

## Chapter 14

### THE GROUP 14 ELEMENTS

#### Exercises

- 14.2 (a)  $\text{Be}_2\text{C}(s) + 4 \text{H}_2\text{O}(l) \rightarrow 2 \text{Be}(\text{OH})_2(s) + \text{CH}_4(g)$   
(b)  $\text{CO}(g) + \text{Cl}_2(g) \rightarrow \text{COCl}_2(g)$   
(c)  $2 \text{Mg}(s) + \text{CO}_2(g) \rightarrow 2 \text{MgO}(s) + \text{C}(s)$   
(d)  $\text{Na}_2\text{CO}_3(s) + 2 \text{HCl}(aq) \rightarrow 2 \text{NaCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$   
(e)  $\text{BaCO}_3(s) \rightarrow \text{BaO}(s) + \text{CO}_2(g)$   
(f)  $\text{CS}_2(g) + 3 \text{Cl}_2(g) \rightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(l)$   
(g)  $\text{SnO}(s) + 2 \text{HCl}(aq) \rightarrow \text{SnCl}_2(aq) + \text{H}_2\text{O}(l)$
- 14.4 (a) Noncrystalline material (usually solid and transparent).  
(b) Zeolites with pore sizes such that molecules in a certain size range will be absorbed.  
(c) Materials containing cemented grains of metals and ceramic compounds.  
(d) Common name for lead(II) sulfide, the major ore of lead.
- 14.6 (a) Diamond has a high thermal conductivity because its structure consists of carbon atoms held in an infinite network by single covalent bonds. Thus any thermal motion at one side of the crystal lattice is quickly transferred through to the other side, making it an excellent thermal conductor.  
(b) According to Le Chatelier's principle, high pressure would favor formation of diamond from graphite because diamond has the higher density. High temperature would be favored, for the phase change has an extremely high activation energy because rearrangement of covalent bonds must occur.
- 14.8 The formation of carbon-carbon chains is favored because the energy of these bonds is little different than that of carbon-oxygen bonds. Thus, on exposure to air, carbon-carbon bonds will be comparatively stable. For silicon, however, silicon-silicon bonds are much weaker than silicon-

oxygen bonds, thus catenated silicon compounds rapidly oxidize in the presence of air.

- 14.10 The unit cell of calcium carbide contains four pairs of ions (as NaCl structure). Thus:

$$\text{Mass} = \frac{4 \times 64.1 \text{ g} \cdot \text{mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 4.26 \times 10^{-22} \text{ g}$$

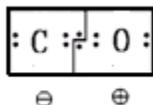
$$\text{Volume} = \frac{4.26 \times 10^{-22} \text{ g}}{2.22 \text{ g} \cdot \text{cm}^{-3}} = 1.92 \times 10^{-22} \text{ cm}^3 = 1.92 \times 10^8 \text{ pm}^3$$

$$\text{Length of side} = \sqrt[3]{(1.92 \times 10^8 \text{ pm}^3)} = 577 \text{ pm}$$

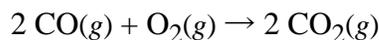
$$\text{Sum of ionic radii} = (577 \text{ pm})/2 = 288 \text{ pm}$$

$$\text{Thus } r(\text{C}_2^{2-}) = 288 \text{ pm} - 114 \text{ pm} = 174 \text{ pm}$$

- 14.12 The formal charge representation is as follows, showing the carbon with a formal negative charge.

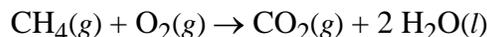


- 14.14 Both gases are colorless and odorless, but carbon monoxide is poisonous as a result of its strong reaction with hemoglobin; carbon dioxide is nontoxic. Carbon monoxide is chemically reactive; for example, it burns in air:



Carbon dioxide is chemically unreactive; for example, it does not react with dioxygen.

- 14.16 The chemical equation is



$$\begin{aligned} \Delta H^\circ &= [1(-394) + 2(-286) - 1(-75) - 1(0)] \text{ kJ} \cdot \text{mol}^{-1} \\ &= -891 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= [1(+214) + 2(+70) - 1(+186) - 1(+205)] \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= -37 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -0.037 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$



- 14.30 The absorption of water must be a very exothermic process (because the expulsion is very endothermic).
- 14.32 Tin forms two oxides, SnO and SnO<sub>2</sub>, while lead forms three, PbO, Pb<sub>3</sub>O<sub>4</sub>, and PbO<sub>2</sub>. For tin, the tin(IV) oxide is the thermodynamically stable oxide; lead(II) oxide is the most stable for lead, the lead(IV) oxide being a good oxidizing agent. The oxide Pb<sub>3</sub>O<sub>4</sub> contains alternating Pb<sup>2+</sup> and Pb<sup>4+</sup> ions.
- 14.34 Lead(IV) fluoride has the characteristic melting point of an ionic compound, while the melting point of lead(IV) chloride is characteristic of a covalent compound. The high charge density lead(IV) ion would be expected to polarize the chloride ions to the point at which covalent bond formation occurs.
- 14.36 In an analogous decomposition (in the absence of atmospheric oxygen) to that of CaCO<sub>3</sub>,
- $$\text{CaCS}_3(s) \xrightarrow{\Delta} \text{CaS}(s) + \text{CS}_2(l)$$
- 14.38 Be<sub>2</sub>C and Al<sub>4</sub>C<sub>3</sub>. They are diagonally related (see Chapter 9).
- 14.40 Tetraethyllead was introduced as a gasoline additive for the enhancement of the octane rating. Though it has been realized that the compound itself is toxic and that its use in gasoline results in elevated lead levels in the environment, TEL is still used in much of the developing countries where environmental controls are less stringent.

### Beyond the Basics

- 14.42 The half-reactions are:



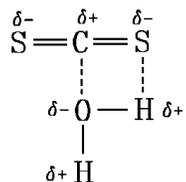
As the E° values sum to a positive value, the iodide ion will spontaneously reduce lead(IV) ion to lead(II) ion (in aqueous solution).

- 14.44 Lead is found in former industrial sites, in old lead-based paint, and in cigarettes. In many parts of the world, lead-containing gasolines are still

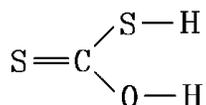
used; thus the motor vehicles in those countries produce high levels of tiny lead particles.



The transition state for the attack is possibly:

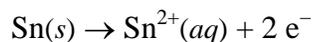


while the possible intermediate follows. This might be feasible, as it has an analogous structure to carbonic acid,  $\text{H}_2\text{CO}_3$ .

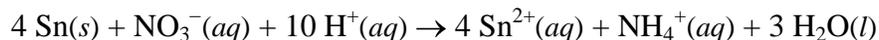


14.48 The structure of methyl isocyanate is what one would expect, but the linear arrangement of silyl isocyanate suggests some multiple bonding involving the *d* orbitals of the silicon.

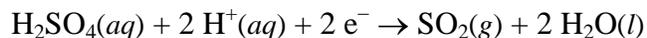
14.50 With dilute nitric acid, half-reactions are



Net ionic equation:



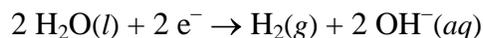
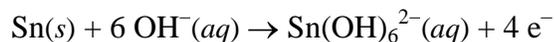
With concentrated sulfuric acid (assuming sulfuric acid is molecular at high concentration), half-reactions are



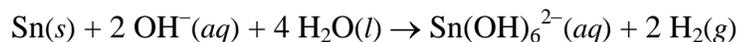
Net ionic equation:



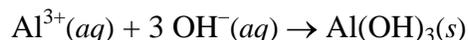
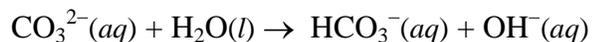
With potassium hydroxide solution, half-reactions are



Net ionic equation:



- 14.52 Because carbonate ion is the conjugate base of the very weak acid, hydrogen carbonate, the following equilibrium lies to the right, and it is the hydroxide ion from this equilibrium that precipitates the aluminum ion. The hydroxide of aluminum must be more insoluble than the carbonate.



- 14.54 We can find the moles of gas X using the Ideal Gas Equation,  $PV = nRT$ :

$$n = \frac{PV}{RT} = \frac{(100 \text{ kPa})(0.244 \text{ L})}{(8.31 \text{ kPa} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} = 9.85 \times 10^{-3} \text{ mol}$$

Thus the molar mass of gas =  $62.9 \text{ g} \cdot \text{mol}^{-1}$

Next we calculate the moles of hydrogen gas:

$$n_{\text{H}_2} = \frac{PV}{RT} = \frac{(100 \text{ kPa})(0.730 \text{ L})}{(8.31 \text{ kPa} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} = 2.95 \times 10^{-2} \text{ mol}$$

and the moles of silicon:

$$n_{\text{Si}} = 1.200 \text{ g} \times \frac{1 \text{ mol SiO}_2}{60.1 \text{ g}} \times \frac{1 \text{ mol Si}}{1 \text{ mol SiO}_2} = 2.00 \times 10^{-2} \text{ mol}$$

Thus in 1 mol of gas X, there are

$$\frac{2.00 \times 10^{-2} \text{ mol Si}}{9.85 \times 10^{-3} \text{ mol X}} : \frac{2.93 \times 10^{-2} \text{ mol H}_2}{9.85 \times 10^{-3} \text{ mol X}} = 2.02 \text{ mol Si} : 2.97 \text{ mol H}_2$$

Molecular formula =  $\text{Si}_2\text{H}_6$

- 14.56 Aluminum has one electron less than silicon, and phosphorus has one electron more than silicon, so one can use the “combo” element analogy similar to the resemblance of boron-nitrogen compounds to those of carbon (Chapter 9). Thus it is not unreasonable for this compound to have the quartz structure with the framework of alternating aluminum and phosphorus atoms substituting for silicon atoms.

- 14.58 The covalent radius of silicon is much greater than that of carbon. Thus the greater mass is more than compensated for by the larger bond lengths.
- 14.60 With each terminal oxygen atom having an oxidation state of  $-2$  and the bridging peroxy- oxygen atoms having a  $-1$  oxidation state, then that of each carbon has to have an oxidation state of  $+3$  (see below).

