Chapter 14

THE GROUP 14 ELEMENTS

Exercises

14.1 (a) $Li_2C_2(s) + 2\ H_2O(l) \rightarrow 2\ LiOH(aq) + C_2H_2(g)$

(b) $SiO_2(s) + 2\ C(s) \rightarrow Si(l) + 2\ CO(g)$

(c) $CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$

(d) $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

$CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca(HCO_3)_2(aq)$

(e) $CH_4(g) + 4\ S(l) \rightarrow CS_2(g) + 2\ H_2S(g)$

(f) $SiO_2(s) + 2\ Na_2CO_3(l) \rightarrow Na_4SiO_4(s) + 2\ CO_2(g)$

(g) $PbO_2(s) + 4\ HCl(aq) \rightarrow PbCl_4(aq) + 2\ H_2O(l)$

$PbCl_4(aq) \rightarrow PbCl_2(s) + Cl_2(g)$

14.3 (a) The ability of an element to form chains of its atoms.

(b) Silicates in which there are numerous cavities in the structure resulting in very low densities.

(c) Non-metallic inorganic compounds prepared by high temperature synthesis.

(d) Chains of alternating silicon and oxygen atoms to which organic (carbon-containing) side groups are attached.

14.5 Diamond is a very hard, transparent, colorless solid that is a good conductor of heat but a non-conductor of electricity. It is insoluble in all solvents and it is chemically unreactive except upon heating in dioxygen. Graphite is a soft, slippery, black solid that is a poor conductor of heat but a good conductor of electricity. It is insoluble in all solvents and will react chemically with only very reactive elements such as dioxygen and difluorine. C_{60} is black and a nonconductor of heat and electricity. It is soluble in many nonpolar and low-polarity solvents and it is quite reactive chemically.

14.7 Diamond and graphite both have network covalent bonded structures. The solvation process cannot provide the energy necessary to break nonpolar covalent bonds. The fullerenes consist of discrete molecules, such as C_{60}.

These individual nonpolar units can become solvated by nonpolar or low-polarity solvent molecules and hence dissolve.

14.9 The three classes are ionic, covalent, and metallic. Ionic carbides are formed by the most electropositive metals. These may contain the dicarbide(2–) ion, C_2^{2-}, or the true carbide ion C^{4-}. Both types of ionic carbides react with water to produce the appropriate hydrocarbon. Covalent carbides are formed by nonmetals, specifically boron and silicon, more electronegative than carbon. These carbides are very hard and have high melting points. The metallic carbides are interstitial carbides, in that the carbon atoms fit in interstices within the metal structure. As such, they have many metallic properties, such as hardness, metallic luster, and electrical conductivity.

14.11 The chemical equation is

$$SiO_2(s) + 3\ C(s) \rightarrow SiC(s) + 2\ CO(g)$$

and with the net increase of two moles of gas, the reaction should be entropy driven. The need for high-temperature synthesis might indicate that there is not only a high activation energy but also the possibility of the reaction being endothermic (according to Le Chatelier's principle).

$$\Delta H^\circ = [1(-65) + 2(-111) - 1(-911) - 3(0)]\ \text{kJ·mol}^{-1}$$
$$= +624\ \text{kJ·mol}^{-1}$$

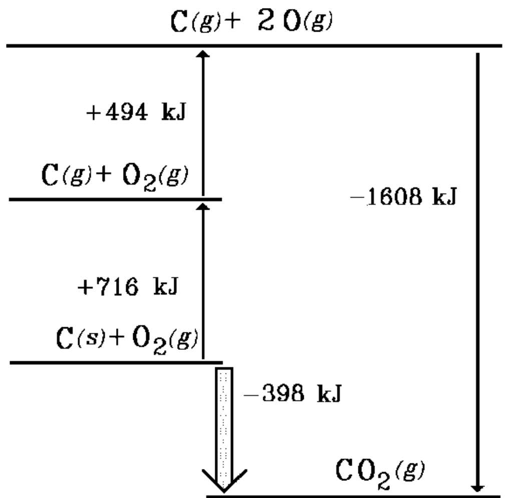
$$\Delta S^\circ = [1(+17) + 2(+198) - 1(+41) - 3(6)]\ \text{J·mol}^{-1}\text{·K}^{-1}$$
$$= +354\ \text{J·mol}^{-1}\text{·K}^{-1} = +0.354\ \text{kJ·mol}^{-1}\text{·K}^{-1}$$

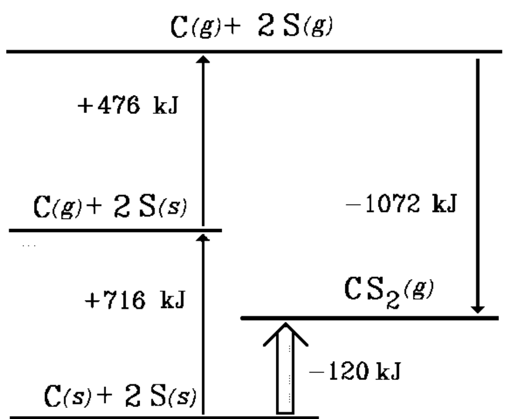
Thus there is indeed a substantial increase in entropy (the driving force for the reaction), while the reaction is also very endothermic.

$$\Delta G^\circ = (+624\ \text{kJ·mol}^{-1}) - (2273\ \text{K})(+0.354\ \text{kJ·mol}^{-1}\text{·K}^{-1})$$
$$= -181\ \text{kJ·mol}^{-1}$$

At this temperature the reaction is spontaneous.

14.13 As can be seen from the enthalpy of the following formation diagrams, it is the lower bond energy of the C=S bond compared to the C=O bond that makes such a large difference in the enthalpy of formation values.





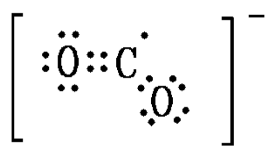
14.15 Because the central carbon atom must form two σ bonds to the sulfur atoms, we assume that *sp* hybrid orbitals are formed. Like carbon dioxide, we consider that the 2*p* orbitals at right angles to the *sp* hybrid orbitals overlap with 3*p* orbitals of the sulfur to provide a pair of π bonds.

14.17 We explain the high activation energy of methane in terms of the lack of any empty orbitals on the carbon atoms that can be used for intermediate formation in the oxidation process. Silicon in the comparable silane molecule has empty 3*d* orbitals that can be involved in the oxidation process.

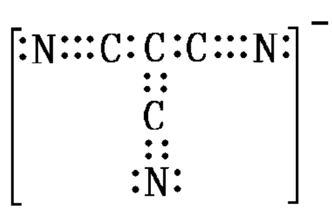
14.19 The synthesis of HFC-134a requires a complex, expensive multistep procedure. Also, higher pressures are necessary for its liquefaction, compared with the CFCs, making it necessary to completely replace the old refrigeration units when changing to HFC-134a.

14.21 Methane is a particularly potent greenhouse gas because it absorbs wavelengths in the infrared region that are currently transparent.

14.23 This ion is isoelectronic with nitrogen dioxide. It has a single unpaired electron, so the bond angle is greater than 120º. The bond order would be about 1½ compared to 2 in carbon dioxide.



14.25 Trigonal planar, because there appear to be three bonding directions around the central carbon. This would be one of three possible resonance structures resulting in an extended π-bond system throughout the ion. The average carbon-carbon bond order is $1^{1}/_{3}$.



14.27 Because the Si_4O_{11} unit has a charge of 6–, for neutrality in the compound the five iron ions must have a total charge of 12+. If the number of Fe^{2+} ions is x and the number of Fe^{3+} ions is y, we can say:

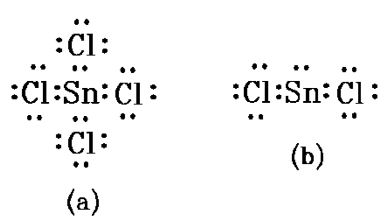
$$x(+2) + y(+3) = +12$$

but $(x + y) = 5$, the sum of the iron ions. Hence by substitution, $x = 3$ and $y = 2$. Thus there are three Fe^{2+} ions and two Fe^{3+} ions per formula.

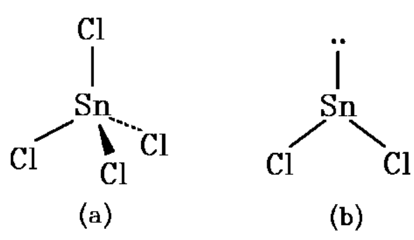
14.29 Zeolites are used as ion exchangers for water; as adsorption agents, particularly for water in organic solvents; for gas separation, particularly dioxygen and dinitrogen from air; and most important, as specialized catalysts, particularly in the oil industry.

14.31 Silicone polymers are very stable chemically. Thus any polymer molecules that leak from the plastic sac in breast implants cannot be broken down by normal bodily processes.

14.33 Electron-dot structures of tin(IV) chloride and tin(II) chloride:



The corresponding molecular shapes (tetrahedral and V-shaped) according to VSEPR theory:



14.35 The half-equations are:

$$PbO(s) + H_2O(l) \rightarrow PbO_2(s) + 2\ H^+(aq) + 2\ e^-$$

$$PbO(s) + 2\ H^+(aq) + 2\ e^- \rightarrow Pb(s) + H_2O(l)$$

14.37 CN^- and CO are the most common species isoelectronic with C_2^{2-}.

14.39 The major problem with inorganic polymer chemistry is the lack of the range of synthetic pathways compared with those available for organic polymer synthesis.

14.41 Carbon:

$4\,CO(g) + Ni(s) \rightarrow Ni(CO)_4(g)$

$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$

$CO(g) + S(s) \rightarrow COS(g)$

$HCOOH(l) \xrightarrow{H_2SO_4} CO(g) + H_2O(l)$

$CO_2(g) + 2\,Ca(s) \rightarrow C(s) + 2\,CaO(s)$

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

$CO(g) + 2\,H_2(g) \xrightarrow{\text{catalyst}} CH_3OH(l)$

$2\,C(s) + O_2(g) \rightarrow 2\,CO(g)$

$C(s) + O_2(g) \rightarrow CO_2(g)$

$Na_2C_2(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + C_2H_2(g)$

$2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l)$

$Al_4C_3(s) + H_2O(l) \rightarrow 3\,CH_4(g) + 4\,Al(OH)_3(s)$

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$

$CH_4(g) + 4\,S(l) \rightarrow CS_2(g) + 2\,H_2S(g)$

$CS_2(g) + 3\,Cl_2(g) \rightarrow CCl_4(g) + S_2Cl_2(l)$

$CS_2(g) + S_2Cl_2(l) \rightarrow CCl_4(g) + 6\,S(s)$

$CH_4(g) + NH_3(g) \rightarrow HCN(g) + 3\,H_2(g)$

$HCN(aq) + H_2O(l) \rightarrow H_3O^+(aq) + CN^-(aq)$

$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$

Silicon:

$Si(s) + HCl(g) \rightarrow SiHCl_3(g) + H_2(g)$

$2\ CH_3Cl(g) + Si(s) \rightarrow (CH_3)_2SiCl_2(l)$

$SiO_2(s) + 2\ C(s) \rightarrow Si(s) + 2\ CO(g)$

$SiO_2(s) + 6\ HF(aq) \rightarrow SiF_6^{2-}(aq) + 2\ H^+(aq) + 2\ H_2O(l)$

$SiO_2(s) + 2\ NaOH(l) \rightarrow Na_2SiO_3(s) + H_2O(g)$

$SiO_2(s) + 3\ C(s) \rightarrow SiC(s) + 2\ CO(g)$

$SiO_2(s) + 2\ Na_2CO_3(l) \xrightarrow{\Delta} Na_4SiO_4(s) + 2\ CO_2(g)$

$2\ SiO_4^{4-}(aq) + 2\ H^+(aq) \rightarrow Si_2O_7^{6-}(aq) + H_2O(l)$

Beyond the Basics

14.43 Lead(II) ion has a similar charge density to that of the calcium ion. Thus it will readily replace calcium ion in the bone structure.

14.45 At high temperatures, the sodium and calcium ions can leach out of the glass structure. This will result in the loss of transparency.

14.47 (a) A six-membered ring structure, Si_3O_3, with alternating silicon and oxygen atoms. Each silicon atom has two singly bonded oxygen atoms attached to it.

(b) $P_3O_9^{3-}$

(c) S_3O_9. In fact, this is the common form of sulfur trioxide; see Chapter 16.

14.49 Tin(II) chloride is the Lewis acid because it is an electron pair acceptor, while the chloride ion, the Lewis base, is an electron pair donor.

14.51 $Mg_2SiO_4(s) + 2$ "$H_2CO_3(aq)$" $\rightarrow 2\ MgCO_3(s) + SiO_2(s) + 2\ H_2O(l)$

14.53 A = CH_4; B = S; C = CS_2; D = H_2S; E = Cl_2; F = CCl_4

$CH_4(g) + 4\ S(s) \rightarrow CS_2(g) + 2\ H_2S(g)$

$CS_2(g) + 2\ Cl_2(g) \rightarrow CCl_4(g) + 2\ S(s)$

$CH_4(g) + 4\ Cl_2(g) \rightarrow CCl_4(g) + 4\ HCl(g)$

14.55 To solve this problem, we need to assume that the ethyl, C_2H_5, unit remains intact. For compound Y,

$$\text{mol Sn} = 0.1240\text{ g} \times \frac{1\text{ mol SnO}_2}{150.5\text{ g}} \times \frac{1\text{ mol Sn}}{1\text{ mol SnO}_2} = 8.239 \times 10^{-4}\text{ mol Sn}$$

We can convert to the mass of tin and subtract from the mass of compound, find the mass of ethyl units, and then determine moles. Alternatively, we can find the molar mass of the compound (assuming it contains one tin), subtract the molar mass of tin, and then determine the number of ethyl units. The latter method will be used here.

$$\text{molar mass Y} = \frac{0.1935\text{ g}}{8.239 \times 10^{-4}\text{ mol}} = 234.9\text{ g}\cdot\text{mol}^{-1}$$

$234.9\text{ g}\cdot\text{mol}^{-1} = [118.7 + n(29.0)]\text{ g}\cdot\text{mol}^{-1}$

$n = 4.00$

Thus the formula of Y is $Sn(C_2H_5)_4$

For compound Z, we will first work out the mass of tin(IV) oxide and silver chloride produced from 1.000 g of Z.

Mass SnO_2 = (0.1164 g)/(0.1865 g Z) = 0.6241 g

Mass AgCl = (0.1332 g)/(0.2240 g Z) = 0.5946 g

$$\text{mol Sn} = 0.6241\text{ g} \times \frac{1\text{ mol SnO}_2}{150.5\text{ g}} \times \frac{1\text{ mol Sn}}{1\text{ mol SnO}_2} \times \frac{118.7\text{ g}}{1\text{ mol Sn}} = 0.4922\text{ g Sn}$$

$$\text{mol Cl} = 0.5946\text{ g} \times \frac{1\text{ mol AgCl}}{143.4\text{ g}} \times \frac{1\text{ mol Cl}}{1\text{ mol AgCl}} \times \frac{35.45\text{ g}}{1\text{ mol Cl}} = 0.1470\text{ g Cl}$$

Mass C_2H_5 = 1.000 g – 0.4922 g – 0.1470 g = 0.3608 g C_2H_5.

$$\text{mole ratios} = \frac{0.4922\text{ g Sn}}{118.7\text{ g}\cdot\text{mol}^{-1}} : \frac{0.1470\text{ g Cl}}{35.45\text{ g}\cdot\text{mol}^{-1}} : \frac{0.3608\text{ g C}_2\text{H}_5}{29.04\text{ g}\cdot\text{mol}^{-1}}$$

$= 4.147\times10^{-3}$ mol Sn : 4.147×10^{-3} mol Cl : 1.242×10^{-2} mol C_2H_5

= 1 Sn : 1 Cl : 3 C_2H_5

Thus the formula of Z is $SnCl(C_2H_5)_3$

Equation for the reaction:

$3\ Sn(C_2H_5)_4(l) + SnCl_4(l) \rightarrow 4\ SnCl(C_2H_5)_3(l)$

This is also compatible with the information that 1.41 g of Y reacts with 0.52 g of tin(IV) chloride to give 1.93 g of Z, since the mass of Z being the sum of the masses of the reactants means there is no other product.

14.57 First we need the values for ΔH° and ΔS° of $Ca(HCO_3)_2$, which we can find by summing the values for the individual ions:

$\Delta H^\circ = [(-543) + 2(-690)]\ kJ{\cdot}mol^{-1} = -1923\ kJ{\cdot}mol^{-1}$

$\Delta S^\circ = [(-56) + 2(+98)]\ J{\cdot}mol^{-1}{\cdot}K^{-1} = +140\ J{\cdot}mol^{-1}{\cdot}K^{-1}$

Now we can find ΔH and ΔS for the reaction:

$\Delta H^\circ = [(-1923) - (-1207) - (-394) - (-286)]\ kJ{\cdot}mol^{-1} = -36\ kJ{\cdot}mol^{-1}$

$\Delta S^\circ = [(+140) - (+93) - (+214) - (+70)]\ J{\cdot}mol^{-1}{\cdot}K^{-1} = -237\ J{\cdot}mol^{-1}{\cdot}K^{-1}$

At 80ºC:

$\Delta G^\circ = -36\ kJ{\cdot}mol^{-1} - (353\ K)(-0.237\ J{\cdot}mol^{-1}{\cdot}K^{-1}) = +48\ kJ{\cdot}mol^{-1}$

A positive value indicates that the decomposition reaction will be favored.

14.59 Bonds in C_2O_4 = 1(C–C) + 1(O–O) + 2(C=C) + 2(C–O)

= [1(346) + 1(142) + 2(799) + 2(358)] $kJ{\cdot}mol^{-1}$

= 2802 $kJ{\cdot}mol^{-1}$

Bonds in $2CO_2$ = 4(C=O)

= [4(799)] $kJ{\cdot}mol^{-1}$ = 3196 $kJ{\cdot}mol^{-1}$

Energy released = [3196 – 2802] $kJ{\cdot}mol^{-1}$ = 394 $kJ{\cdot}mol^{-1}$