	577	143
	Ga	577	153
	In	556	167
	Tl	590	171
Group 14	C	1090	77
	Si	786	118
	Ge	784	122
	Sn	707	158

- (b) The ionization energies generally decrease down a group. As the atomic number of an element increases, atomic shells and subshells that are farther from the nucleus are filled. The outermost valence electrons are consequently easier to remove. The radii increase down a group for the same reason. The radii are primarily determined by the outer shell electrons, which are farther from the nucleus in the heavy elements.
- (c) The trends correlate well with elemental properties; for example, the greater ease of outermost electron removal correlates with increased metallic character, that is, the ability to form positive ions by losing one or more electrons.

14.91 In the majority of its reactions, hydrogen acts as a reducing agent, that is, $\text{H}_2(\text{g}) \rightarrow 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$, $E^\circ = 0 \text{ V}$. In these reactions, hydrogen resembles Group 1 elements, such as Na and K. However, as described in the text and in the answer to Exercise 14.79, it may also act as an oxidizing agent; that is, $\text{H}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{H}^-(\text{aq})$, $E^\circ = -2.25 \text{ V}$. In these reactions, hydrogen resembles Group 17 elements, such as Cl and Br. Consequently, H_2 will oxidize elements with standard reduction potentials more negative than -2.25 V , such as the alkali and alkaline earth metals (except Be). The compounds formed are hydrides and contain the H^- ion; the singly charged negative ion is reminiscent of the halide ions. Hydrogen also forms diatomic molecules and covalent bonds like the halogens. The atomic radius of H is 78 pm, which compares rather well to that of F (64 pm) but not as well to that of Li (157 pm). The ionization energy of H is $1310 \text{ kJ} \cdot \text{mol}^{-1}$, which is similar to that of F ($1680 \text{ kJ} \cdot \text{mol}^{-1}$) but not similar to that of Li ($519 \text{ kJ} \cdot \text{mol}^{-1}$). The electron affinity of H is $+73 \text{ kJ} \cdot \text{mol}^{-1}$, that of F is $+328 \text{ kJ} \cdot \text{mol}^{-1}$, and that of Li is $60 \text{ kJ} \cdot \text{mol}^{-1}$. So in its atomic radius and ionization energy, H more closely resembles the Period 2 halogen, fluorine, in Group 17, than

the Period 2 alkali metal, lithium, in Group 1; whereas in electron affinity, it more closely resembles lithium, Group 1. In electronegativity, H does not resemble elements in either Group 1 or Group 17, although its electronegativity is somewhat closer to those of Group 1. Consequently, hydrogen could be placed in either Group 1 or Group 17. But it is best to think of hydrogen as a unique element that has properties in common with both metals and nonmetals; therefore, it should probably be centered in the periodic table, as it is shown in the table in the text.

14.93

(a) Radius, Polarizing ability			Radius, Polarizing ability		
Ion	pm	($\times 1000$)	Ion	pm	($\times 1000$)
Li ⁺	58	17	Be ²⁺	27	74
Na ⁺	102	9.80	Mg ²⁺	72	28
K ⁺	138	7.25	Ca ²⁺	100	20.0
Rb ⁺	149	6.71	Sr ²⁺	116	17.2
Cs ⁺	170	5.88	Ba ²⁺	136	14.7

(b) These data roughly support the diagonal relationship. Li⁺ is more like Mg²⁺ than Be²⁺, and Na⁺ is more like Ca²⁺ than Mg²⁺; but further down the group, the correlation fails. Charge divided by r^3 would be a better measure of polarizing ability.



$$\begin{aligned} \text{number of moles of HBr} &= (0.135 \text{ L H}_2) \left(\frac{1 \text{ mol H}_2}{22.4 \text{ L H}_2} \right) \left(\frac{2 \text{ mol HBr}}{1 \text{ mol H}_2} \right) \\ &= 0.0121 \text{ mol} \end{aligned}$$

$$\text{molar concentration of HBr} = \frac{0.0121 \text{ mol}}{0.225 \text{ L}} = 0.0538 \text{ mol} \cdot \text{L}^{-1}$$

14.97 The smaller the cation, the greater is the ability of the cation to polarize and weaken the carbonate ion, CO₃²⁻. On that basis, we would predict

that within a group the carbonates of the first members of the group are less stable than those of the later members. Thus, $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$ and $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$. Between groups, we would expect the stability of the carbonates in one period to decrease from Group 1 to Group 13 because of the smaller size of Group 13 ions. Thus, $\text{Al}_2(\text{CO}_3)_3 < \text{MgCO}_3 < \text{Na}_2\text{CO}_3$. Carbonates of Group 13 M^{3+} ions are, in fact, so unstable that they do not exist. Tl_2CO_3 where Tl has an oxidation number of +1 is known, however.

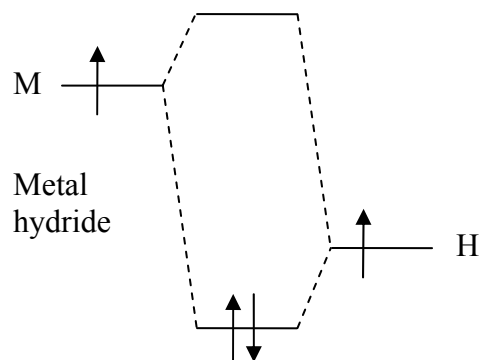
- 14.99** (a) The unit cell described will contain a total of 4 B atoms and 4 N atoms. The volume of the cell is $(361.5 \text{ pm})^3 = (3.615 \times 10^{-8} \text{ cm})^3 = \text{or } 4.724 \times 10^{-23} \text{ cm}^3$. The mass in the unit cell will be

$$(4 \times 10.81 \text{ g} \cdot \text{mol}^{-1} + 4 \times 14.01 \text{ g} \cdot \text{mol}^{-1}) \div 6.022 \times 10^{23} \text{ mol}^{-1} = 1.649 \times 10^{-22} \text{ g}.$$

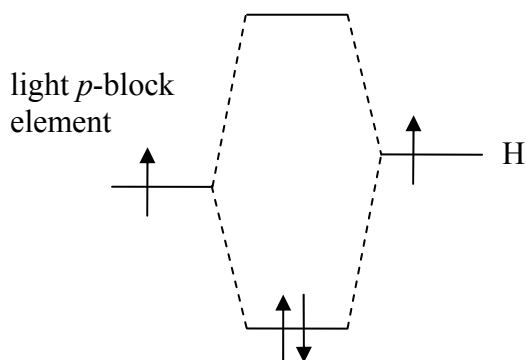
$$d = \frac{1.649 \times 10^{-22} \text{ g}}{4.724 \times 10^{-23} \text{ cm}^3} = 3.491 \text{ g} \cdot \text{cm}^{-3}$$

- (b) Because the density of cubic boron nitride is greater than that of hexagonal BN, we would expect the cubic form to be favored at high pressures, exactly as found for the cubic (diamond) and hexagonal (graphite) forms of carbon.

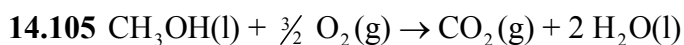
- 14.101** The metal hydride compounds have a molecular orbital structure that is very asymmetric. Because the hydrogen atom is much more electronegative than the metal atom, its orbital lies much lower in energy. Consequently, when a bond is formed, it is a strongly ionic bond with the electrons heavily localized on the H atom.



However, in the case of the lighter *p*-block elements, the electronegativity difference is not so great and the bonding is much more covalent. If anything, the *p*-block element is more electronegative than hydrogen; the bond polarity would lie in the other direction but would be much less pronounced than in the saline hydrides.



14.103 Species (a), (b), (c) and (d) can all function as greenhouse gases while (e) cannot. Any molecule other than a homonuclear diatomic can exhibit a changing dipole moment as it vibrates with certain vibrational modes. Since argon is monoatomic it has no covalent bonds, no vibrational modes, and no dipole moment.



$$\begin{aligned}
 \text{number of kg CO}_2 &= 1.00 \text{ L CH}_3\text{OH} \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{0.791 \text{ g CH}_3\text{OH}}{1 \text{ mL CH}_3\text{OH}} \right) \\
 &\quad \times \left(\frac{1 \text{ mole CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \right) \left(\frac{1 \text{ mole CO}_2}{1 \text{ mole CH}_3\text{OH}} \right) \\
 &\quad \times \left(\frac{44.02 \text{ g CO}_2}{1 \text{ mole CO}_2} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) \\
 &= 0.988 \text{ kg CO}_2
 \end{aligned}$$

This mass of carbon dioxide is about half the amount generated by combusting an equivalent volume of octane (2.16 kg per liter).

However, we also need to consider how much energy is produced per liter of fuel and how the mass of carbon dioxide produced compares for a given amount of energy produced. Standard enthalpies of combustion given in Appendix 2 are

$\Delta H_c^\circ = -5471 \text{ kJ} \cdot \text{mol}^{-1}$ for octane and $\Delta H_c^\circ = -726 \text{ kJ} \cdot \text{mol}^{-1}$ for methanol.

$$\begin{aligned}
 \text{energy per L methanol} &= 1.00 \text{ L CH}_3\text{OH} \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{0.791 \text{ g CH}_3\text{OH}}{1 \text{ mL CH}_3\text{OH}} \right) \\
 &\quad \times \left(\frac{1 \text{ mole CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \right) \left(\frac{726 \text{ kJ}}{1 \text{ mole CH}_3\text{OH}} \right) \\
 &= 1.79 \times 10^4 \text{ kJ} \\
 \text{energy per L octane} &= 1.00 \text{ L C}_8\text{H}_{18} \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{0.703 \text{ g C}_8\text{H}_{18}}{1 \text{ mL C}_8\text{H}_{18}} \right) \\
 &\quad \times \left(\frac{1 \text{ mole C}_8\text{H}_{18}}{114.22 \text{ g C}_8\text{H}_{18}} \right) \left(\frac{5471 \text{ kJ}}{1 \text{ mole C}_8\text{H}_{18}} \right) \\
 &= 3.37 \times 10^4 \text{ kJ}
 \end{aligned}$$

So the combustion of octane produces almost twice as much energy per liter as methanol.

(octane/methanol=1.88)

For an equivalent amount of combustion energy, methanol produces $1.88 \text{ L} \times 1.09 \text{ kg CO}_2 \cdot \text{L}^{-1} = 2.05 \text{ kg CO}_2$, which is still slightly less than octane. (However, it requires that the vehicle carry about 90% more fuel

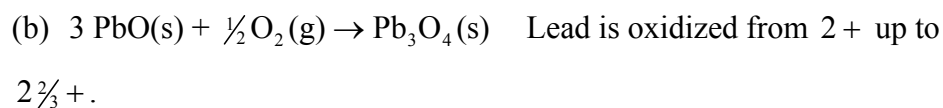
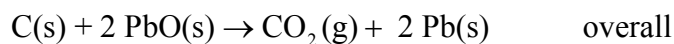
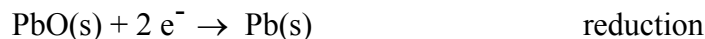
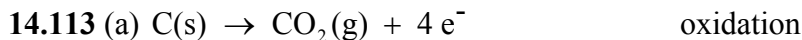
by volume, 1.9 vs. 1 L, and more than twice as much fuel by mass, 1.5 kg vs. 0.7 kg.)

14.107 (a) Diborane, B_2H_6 , and $Al_2Cl_6(g)$ have the same basic structure in the way in which the atoms are arranged in space. (b) The bonding between the boron atoms and the bridging hydrogen atoms is electron deficient. There are three atoms and only two electrons to hold them together in a 3-center-2-electron bond. The bonding in Al_2Cl_6 is conventional in that all the bonds involve two atoms and two electrons. Here, the lone pair of a Cl atom is donated to an adjacent Al. (c) The hybridization is sp^3 at the B and Al atoms. (d) The molecules are not planar. The Group 13 element and the terminal atoms to which it is bound lie in a plane that is perpendicular to the plane that contains the main group element and the bridging atoms.

14.109 (a) By viewing the unit cell from different directions, it is clear that it belongs to a hexagonal crystal system. (b) There are eight carbonate ions on edges, giving $\frac{1}{4} \times 8 = 2$ carbonate ions, plus there are four carbonate ions completely within the unit cell. The total number of carbonate ions in the unit cell is six. Calcium ions lie at the corners of the unit cell ($\frac{1}{8} \times 8 = 1$) as well as on the edges ($4 \times \frac{1}{4}$) and within the cell (4). The total number of calcium ions in the cell is six, agreeing with the overall stoichiometry of calcite, $CaCO_3$.

14.111 There are two Ca^{2+} ions located completely within the cell plus four located on faces ($4 \times \frac{1}{2}$) for a total of four Ca^{2+} ions in the unit cell. Similarly, there are two sulfate ions located completely within the unit cell and four on faces, also giving a total of four sulfate ions in the unit cell.

There are eight water molecules completely inside the unit cell. The overall formula is $\text{Ca}_4(\text{SO}_4)_4(\text{H}_2\text{O})_8$ or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.



$$\begin{aligned} \text{electrons transferred} &= 5.0 \text{ g PbO} \left(\frac{1 \text{ mole PbO}}{223.2 \text{ g PbO}} \right) \left(\frac{1 \text{ mole Pb}_3\text{O}_4}{3 \text{ mole PbO}} \right) \\ &\quad \times \left(\frac{2 \text{ mole e}^-}{1 \text{ mole Pb}_3\text{O}_4} \right) \\ &= 1.5 \times 10^{-2} \text{ mole electrons} \end{aligned}$$

14.115 The spherical structures require the formation of five-membered rings (see structure **10**, C_{60}). Boron nitride cannot form these rings because they would require high-energy boron-boron or nitrogen-nitrogen bonds.