

**K. ALEX MÜLLER** (1927–) was born in Basel, Switzerland. His mother died when he was 11, at which time he enrolled in the Evangelical College in Schiers (eastern Switzerland). After graduating and then fulfilling his obligation to the Swiss military, he attended the Swiss Federal Institute of Technology (ETH) in Zurich, where Wolfgang Pauli was one of his teachers. He received both his undergraduate degree and his doctorate (in 1958) from ETH. In 1963, Müller accepted a position at the IBM Zurich Research Laboratory, where he remained until his retirement. For 15 years, the main focus of his research was on the ceramic SrTiO<sub>3</sub> and related perovskite compounds.

J. GEORG BEDNORZ (1950–) was born in Neuenkirchen, North-Rhine Westphalia, in what was then West Germany. Although he developed an interest in chemistry in high school, he ended up taking his undergraduate degree in crystallography at the University of Münster. In 1972 Bednorz spent the summer at the IBM Zurich Research Laboratory, where he first met K. Alex Müller. After subsequent stints at IBM, where Bednorz worked with SrTiO<sub>3</sub>, he began his doctorate research at ETH Zurich under the supervision of Heini Gränicher and Müller.

After obtaining his Ph.D. in 1982, Benorz joined the IBM lab and worked with Müller on the electrical properties of ceramics made from transition metal oxides. In 1986 they prepared a lanthanum barium copper oxide whose critical temperature (the temperature at which it becomes superconducting) was 35 K. This was 12 K higher than the previous record and stimulated much additional research into high-temperature superconductivity, yielding materials with higher and higher critical temperatures. Müller and Bednorz were awarded the 1987 Nobel Prize in Physics for their work.

## **CHAPTER 8**

## Oxides and Silicates as Materials

This chapter applies concepts from many of the previous chapters to a major area of current research: materials science. Because this area is very broad, we focus on one type of material: the oxides of the elements (including the geochemically important silicates). Sections 8.1 and 8.2 set the basis for the study of materials science, using oxides as examples. Section 8.1 sets the background by asking, "What is a material? What are the physical properties we look for in a material? What kinds of structures can have these desirable properties? Why are some substances solids that are considered materials, while others are gases that are not of interest to materials science?" Section 8.2 then applies the background questions specifically to oxides. We extend the process of drawing Lewis structures (Section 3.1) to allow for the possibility that the ionic or covalent formula unit may polymerize, and derive principles that allow us to predict periodic trends in useful physical properties of oxides.

Sections 8.3 and 8.4 zero in on some properties of ionic solids that contribute to the properties of solid oxides as materials. In Section 8.3 we examine the ability of more than one kind of metal ion to fit in oxide lattices to give mixed-metal oxides, and we look at important types of mixed-metal oxide lattices. These concepts are applied to radiochemistry, the doping of crystals in physics, physical chemistry and bioinorganic chemistry, and the technologies of microphones and loudspeakers. Section 8.4 looks at the electrical and magnetic properties of metal oxides, which are extremely important in modern-day technology. What are high-temperature superconductors? How can electronic production of sound work? The principles of this section are applied to conduction in lithium-ion batteries and solid oxide-ion conductors in the control of pollution from automobile exhausts and the building of maglev trains.

Although the emphasis here in Chapter 8 is on physical properties of oxides, the chemical reactivity of oxides must be taken into account. Section 8.5 discusses the acid–base reactivity, solubility properties, and contributions to the atmospheric chemistry of oxides of the elements, including cement chemistry and the failure of Biosphere II. In reading Section 8.5D, note what nonchemical considerations are also very important in successful pollution control.

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Sections 8.6 and 8.7 roll back the calendar a few billion years and talk about the materials that are most important in the formation of the solid Earth: the simple, oligomeric, and polymeric silicates (Section 8.6) and aluminosilicates (Section 8.7). What silicate "lasts forever"? In Section 8.6 we address questions about the following applications: Which silicates were manufactured many thousands of years ago for use as pigments? How might the transformation of silicates be related to deep earthquakes? For what chemical reason do people choose to live on the slopes of very dangerous volcanoes? What minerals are being found on Mars, and what do they tell us about the early history of Mars? In Section 8.7 we discuss the chemistry of water softening, soil fertility, converting petroleum to gasoline, and try to answer questions, such as could silicates have had any role in the origin of life on Earth? What type of silicate is valued as much for what is not there as for what is present in the silicate?

#### 8.1. Materials and Their Physical Properties

**OVERVIEW.** In modern materials science we look for specific physical properties in chemical substances such as oxides. Predicting substances likely to show such properties begins with an understanding of the relationship between physical properties and the structure type of a substance. The structure type is shown pictorially in Figure 8.1 and can be indicated in formulas using dimensionality prefixes such as  $\frac{2}{\infty}$ . You may practice applying these classifications by reading Section 8.1A and trying the "(a)" parts of Exercises 8.1, 8.2, and 8.4. Selected physical properties of oxides are discussed in Section 8.1B and summarized in Tables 8.1 and 8.2. In this subsection you can learn to predict likely structure types and physical properties for a given oxide by trying Exercises 8.1– 8.7. Materials scientists can achieve unusual physical properties for a structure type by making unusual changes in the basic structural unit, as in the example of ionic liquids (Section 8.1C; Exercises 8.8–8.9).

In Section 8.1C you again employ the concept of lattice energies from Section 4.2 and the concept of speciation (Section 3.8) as applied to structural units. The concepts of Section 8.1 involving physical properties, structural types, linkage, and physical properties will be used again in extensively in Chapter 12.

In the remainder of this chapter we will be concerned with the physical properties of compounds such as oxides. Many of these are of interest to **materials science**. Substances considered to be materials have more complex or extended structures than simple gaseous molecules or ion pairs or multiplets, or than simple molecular liquids, and are valued principally for their physical (rather than chemical) properties. Most materials of interest are solids, but these also include some liquids with unusual structures (e.g., liquid crystals). In this section we discuss some general principles that affect the physical properties of inorganic materials. The earth we stand on and many of the materials out of which we build the edifices of modern civilization consist of inorganic materials. For many modern purposes (in electronics, spacecraft, and so on) the properties must be such as to withstand extreme conditions, or to show great strength and lightness, or to have various unusual combinations of properties. The principles in this section would be of use in suggesting the kinds of new materials that you would want to synthesize if you were seeking new materials with certain unusual physical properties.

**8.1A. Structural Types.** Fundamentally, many of the physical properties of materials depend on how extensively its **structural units** ( $MO_x$  in an oxide; M in a metal) are **linked** together by intermolecular forces or chemical bonds. In Figure 8.1, we categorize eight structural types (a) through (h) in which the same structural unit (shown as a sphere) is linked in different ways and to increasing extents.

At one extreme, the bulk material (e.g., a crystal) may consist of numerous, separate, much smaller molecules linked only very loosely together by **intermolecular attractions** (Section 8.1B). In these **monomeric molecular** substances (Figure 8.1a), the structural unit is a (at least fairly) simple molecule.

At the other extreme, the entire piece (e.g., the crystal) may consist of structural units that are linked into one giant three-dimensional **network polymer** (Figure 8.1g) or **ionic lattice** (Figure 8.1h) by strong chemical-bonding forces.

Between these extremes there are several intermediate possibilities, as illustrated in Figure 8.1. Next in complexity after the monomers are the **oligomeric** molecules or ions (Figure 8.1b, c, and d), which contain a few structural units linked together. In **chain oligomeric** molecules or ions (Figure 8.1b), each central structural unit is linked to *two* others, but after a definite number of units have been linked, the chain is terminated by a slightly different unit with only *one* link. (Examples include the homopolyatomic ions discussed in Section 3.1A.) In **cyclic oligomeric** molecules or ions (Figure 8.1c), all units are linked to *two* others and form a ring, so there are no terminal



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units. In **polyhedral oligomeric** molecules or ions (Figure 8.1d) the units are linked in a small three-dimensional assembly to *three* or more other units.

Next in complexity are **polymeric** substances (Figure 8.1e–h). These can be divided into four categories. In **linear** or **chain** or **one-dimensional polymers** (Figure 8.1e), each structural unit is linked to *two* others to give long-chain molecules or ions. Their one-dimensional polymerization is often denoted with  $\frac{1}{\omega}$  in front of the formula of the structural or simplest-formula unit—for example,  $\frac{1}{\omega}$  [CH<sub>2</sub>CH<sub>2</sub>] for polyethylene. Sometimes a subscript *n* is used instead—for example, (CH<sub>2</sub>CH<sub>2</sub>)<sub>*n*</sub>. In **layer** or **sheet** (or **two-dimensional**) **polymers** (Figure 8.1f) (denoted with  $\frac{2}{\omega}$ , such as  $\frac{2}{\omega}$ [C] for graphite), many or all structural units are linked to *three* other units, so the molecule or ion extends indefinitely in two dimensions. In either **ionic** (Figure 8.1h) **network** (or **three**-**dimensional**) **polymers** (Figure 8.1g) (denoted with  $\frac{3}{\omega}$ , such as  $\frac{3}{\omega}$ [SiO<sub>2</sub>] for silicon dioxide), the individual structural units have enough links with orientations allowing the molecule or ionic lattice to extend indefinitely in three dimensions.

## **EXAMPLE 8.1**

Which pairs of structure types in Figure 8.1 represent polymorphs of each other (Section 4.1C)?

**SOLUTION:** In Section 4.1C polymorphs are defined as different atomic arrangements (of a given structural unit) involving the same coordination numbers (of the unit's central atom). Let us take for granted that each structure type in Figure 8.1 has the same structural unit, with the same number x of terminal atoms bonded to the central atom. In addition, the central atom contains a certain number  $\ell$  of links. (As a result, the coordination number of the central atom of each structural unit equals  $x + \ell$ .) Polymorphs have the same number of links  $\ell$ . There are two pairs of polymorphs in Figure 8.1: cyclic molecules (Figure 8.1c) and linear polymers (Figure 8.1e), with two links to each central atom or structural unit, and polyhedral molecules (Figure 8.1d) and layer polymers (Figure 8.1f), with three links.

**8.1B. Physical Properties.** In Table 8.1 we summarize these eight categories of structure type, their structural units, links, what must happen to break the links, and then three important physical properties: hardness, electrical conductivity, and solubility.

As postulated in the ideal **kinetic-molecular theory** of gases, molecules capable of existing in the gaseous state exert no attractive forces on each other, move independently of each other, and remain relatively far apart. In practice, however, there are attractive forces between molecules (**intermolecular attractions**). The weakest of these is the van der Waals force, which occurs between molecules of all substances. The van der Waals force results when a momentary unsymmetrical distribution of electrons in one molecule (a temporary dipole) induces an opposed momentary unsymmetrical distribution of electrons in a neighboring molecule. The momentarily oppositely charged ends of the two molecules then attract each other. In small molecules the van

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Material Typeª	Structural Units	Held Together By	Vaporization Processes	Hardness	Electrical Conductivity	Solubility
Molecular (a)–(d)	Molecules	London forces, hydrogen bonds	Break these intermolecular forces	Soft	Poor	In appropriate solvents
Metallic ( <b>g</b> ) (Chapter 12)	Atoms (or ions)	Covalent bonds (or sea of electrons)	Break metallic bonds → M, M₂	Variable	Good	In other metals
Covalent network ( <b>g</b> ) (Chapter 12)	Atoms or molecular fragments (MO <sub>x</sub> )	Covalent bonds	Break covalent bonds → monomers, oligomers	Hard	Usually poor	Insoluble in all solvents
Ionic ( <b>h</b> ) (Chapter 4)	Oppositely charge ions	Attractions of opposite charges	Lattices → ion pairs or multiples	Variable, brittle	Usually poor (good as liquid)	Sometimes in water
Chain (e)	Atoms or molecular fragments (MO <sub>x</sub> )	Covalent bonds, van der Waals forces	Break covalent bonds → monomers, oligomers	Soft	Usually poor	In appropriate solvents
Layer (f)	Atoms or molecular fragments (MO <sub>x</sub> )	Covalent bonds, van der Waals forces	Break covalent bonds → monomers, oligomers	Soft, slippery	Usually poor, can be good	Insoluble in all solvents

TABLE 8.1. Structure Types and Typical Properties of Solids

<sup>*a*</sup> The boldfaced letters in parentheses refer to the structure types in Figure 8.1.

der Waals force is very weak as compared to the average kinetic (thermal) energies that the molecules possess at room temperature. But in very large molecules with numerous highly polarizable (relatively loosely bound) electrons, the van der Waals forces may be so substantial that the kinetic energy available to molecules at room temperature is not enough to overcome such an attraction. Hence monomeric or oligomeric substances consisting of sufficiently large molecules are not gaseous at room temperature and atmospheric pressure.

The kinetic-molecular picture of the liquid state postulates that molecules or ions are held close by forces that are strong compared with the thermal energy at that temperature. But the molecules or ions are free to flow around each other, which implies that their intermolecular attractive forces can be stretched and modified. The molecules or ions must also either be relatively small, or if they are chain polymers, the chains must not be rigid; they cannot be layer or network polymers. Medium-sized molecular substances, or smaller molecules linked by somewhat stronger forces such as dipole–dipole forces and hydrogen bonding (i.e., water and alcohols), are most likely to be liquids at room temperature.

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In the solid state molecules or ions are packed closely together and exert attractive forces on one another that are strong enough to hold the units in position in a lattice despite their vibrational energies. Large covalent molecules often have strong enough van der Waals forces to be solids at room temperature, but these forces seldom rival in strength the inter-unit covalent bonds or Coulombic forces found in the high-melting solid two- or three-dimensional polymeric substances.

Thus, *molecular substances* (Figure 8.1a–d), and especially monomeric molecular substances (Figure 8.1a), tend to be gases, liquids, or low-melting (i.e., below 300°C) solids at room temperature, and they have relatively low heats of fusion and heats of vaporization. As specific examples (Table 8.2) we may cite  $F_2$  (in which the weak intermolecular attractions are due to van der Waals forces) and glycerol [ $C_3H_5(OH)_3$ ], in which the stronger intermolecular forces are due to hydrogen bonding. Other properties generally follow from the absence of strong intermolecular attractions. Molecular substances tend to have higher solubilities and may even be soluble in nonpolar solvents. Like a brick wall with no mortar, these substances are lacking in structural strength, so they are deformable (soft in a mechanical sense, such as wax).

At the other extreme, the structural units of *three-dimensional network* or *ionic* substances (Figure 8.1g, h) are held together by strong chemical forces—namely, covalent or ionic bonding, which extends throughout the grain or crystallite of the

Class <sup>a</sup>	Example	ΔH <sub>fus</sub> (kJ mol⁻¹)	Melting Point (°C)	ΔH <sub>vap</sub> (kJ mol <sup>-1</sup> )	Boiling Point (°C)
Molecular ( <b>a</b> )	F <sub>2</sub>	0.5	~218	6.6	~188
	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub>	18.3	18	61	290
Chain (e)	Selenium	6.69	220	96	685
Layer (f)	CdI <sub>2</sub>	15.3	387	115	742
	Graphite	117	4489		
Metallic ( <b>g</b> )	Na	2.6	98	99	1052
	W	52.3	3422	824	5500
Covalent Network ( <b>g</b> )	Diamond			~713	4350
	Cristobalite	9.6	1722	516	3270
Ionic ( <b>h</b> )	NaCl	28.2	801	170	1465
	SrF <sub>2</sub>	28.5	1477	297	2477
	ZrO <sub>2</sub>	87	2709		4300

## TABLE 8.2. Examples of Different Classes of Solids and Thermal Data Relating to Their Ease of Vaporization

*Source of thermal data:* D. R. Lide, Ed., *CRC Handbook of Chemistry and Physics*, 84th ed., CRC Press: Boca Raton, FL, 2003, pp. 6-109–6-139.

<sup>a</sup> The boldfaced letters in parentheses refer to the structure types in Figure 8.1.

substance. It is very difficult for the structural units to acquire mobility with respect to each other. At room temperature these substances are high-melting solids with high heats of fusion and vaporization (Table 8.2).

The subcategories of polymers have some characteristic variations on the typical properties of polymers. The one-dimensional chain polymers (Figure 8.1e) typically differ from other polymers in that the bonding usually does not give rigidity to the material. Consequently, chain polymers can be mechanically soft and have low melting points. As liquids they are viscous, since the long, spaghetti-like molecules can easily become entangled and hence resistant to flow. (The most familiar examples of these properties include thermoplastic organic polymers such as polyethylene.)

The two-dimensional layer polymers (Figure 8.1f) tend to be rigid in those two dimensions, but not in the third. These often consist of flat sheets that readily slide over each other (some are used as lubricants). They are mechanically soft in the third dimension. Examples include graphite,  $CdCl_2$ , and  $CdI_2$  (Figure 4.5c; Section 4.1c).

The process of melting network polymeric (Figure 8.1g) and ionic (Figure 8.1h) solids requires stretching and bending strong inter-unit attractions, so it occurs at high temperatures (Table 8.2). This can happen for ionic solids, because Coulombic attractions are omnidirectional, and another attraction can replace the one lost when an ion becomes mobile. When *covalent* layer or network solids are melted, however, numerous covalent bonds must be ruptured. At this high temperature, any remaining linking covalent bonds may also be ruptured, so gaseous small molecules are formed. Hence, covalent layer or network solids frequently **sublime** (pass directly from the solid to the gaseous state) or decompose at high temperatures, rather than truly melting and boiling.

**Densities.** The distances between the separate molecules (Figure 8.1a–d) in the solid (or liquid) phase are governed by the relatively long van der Waals radii of whatever atoms are on the outside of the units, so molecular substances tend to have relatively low densities. Among the subcategories of polymers, the more-polymerized form tends to have the higher density and greater structural strength and mechanical hardness (Section 8.2B). Because the structural units are strongly bonded together at distances that are the sums of relatively short covalent or ionic radii, these materials have relatively high densities. As examples of the density trend involving the same structural unit, we may compare diamond,  $^{3}_{\infty}$ [C] (density 3.51 g cm<sup>-3</sup>), with graphite,  $^{2}_{\infty}$ [C] (2.25 g cm<sup>-3</sup>), and polyhedral molecular C<sub>60</sub>, (1.65 g cm<sup>-3</sup>).

## **EXAMPLE 8.2**

Molybdenum(IV) sulfide is a solid (mp 1750°C) that is slippery; it is used as a lubricant in products such as WD40<sup>TM</sup>. (a) To which category in Figure 8.1 does this solid likely belong? (b) Which would be the best concise way of indicating this category of solid:  $MoS_2$ ,  $Mo_4S_8$ ,  $\frac{3}{\infty}[MoS_2]$ , or  $\frac{2}{\infty}[MoS_2]$ ?

**SOLUTION:** The very high melting point suggests a polymeric structure (but probably not one-dimensional). The property of being slippery suggests a two-dimensional layer structure (Figure 8.1f) with weak intermolecular forces between the layers—hence,  $\frac{2}{\infty}$ [MoS<sub>2</sub>].

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**8.1C. New Physical Properties for Old Structure Types: Ionic Liquids.** The properties typically associated with a given structural type can often be modified considerably by changing details of the structures, or by making *composites* of two structure types. For example, ionic liquids<sup>1</sup> comprise an important group of exceptions to the general trends discussed above. When (nonacidic) cations and (nonbasic) anions are both *very* large, the lattice energies of their salts can become low enough to allow melting at less than 100°C or even below room temperature.<sup>2</sup> In practice, ionic liquids contain large nonacidic organic cations such as  $R_4N^+$  (tetraalkylammonium) (Figure 8.2a),  $R_4P^+$  (tetraalkylphosphonium) (Figure 8.2b),  $C_5H_5NR^+$  (alkylpyridinium) (Figure 8.2c), and most frequently  $C_3H_3(NCH_3)(NR)^+$  (1-alkyl-3-methylimidizolium) (Figure 8.2d), along with large nonbasic inorganic or fluorinated organic anions such as  $Al_2Cl_7^-$  (Figure 8.2e),  $AlCl_4^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CF_3CO_2^-$  (Figure 8.2f),  $CF_3SO_3^-$  (Figure 8.2g),  $BF_4^-$ , and  $PF_6^-$ .

The lattice energy of CsCl, with a large cation–anion distance of 348 pm, is –670 kJ mol<sup>-1</sup> and its melting point is 645°C (918 K). 1-Ethyl-3-methylimidizolium (Figure 8.2d) hexafluorophosphate ( $PF_6^-$  anion) is anticipated to have a similar "radius" ratio to CsCl, but a much longer cation–anion distance of around 510 pm.<sup>3</sup> Proportionately its lattice energy might be expected to be in the neighborhood of –450 kJ mol<sup>-1,4</sup> its melting point is 60°C (333 K). However, the lattice energy is still much larger than the London, dipole–dipole, or hydrogen-bonding forces that hold molecules in the liquid state, so ionic liquids have essentially zero vapor pressure. They therefore do not contribute to air pollution and are considered to be *green solvents*. Their major disadvantage is that they are quite viscous due to the cation–anion attractions that are present.





## **EXAMPLE 8.3**

Let us contrast the properties of the two ionic compounds,  $BaI_2$  and  $[Ba(18-crown-6)(H_2O)_2]$ (AlI<sub>4</sub>)<sub>2</sub>. Compared to  $BaI_2$ ,  $[Ba(18-crown-6)(H_2O)_2](AlI_4)_2$  should have (a) a higher or lower lattice energy, (b) a higher or lower melting point, and (c) a higher or lower vapor pressure?

**SOLUTION**: With the larger cation and the larger anions,  $[Ba(18-crown-6)(H_2O)_2](AII_4)_2$  is more likely to be an ionic liquid. Therefore, it should have (a) a lower lattice energy, (b) a lower melting point, but (c) a faintly higher but still negligible vapor pressure.

### **Solubility and Ionic Liquids**

Ionic liquids tend to be immiscible with nonpolar organic solvents. They somewhat resemble moderately polar organic solvents in being good solvents for many organic molecules.<sup>5</sup> Their miscibility with water and their ability to dissolve inorganic salts can be modified by the choice of the anion. With the Lewis base Cl<sup>-</sup> as the anion, the ionic liquid is miscible with water. It is Lewis basic and can coordinate to acidic cations, dissolving (for example) acidic metal halides by forming halometallate anions:

$$AlCl_{3}(s) + (EMIM)^{+}Cl^{-}(l) \rightarrow (EMIM)^{+}[AlCl_{4}]^{-}$$

$$(8.1)$$

[(EMIM)<sup>+</sup> is the cation shown in Figure 8.2d when R is the ethyl group, -CH<sub>2</sub>CH<sub>3</sub>.] With excess AlCl<sub>3</sub>, the anion [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> (Figure 8.2e) is formed, which tends to dissociate in solution to AlCl<sub>4</sub><sup>-</sup> and AlCl<sub>3</sub>. The latter is a strong Lewis acid, so the ionic liquid is a Lewis acid. With large nonbasic anions such as [PF<sub>6</sub>]<sup>-</sup>, the ionic liquids are neither acidic nor basic; these salts are water insoluble by Solubility Tendency III (Section 4.3).

Given this variability of acid–base properties and miscibilities, it is often possible to find an ionic liquid to dissolve nonpolar organic substrates and ionic metal salts (as reactants or catalysts) in the same (ionic liquid) phase. After the reaction is complete, a nonpolar organic product can be extracted by an immiscible nonpolar liquid, such as hexane or supercritical  $CO_2$ , and recovered by evaporation. The remaining inorganic salt can be extracted with immiscible water, leaving the pure ionic liquid for reuse. If supercritical  $CO_2$  has been used, there has been no air pollution.

# 8.2. The Structure Types and Physical Properties of the Oxides of the Elements

**OVERVIEW.** There are dramatic changes in structure types on crossing certain boundaries in the periodic table of the highest oxides of the elements (Table 8.3; Section 8.2A). Possible structure types can be predicted using an expansion of the procedure for drawing Lewis dot structures, which tends to assume a total coordination number of four. Higher total coordination numbers can be predicted in later periods of the periodic table using either the concept of changes in maximum/penultimate total coordinate-covalent links units form to each other via bridging fluorine or oxygen atoms. Hence, we can predict periodic trends in structure types. Section 8.2 also gives you a good chance to review the interpretation of observed bond lengths and bond angles. You may review these concepts by working Exercises 8.10–8.19.

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You can then predict periodic trends in physical states, melting points and boiling points, enthalpies of fusion and vaporization, and usefulness as ceramics among fluorides or oxides as a function of their degrees of polymerization. Details of the effects of pressure on polymerization isomerism, and properties of ceramics such as brittleness and preparation by sintering, can be understood (Section 8.2B). You may try predicting these trends with Exercises 8.20–8.24.

Section 8.2 builds upon earlier concepts of covalent radii (Section 1.5B), electronegativity differences (Section 1.6), drawing Lewis structures (Section 3.1), total coordination numbers (Sections 3.4 and 3.5), and radius ratios and polymerization isomers (Section 4.1). Periodic trends in structure types will appear again in Section 12.1.

**8.2A. Predicting Trends in Structure Types of Oxides.** The overall goal in this section is to see (by example) *why* some oxides are materials and others are molecular. There are too many oxides of elements to enumerate or describe them all; Table 8.3 summarizes structural features of the oxides of elements in their highest oxidation states. Oxides in taller columns have greater molecularity.

The oxides in the shaded boxes have molecular structures, as also indicated at the bottom of the tallest columns. The large majority of the highest oxides are in short columns, which signifies polymeric structures. At the bottom of each box the type of polymeric structure of the major polymerization isomer is indicated. In this subset of oxides of the elements we may note three trends:

1. There are relatively *few molecular oxides* (taller columns in Table 8.3); these tend to be associated with relatively high oxidation states.



## TABLE 8.3. Highest Oxide of Each Element and Its Structure Type<sup>a,b</sup>

Source of most data: A.F. Wells, Structural Inorganic Chemistry, 5th ed., Oxford University Press: Oxford, UK, 1983. <sup>a</sup> Solid-state structure types are as indicated in Figure 8.1 except as follows: **?** = unknown structure; **gh** = network (**g**) or ionic (**h**) structure.

<sup>b</sup> Entries in **brown** are for oxides in which the oxidation number is below the group number.

- 2. There are *numerous polymeric oxides* (shorter columns in Table 8.3), which might capture the interest of materials scientists. Among the polymeric oxides, the large majority have three-dimensional network covalent (Figure 8.1g) or ionic (Figure 8.1h) structures.
- 3. The transitions from the molecular structure types in Table 8.3 to ionic/ network covalent structure types are often abrupt and result mainly from changes in oxidation number (and therefore structural unit).

Table 8.3 suggests that the overwhelming majority of oxides involve extensive bridging of structural units by oxygen atoms or ions to give *polymeric solid materials*. The  $O^{2-}$  ion is a very strongly basic anion, and it very frequently acts as a bridging ligand. Every time it forms a bridge to the central atom of another  $MO_x$  structural unit, it does so via a coordinate covalent bond, donating an electron pair to an empty orbital (a **vacant coordination site**, VCS) on another M oxide structural unit.

In a few cases (Table 8.3) oxides form chain polymers (Figure 8.1e). Examples include  ${}^{1}_{\infty}[SO_{3}], {}^{1}_{\infty}[CrO_{3}]$ , and  ${}^{1}_{\infty}[HgO]$ . In a few cases oxides form layer polymers (Figure 8.1f); examples include  ${}^{2}_{\infty}[Re_{2}O_{7}], {}^{2}_{\infty}[V_{2}O_{5}], {}^{2}_{\infty}[P_{2}O_{5}]$ , and  ${}^{2}_{\infty}[P_{2}O_{3}]$ . (Notice that these are close to the network covalent or ionic structures in the periodic table of Table 8.3.)

Because Table 8.3 only shows a subset of oxides, we need a procedure to make predictions that apply to any binary compound. In many ways the procedure is similar to that for drawing Lewis structures (Section 1.4), but it adds three options. First, it is applicable both to ionic and covalent compounds. Second, it clarifies when the central atom may have more than an octet of electrons. Third, it allows a molecule/structural unit to undergo polymerization. Here we illustrate and apply the abstract principles of Section 8.1 to the prediction and understanding of structure types and the resulting trends in physical properties of the oxides of the elements.

A procedure for generating plausible structures for oxides (or fluorides) is outlined in Figure 8.3. The procedure may generate more than one plausible structure/polymerization isomer, but these should not be wildly different (e.g., not the structure types in Figures 8.1a and 8.1g), and should guide us to reasonable expectations of properties that are observed (Section 8.2B).



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Step 1. Start with the structural unit  $(:)_n MO_x$  with only one M atom and x oxygen atoms (x can be a fraction). Generate one or two predictions of the total coordination number (TCN) of the central (normally the metal) atom or ion. One prediction is based on the radius ratio (Section 4.1). The other prediction is based on the expected penultimate TCN (Section 3.5).

The radius-ratio prediction is based on a presumption of ionic bonding. Because the ionic radius of oxide ion is 126 pm (Table C), use of the radius-ratio principle predicts eight-coordination for metal ions that are larger than  $0.714 \times 126$  pm = 92 pm. Six-coordinate metal ions are predicted to be those with radii between  $0.414 \times 126$  pm = 52 pm and 92 pm. Four-coordinate metal ions are predicted for ions with radii between  $0.255 \times 126$  pm = 28 pm and 52 pm. If a metal ion is close to one of these boundaries, it is best to carry forth *both* predicted coordination numbers, because the radius ratio does not give precise results, and there may be polymerization isomers.

Step 2. The number of vacant coordination sites (VCS) of the central atom in the structural unit  $(:)_n MO_x$  is then obtained by subtracting the number of oxygen (or other outer) atoms *x*, the number of central-atom unshared *sp* electron pairs *n*, and the number of M–O  $\pi$  bonds in the structural unit from the expected total coordination number obtained in Step 1:

VCS = Links per (:)<sub>n</sub>MO<sub>x</sub> = TCN - 
$$x - n - \pi$$
 (8.2)

Step 3. Select the structure type based on the number of VCS calculated from Equation 8.2: If VCS = 0, then the predicted structure type is a monomeric molecule (Figure 8.1a). If VCS is a fraction, then it is a chain oligomer (Figure 8.1b). If VCS = 1, then we predict a cyclic oligomer (Figure 8.1c) or a chain polymer (Figure 8.1e). If VCS = 1.5 or more, then we predict a polymer: a polyhedral oligomer (Figure 8.1d), a layer polymer (Figure 8.1f), a network polymer (Figure 8.1g), or an ionic solid (Figure 8.1h). Higher VCS numbers suggest higher degrees of polymerization. (However, a distinction between Figure 8.1g and Figure 8.1h is not expected yet.) Rarely, a *negative* VCS number may be computed, in which case one of the outer atoms in the structural unit is *expelled* and the compound is ionic—for example, NF<sub>5</sub> has TCN = 4, so VCS = -1. The compound is  $[NF_4^+](F^-)$ .

Step 4. If different predictions (e.g., Figure 8.1g, h) have resulted starting from the ionic-based radius-ratio rule and the covalent-based penultimate TCN, the electronegativity difference may now help narrow the choice of the more likely structure type and (if desired) the lattice type. This choice is illustrated in Example 8.5, in which the large Mg–O electronegativity difference leads us to favor the results of the radius-ratio calculation, the six-coordinate NaCl lattice type, over the four-coordinate prediction based on the penultimate TCN. Also, recall from Section 4.1C how, for a metal TCN of six in  $MX_2$  or  $MX_3$ , increasing covalency favors layer structures (Figure 4.6b) over the ionic TiO<sub>2</sub> (Figure 4.2) or AlF<sub>3</sub> structures. Sometimes the same structure type is chosen regardless of the covalency: One of the ZnS structures (Figure 4.2) may be chosen for TCN = 4 regardless of the electronegativity difference (it is found both for oxides and sulfides). Step 4 is illustrated in Example 8.5 and Figure 8.4.

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## **EXAMPLE 8.4**

Without using radius ratios, calculate the numbers of VCS or links per structural unit for the (real or imaginary) oxides of third-period elements: MgO, SiO<sub>2</sub>, SO<sub>3</sub>, ClO<sub>3.5</sub>, and "ArO<sub>4</sub>."

**SOLUTION**: If we assume a constant penultimate TCN of four for these central atoms (Step 1), we see that this is achieved in the structural unit only in the hypothetical  $ArO_4$ ; this is the only one of these oxides with no VCS or links and a monomeric molecular structure (Figure 8.1a). In all other cases the central atom falls short of its expected (penultimate) coordination number (corresponding to an octet of electrons). Thus, the central atoms of these oxide structural units have 3, 2, 1, and 0.5 VCS, respectively (Step 2). We can represent these potential Lewis-acid sites by empty parentheses: ()<sub>3</sub>MgO, ()<sub>2</sub>SiO<sub>2</sub>, ()SO<sub>3</sub>, and ()<sub>0.5</sub>ClO<sub>3.5</sub>. If  $\pi$  bonding is excluded, then the only way of achieving octets is by linking with neighboring structural units through bridging oxygen atoms or oxide ions.

## **EXAMPLE 8.5**

Extend the results of Example 8.4 to predict the likely structure types for the remaining oxides:  $ClO_{3.5}$ ,  $SO_3$ ,  $SiO_2$ , and MgO.

**SOLUTION:** By Step 3, ()<sub>0.5</sub>ClO<sub>3</sub> forms one oxygen link between two structural units, which produces an  $O_3$ Cl-O-ClO<sub>3</sub> (Cl<sub>2</sub>O<sub>7</sub>) "dimer" (Figure 8.4a). This conclusion is supported because we can draw a good Lewis structure for Cl<sub>2</sub>O<sub>7</sub>.

( )SO<sub>3</sub> has one VCS per structural unit. Each ( )SO<sub>3</sub> structural unit donates an electron pair from one of its oxygen atoms to form an oxygen link and accepts an electron pair from an oxygen atom of another ( )SO<sub>3</sub> structural unit to form another link, resulting in doubly linked structural units (Figure 8.4b). As shown there, at least two polymorphs can result: cyclic S<sub>3</sub>O<sub>9</sub> and chain  $\frac{1}{\infty}$ [SO<sub>3</sub>]. Both conclusions are supported, because we can draw good Lewis structures for both.

()<sub>2</sub>SiO<sub>2</sub> (Figure 8.4c) has *two* VCS, so we anticipate correctly that it is likely to polymerize to a greater extent than does ()SO<sub>3</sub>, using every oxygen atom and every VCS in quadruply linking the structural units, and giving each bridging oxygen atom a coordination number of *two*. Figure 8.4c shows the first step in polymerization to form large hexameric rings,  $(SiO_2)_{6}$ , of varying conformations. Formation of the six links to give this ring takes care of one VCS and one oxygen atom per SiO<sub>2</sub> unit. The other vacant site and oxygen atom per unit leads to three-dimensional polymerization to give the SiO<sub>2</sub> polymorphs shown in Figure 4.7a–c.

The ()<sub>3</sub>MgO structural unit has three VCS if its TCN is four. But (Step 4) radius-ratio calculations predict a TCN of six. In either case we predict polymerization in three dimensions to give a network or an ionic solid. Because the electronegativity difference of Mg and O is large, the radius-ratio calculations are more likely to be correct. In practice, MgO exhibits six-coordination for both Mg and O in a NaCl ionic lattice.

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## **EXAMPLE 8.6**

isomers.

Use radius ratios and the ions in Table C to predict the identities of the monomeric hexafluorides of the elements. Compare your predictions with the predictions you would obtain using maximum total coordination numbers.

SOLUTION: To be monomeric molecular, the coordination number of M in the structural unit must equal the number of F atoms in the formula. To obtain an MF<sub>6</sub>, the radius ratio should be more than 0.414 but less than 0.732, so the radius of M<sup>6+</sup> should be between 49 pm and 87 pm. There are a number of qualifying M<sup>6+</sup> ions in Table C, including all of those of Groups 6, 16/VI, and the seventh-period elements of Groups 6F-8F. In practice, over a dozen monomeric MF<sub>6</sub> molecules are known.<sup>6</sup> This is more than would be expected based on maximum coordination numbers exceeding six for fifth-period elements or below. (The very electronegative fluorine atom of covalent fluorides is a very poor donor atom and thus is a very poor bridging atom.)

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**8.2B.** Oxides and Their Physical Properties. In Figure 8.5 we show examples of structurally well-characterized molecular oxides of the elements. In Table 8.4 we tabulate ranges of important physical properties (melting points and boiling points, and heats of fusion and vaporization) of molecular and polymeric oxides.



(b) Dimeric molecular oxides



(c) Cyclic oligomeric oxides



(d) Polyhedral oligomeric oxides



**Figure 8.5.** Examples of monomeric, dimeric, cyclic oligomeric, and polyhedral oligomeric oxides. The letters in parentheses refer to the structure types in Figure 8.1. Where known, bond lengths and angles are also shown.

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Structure Type <sup>a</sup>	Range of Oxides	∆H <sub>fus</sub> (kJ mol⁻¹)	Melting Point (K)	∆H <sub>vap</sub> (kJ mol⁻¹)	Boiling Point (K)
Monomeric ( <b>a</b> )	CO to OsO <sub>4</sub>	0.8-9.8	68-313	6-39.5	82-303
Dimeric ( <b>b</b> )	$F_2O$ to $Tc_2O_7$		39-392	26-59	128-485
Cyclic or Cluster ( <b>c</b> and <b>d</b> )	S <sub>3</sub> O <sub>9</sub> to Sb <sub>4</sub> O <sub>6</sub>			40-109	318-633
Ionic $M^{2+}O^{2-}(\mathbf{h})$	BaO to BeO	46-86	2193-2803	151-309	3023-4123
Ionic $(M^{3+})_2(O^{2-})_3$ ( <b>h</b> )	Ga <sub>2</sub> O <sub>3</sub> to Y <sub>2</sub> O <sub>3</sub>	105–111	2019–2711	290-402	2723
Ionic $(M^{4+})(O^{2-})_2(\mathbf{h})$	ThO <sub>2</sub> to ZrO <sub>2</sub>	87	2992-3763	514-567	4673-5123

TABLE 8.4 Trends in Selected Physical Properties of Oxides by Structure Type

<sup>*a*</sup> The boldfaced letters in parentheses refer to the structural types in Figure 8.1.

**Physical Properties of Monomeric Molecular Oxides.** The simplest monomers are XeO<sub>4</sub>, RuO<sub>4</sub>, OsO<sub>4</sub>, IrO<sub>4</sub>,<sup>7</sup> and :XeO<sub>3</sub>. Because oxygen is good at forming  $\pi$  bonds, there are also doubly bonded and triply bonded monomeric molecular oxides, such as SO<sub>3</sub> (one polymerization isomer), :SO<sub>2</sub>, CO<sub>2</sub>, and :CO (Figure 8.5a). Also there are some simple oxides that not only involve  $\pi$  bonds but also are stable free *radicals* with odd numbers of valence electrons—namely, NO<sub>2</sub>, ClO<sub>2</sub>, and NO. For the monomeric molecular oxides, the structural unit is the molecule, so (except for the free radicals) it should be possible to draw a good Lewis structure for the structural unit.

The monomeric oxides have relatively low melting points, boiling points, enthalpies of fusion, and enthalpies of vaporization (Table 8.5)—it requires but little energy to overcome the weak intermolecular forces holding these molecules together in the liquid or solid.

**Physical Properties of Dimeric Molecular Oxides.** When the element of the oxide has an odd oxidation state, this requires the presence of two atoms of the element, and of one bridging oxygen atom to link the two element atoms in the dielement hepta–, penta–, and monoxides  $M_2O_7$  (M = Cl, Mn, Tc),  $Br_2O_5$ , and  $M_2O$  (M = F, Cl, Br), respectively. The structures of the dinitrogen oxides differ, however, in having nitrogen-nitrogen bonds as the linking element instead of bridging oxygen atoms (Figure 8.5b). Again we can draw good Lewis structures for these dimeric molecular oxides  $M_2O_{2x}$ . Because the dimeric molecules are somewhat larger than the monomeric oxides, they have somewhat higher melting points and boiling points, and enthalpies of fusion and vaporization.

**Physical Properties of Cyclic and Polyhedral Oligomeric Molecular Oxides.** Some nonmetal oxides have cyclic oligomeric polymerization isomers, such as  $S_3O_9$ , and  $Se_4O_{12}$ . Others have polyhedral polymerization isomers, such as  $P_4O_{10}$ ,  $:P_4O_6$ ,  $:As_4O_6$ ,  $:Sb_4O_6$ , and  $I_4O_{16}$ . In the first four of these M has a TCN of four, and good Lewis structures can be drawn (Figure 8.5c, d). These molecules are large enough to have substantial intermolecular attractions, so they are low-melting solids with medium enthalpies of vaporization. (The trends in the apparent melting points and enthalpies of fusion are complicated by the tendency of these oxides to convert to other polymerization isomers rather than to melt.)

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#### Physical Properties of Network and Ionic Oxides-Heat Resistance and

**Mechanical Hardness.** As seen in Table 8.4, network (Figure 8.1g) and ionic (Figure 8.1h) oxides have extraordinarily high melting points, boiling points, heats of fusion, and heats of vaporization. **Ceramics** are compounds of metals and metalloids with small nonmetal atoms such as boron, carbon, nitrogen, or oxygen. Nowadays ceramics are used for making far more than pottery and china: Advanced ceramics are used in abrasives, cutting tools, electrical insulators, heat shields, nuclear fuels, bone implants, and lasing crystals. The short, strong bonds in such materials give them not only very high melting points, but also the ability to keep their strength and mechanical hardness even when very hot (in contrast to most organic polymers). Hardness in this sense is the resistance of one body to indentation, scratching, cutting, abrasion, or wear by another body. The hardest materials are considered to be diamond,  $\frac{3}{\infty}$ [C], followed by the cubic polymerization isomer of boron nitride,  $\frac{3}{\infty}$ [BN]. Other very hard carbide ceramics include B<sub>4</sub>C, SiC, TiC, Be<sub>2</sub>, ZrC, TaC, and WC. Very hard borides include AlB and ZrB<sub>2</sub>; very hard nitrides include not only BN, but also TiN. Now, however, we emphasize very hard oxide ceramics.

Perhaps the hardest oxide is *alumina* ( $Al_2O_3$ ), with *beryllia* (BeO) and *zirconia* ( $ZrO_2$ ) not far behind. (Note the common industrial nomenclature by which the most common oxide of a metallic element is named by substituting "–ia" for "–ium" in the name of the metallic element.) Among the best known of these is silica.

The silica polymorphs quartz, tridymite, and cristobalite are not as hard because their structures (Figure 4.6) contain a good deal of empty space within the  $(SiO_2)_6$ rings. The polymerization isomer stishovite, with six-coordinate silicon in a denser rutile lattice, has been found to be comparable in hardness to cubic boron nitride.<sup>8</sup> By the application of ultra-high pressure, solid molecular CO<sub>2</sub>, a very soft material, is reduced in volume by 15% and is converted (reversibly) to  $\frac{3}{\infty}$ [CO<sub>2</sub>], a much harder polymerization isomer of carbon dioxide having the tridymite structure with fourcoordinate carbon atoms.<sup>9</sup>

The very high melting points and low volatility of these oxides make some of them (such as MgO) useful as **refractories** for providing surfaces capable of withstanding very high temperatures. MgO is used not only to line furnaces but also to cover the heating elements of electric ranges, because it conducts heat much more readily than it conducts electricity. A related use is that of *thoria* (actually 99% ThO<sub>2</sub> + 1% CeO<sub>2</sub>) to provide luminosity to gas flames for lighting purposes: The oxides become white-hot without melting.

*Brittleness* is an unfortunate characteristic physical property found in ionic solid oxides. The mechanical strength of ionic materials stems from the large amount of work that has to be done to increase their cation–anion distances. However, if the mechanical stress is sufficient to overcome these attractions, the layers of ions then may slip to an arrangement in which cations are next to cations and anions are next to anions. Suddenly the attractions are replaced by repulsions, and the material shatters.

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## Difficulties of Synthesis

Because ceramics are hard and brittle, they cannot be formed into useful objects by some of the methods used with organic polymers, such as extrusion through holes or into molds; unlike metals, they are difficult to machine into shape. Because their melting points are so extraordinarily high, they are difficult to prepare from molten materials. So, often they are synthesized by **sintering**: heating finely divided powders in furnaces for long periods of time at very high temperatures (up to 2500°C), which are nonetheless well below the melting point of the oxide. Under these conditions the ions from different granules gradually diffuse and "weld" together the granules having dimensions of 100–10,000 nm to give a coherent solid. Between the grains impurities tend to congregate as defects that readily undergo failure when subjected to a stress.

Much modern research in ceramics deals with ways to generate fine, homogeneous *nanoparticles* of 1–100 nm dimensions of starting oxides that will sinter together (at lower temperatures) to give dense, strong ceramics with fewer defects. Alternatively, some of these problems can be overcome by creating **composites** of ceramics with either metals or organic or other polymers that are not brittle.

## **EXAMPLE 8.7**

Predict the coordination numbers, the physical states, and the relative melting points and boiling points of the oxides of the second-period elements in their maximum oxidation state. State whether each should be monomeric, oligomeric, or polymeric or ionic.

**SOLUTION**: From Table 8.3 we see that these oxides are  $Li_2O$ , BeO,  $B_2O_3$ ,  $CO_2$ , and  $N_2O_5$ . Six-coordinate metal ions are predicted to be those with radii between 52 pm and 92 pm; from Table C,  $Li^+$  and  $Be^{2+}$  qualify (for  $Li_2O$ , this number would apply to the oxide ion, while  $Li^+$  would have three-coordination). Four-coordinate metal ions are predicted for ions with radii between 28 pm and 52 pm;  $B^{3+}$  and  $C^{4+}$  qualify. Three-coordination is expected for  $N^{5+}$ . In contrast, the penultimate TCN for Period 2 is three.

We now compute the number of VCS per structural unit (Step 2 in Figure 8.3): 2.5 for Li in  $\text{LiO}_{0.5}$ ; 5 or 2 for Be in BeO; 2.5 or 1.5 for B in BO<sub>1.5</sub>. For CO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> we should consider the number of  $\pi$  bonds in the structural unit—namely, two in CO<sub>2</sub> and one per N in N<sub>2</sub>O<sub>5</sub>. The resulting numbers of VCS by Equation 8.2 are 0 for CO<sub>2</sub> and 0.5 for NO<sub>2.5</sub>.

Step 3 of Figure 8.3 is next. The oxides of Li, Be, and B have enough VCS for polymeric (ionic) structures to be likely, so we predict that these will be solids at room temperature, with high melting points and high boiling points. Our first three predictions are verified for these solids: Li<sub>2</sub>O has a melting point of 1427°C, BeO of 2530°C, and B<sub>2</sub>O<sub>3</sub> of 450°C (but with a boiling point of 1860°C). CO<sub>2</sub> is actually a gaseous monomeric molecule at room temperature, which sublimes at  $-79^{\circ}$ C at atmospheric pressure. For dinitrogen pentoxide, the prediction is partially correct: In the gas phase one of the five oxygens bridges or links the two nitrogens, while each of the other oxygen atoms is bonded to only one nitrogen atom; each nitrogen has a coordination number of three. The solid form of this compound consists of NO<sub>2</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions, with  $\pi$  bonding in each ion.

## **EXAMPLE 8.8**

Predict the coordination numbers, the physical states, and the trends in structures and melting points of the oxides of vanadium in its different oxidation states (II through V). Supplement this list by adding the oxides of Cr(VI) and Mn(VII).

**SOLUTION**: All of these would have the same penultimate coordination number, four, whereas the radii of the ions do decrease as the charge increases. For this reason, a more subtle prediction is possible using the trends in radius ratio. Of the ions involved, only V<sup>2+</sup> might possibly be large enough for eight-coordination (six-coordination is actually found). The Cr<sup>6+</sup> and Mn<sup>7+</sup> ions are only a little larger than 52 pm, so they might be and are four-coordinate. The remainder should be six-coordinate. For most of these oxide structural units, the numbers of VCS are predicted to be greater than two, so that three-dimensional ionic or network covalent lattices are predicted. With only 1.0 and 0.5 VCS, the CrO<sub>3</sub> and MnO<sub>3.5</sub> structural units are expected to give either *cyclo*-(CrO<sub>3</sub>)<sub>n</sub> or  $\frac{1}{\infty}$ [CrO<sub>3</sub>] and Mn<sub>2</sub>O<sub>7</sub>, respectively. Any of these latter structures should have greatly reduced melting points—even a chain polymer such as  $\frac{1}{\infty}$ [CrO<sub>3</sub>] could readily become mobile by twisting, in much the same way that the chain polymer, spaghetti, easily becomes fluid upon stirring.

The observed melting points are very high—1789° C and above for the first three oxides, VO,  $V_2O_3$ , and  $VO_2$ . The layer polymer  $^2_{\infty}[V_2O_5]$  has a lower melting point (670°C). The chain polymer  $^1_{\infty}[CrO_3]$  has a much lower melting point of 197°C, followed by dimeric molecular Mn<sub>2</sub>O<sub>7</sub> at 6°C.

## 8.3. Close Packing of Anions: Isomorphous Substitution in Mixed-Metal Oxides

**OVERVIEW.** The structures of many oxides can be described as based on a lattice of close-packed large oxide ions (Section 8.3A). Smaller cations can fit in some or all of the small tetrahedral holes between anions in two layers; there are two tetrahedral holes per anion. Larger cations can fit in the larger octahedral holes; there is one octahedral hole per anion. You may try such identifications with Exercises 8.27–8.31.

Mixed-metal oxides have more than one kind of metal ion in different hole types. Two common lattice types for mixed-metal oxides are the spinel structure  $(AB_2O_4)$  and the perovskite structure  $(ABO_3)$ . Nonstoichiometric oxides can arise when a given metal ion (usually from the *d* block) has two different adjacent oxidation states; then a smaller number of the higher-charged ions, plus a *defect* (missing ion) can replace a larger number of the lower-charged ions. Ions (usually cations) in a lattice can sometimes move into holes (such as vacant tetrahedral or octahedral sites) in the solid state, conducting electricity even in the solid state. You may practice identifying these structure types in Section 8.3B with Exercises 8.32–8.38.

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Oxides often employ substitution of one cation for another of similar size according to the first and second principles of isomorphous substitution (Section 8.3C). With the first principle, the two cations have the same charge. The second principle substitutes pairs of ions for other pairs of ions of the same *total* charge. You may try predicting cases of isomorphous substitutions with Exercises 8.39–8.50.

This section includes Connections to biochemistry, physical chemistry, radiochemistry, and three Connections to materials science. This section uses the deduction of ionic charges from Section 1.4, ionic radii from Section 1.5, the lattice types and unit cells introduced in Section 4.1, oxidation–reduction half-reactions from Section 6.1, and charge-transfer absorptions from Section 6.4. The concepts of defects and holes in lattices will appear again in Chapter 12.

**8.3A. Close Packing of Anions.** Before we look at some additional types of ionic oxides of metals and their physical properties, we need to mention an alternative way of looking at crystal lattices that is useful for many ionic compounds. Anions are normally larger than cations and are often in contact with each other in layers in which each anion touches six other anions (Figure 8.6a.) Each anion of a second layer of anions then can contact three anions in the layer below it, falling in the center of each triangle of the first layer (Figure 8.6b).



**Figure 8.6.** Close packing of atoms or (an)ions. (a) First layer. (b) Second layer (in **light brown**), with each atom of the second layer centered on an indentation between three atoms in the first layer. (c) Third layer (in **brown**) over indentations of the second layer, such that atoms of the third layer are directly over atoms of the first layer. This is the pattern of **hexagonal close packing**. (d) Third layer (in **gray**) also over indentations of the second layer, such that atoms of the third layer are also directly over indentations of the first layer. This is the pattern of **cubic close packing**. [Adapted from D. W. Oxtoby, H. P. Gillis, and A. Campion, *Principles of Modern Chemistry*, 7th ed., Brooks/Cole Cengage Learning: Belmont, CA, 2011, p. 1045.]

8.3. CLOSE PACKING OF ANIONS: ISOMORPHOUS SUBSTITUTION IN MIXED-METAL OXIDES 465



There are two possible patterns of close packing of a third layer of anions over the first and second layers. With one possibility, called **hexagonal close packing** (hcp) (Figure 8.6c), the third (top, **brown**) layer is matched up exactly with the first (bottom, **brown**) layer. This pattern is then normally continued throughout the whole crystal, with layers of spheres alternately in the A position (**brown**) and B position (**light brown**). The packing sequence of layers can be described as "...ABAB...."

In the alternate pattern of close packing, called **cubic close packing** (ccp) (Figure 8.6d), the third (top, **gray**) layer does not directly coincide with either the bottom or the middle layer. Instead, the anions of the third layer fall directly over the three-sided cavities of both the lower and the middle layers (Figure 8.6d). Finally the fourth layer directly matches the first layer, so that the packing sequence of layers can be described as "...ABCABC...."

Lattices of anions only would be unstable, having only repulsions; an equal total charge of cations must be included. The much smaller cations can then fill some of the **holes** or interstices between the anions. Thus, if we were packing basketballs (e.g., anions) and baseballs and golf balls (e.g., cations) for shipment in the same large box, we would figure out first how to pack the larger basketballs (anions) in the most efficient way possible, with confidence that the baseballs and golf balls (cations) would fit in the spaces between the larger spheres.

There are two types of holes in the hcp and ccp lattices: smaller tetrahedral holes and larger octahedral holes. The locations of these may be seen using Figure 8.6b. Between three anions in the first layer drawn in **brown** and *directly below* the anion in the second neighboring layer drawn in **light brown**, there is a small open space. It is called a **tetrahedral hole**, because it is surrounded by four large anions. A small cation (e.g., a golf ball) put in here has a coordination number of four.

As can be seen from Figure 8.6b, there is a white channel that falls between three ions in the first (**brown**) layer of anions *and* between three ions in the second (**light brown**) layer of anions. A cation centered in this cavity has a coordination number of six and an octahedral geometry. This **octahedral hole** is larger (suitable for a baseball); this is easier to see with the Polyhedral Model Kit.

For each sphere in a given layer, there are *two* tetrahedral holes but only one octahedral hole. The stoichiometry of the salt does not normally allow all of the holes to be filled with cations, but (if close packing is utilized) the structure can be described in terms of the type and fraction of holes occupied.

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## **EXAMPLE 8.9**

Which of the following structural descriptions are inconsistent with the stoichiometry of the salt being described? (a)  $Al_2O_3$  adopts an hcp lattice of oxide ions in which two-thirds of the octahedral holes are occupied by aluminum ions. (b)  $HgI_2$  adopts a ccp lattice of iodide ions in which half of the tetrahedral holes are occupied by  $Hg^{2+}$  ions. (c)  $SnBr_4$  adopts an hcp lattice of bromide ions in which one-eighth of the tetrahedral holes are occupied by  $Sn^{4+}$  ions.

**SOLUTION**: Recall that there are two tetrahedral and one octahedral holes per anion. (a) Two-thirds of an Al<sup>3+</sup> ion has two positive charges, which match the two negative charges of the oxide ion. This description is *consistent* with the stoichiometry of the salt. (b) Filling one-half of the two tetrahedral holes per anion with Hg<sup>2+</sup> ions gives two positive charges, which is *inconsistent* with the charge of the iodide ion, -1. (c) Filling one-eighth of two holes with Sn<sup>4+</sup> ions generates one positive charge, which is *consistent* with the one negative charge of the bromide ion. (If these holes are filled properly, a molecular structure results, as is observed.)

## 8.3B. Mixed-Metal Oxides—Spinels, Perovskites, and Nonstoichiometric Oxides.

There are a number of technologically important oxides, the simplest formulas of which look like oxo salts (e.g., BaTiO<sub>3</sub>), but which do not involve identifiable oxo anions. Such compounds are called mixed-metal oxides. The mixed-metal oxides are best regarded as consisting of lattices of oxide ions together with two (or more) different types of metal ions. In many of these, the oxide ions are close packed, and one kind of metal ion may occupy tetrahedral holes and the other kind, octahedral holes in the close-packed structure. An important class of over 100 mixed-metal oxides (and 30 mixed-metal sulfides) is known as the **spinels**\*, AB<sub>2</sub>O<sub>4</sub>. (Structures indicated with asterisks, \*, can be built using the Polyhedral Model Kit.) Spinels are very important in the solid-state electronics industry for their electric and magnetic properties (Section 8.4). In spinels the oxide ions are cubic close packed. Normally the A metal ions are +2-charged ions of radius between 80 and 110 pm, which occupy one-eighth of the tetrahedral holes in the oxide-ion lattice. Spinels are known in which the A metal ions are the +2 ions of Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Sn. Normally the B metal ions are +3-charged ions of radius between 75 and 90 pm, which occupy one-half of the octahedral holes; these include the +3 ions of Ti, V, Cr, Mn, Fe, Co, Ni, Rh, Al, Ga, and In.

Of particular interest are spinels in which both A and B are the same element: They form compounds of stoichiometry  $M^{2+}(M^{3+})_2(O^{2-})_4$  or  $M_3O_4$ , which have fractional average oxidation numbers because of the presence of two different oxidation states in the same compound.  $Mn_3O_4$  (hausmannite), Fe<sub>3</sub>O<sub>4</sub> (magnetite<sup>\*</sup>), and Co<sub>3</sub>O<sub>4</sub> are all intensely black, and much darker than the simple oxides of these metals, due to charge-transfer absorptions (Section 6.4B).

Another important class of mixed-metal oxides is the **perovskites**<sup>\*</sup> (ABO<sub>3</sub>), of which the prototype is CaTiO<sub>3</sub> (perovskite). It has an unusual cubic close-packed lattice of oxide *and* calcium ions (Figure 8.7), in the octahedral holes of which the much smaller Ti<sup>4+</sup> ions can "rattle around." In this lattice the very large A ion ideally has a coordination number of 12.





**Figure 8.7.** The structure of perovskites,  $ABO_3$ (e.g.,  $A = Ca^{2+}$  and  $B = Ti^{4+}$  in  $CaTiO_3$ ). Oxide ions are shown in **brown**. Larger A ions ( $Ca^{2+}$ ) are shown in **light gray**, at the center of dodecahedral (12) coordination by oxide ions. Smaller B ions ( $Ti^{4+}$ ) are shown in **dark gray**, at the center of the octahedral coordination by oxide ions. [Adapted from D. W. Oxtoby, H. P. Gillis, and A. Campion, *Principles of Modern Chemistry*, 7th ed., Brooks/Cole Cengage Learning: Belmont, CA, 2011.]

## **EXAMPLE 8.10**

Choose the appropriate classification—perovskite, spinel, or neither—for each of the following metal oxides: (a)  $BaCO_3$ ; (b)  $RaTiO_3$ ; (c)  $BaThO_3$ ; (d)  $TiBa_2O_4$ ; (e) hausmannite,  $Mn_3O_4$ ; (d)  $Tl_2SiO_4$ .

**SOLUTION**: (a), (b), and (c) all have the stoichiometry to be perovskites, but the cation sizes may not be suitable. The Ba<sup>2+</sup> and Ra<sup>2+</sup> ions are very large +2 ions, so they are acceptable. There should also be a much smaller +4-charged metal ion. C<sup>4+</sup> is not a realistic metal ion, however, and we may recognize that  $CO_3^{2-}$  is the polyatomic carbonate ion, so (a) is *neither*. The Ti<sup>4+</sup> is indeed a much smaller metal ion, so (b) is a *perovskite*. It has an acceptable radius for a perovskite. The Th<sup>4+</sup> ion has a quite large radius of 108 pm, on the other hand, so (c) is *neither*. (d), (e), and (f) have the correct overall stoichiometry to be spinels. In (d), however, the A ion is Ti<sup>4+</sup> which is not a +2 ion between 80 and 110 pm, and Ba<sup>2+</sup> is not a +3 ion between 75 and 90 pm, so this salt is *neither*. In hausmannite the A ion is Mn<sup>2+</sup>, which has the correct size and charge, and the B<sub>2</sub> ions are Mn<sup>3+</sup>, which have the correct charge and size, so (e) is a *spinel*. In (f) the B<sub>2</sub> ions are Tl<sup>+</sup>, which are too low in charge and too large in size. The A ion is Si<sup>4+</sup>, which is too high in charge and too small in size. Indeed, you may recognize this as the *silicate* ion. So this is *neither*—it is the salt barium silicate.

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## A CONNECTION TO MATERIALS SCIENCE

## **Microphones and Loudspeakers**

If the temperature is not too high, the Ti<sup>4+</sup> ions of perovskite itself tend to be off the center of the lattice unit cell, giving rise to an electric charge separation or dipole; such materials are known as **ferroelectrics**. Application of mechanical pressure to one side of a perovskite crystal causes the Ti<sup>4+</sup> ions to migrate, generating an electrical current; application of an electric current causes mechanical motion of the ions. The pressure effect, known as the **piezoelectric effect**,<sup>10</sup> makes perovskites useful in converting mechanical energy to electric energy, as in microphones, sonar, and vibration sensors, or vice versa. The conversion of electrical energy to mechanical energy is useful in sonic and ultrasonic transducers and in headphones and loudspeakers.

Perhaps the easiest mixed-metal-ion oxides to prepare are the **nonstoichiometric oxides** of metals that have cations of more than one oxidation state. Iron(II) oxide as normally prepared gives an actual elemental analysis corresponding approximately to  $Fe_{0.95}O$ ; there is a **defect** consisting of missing iron atoms. The compound, however, must still be electrically neutral; this is accomplished by the replacement of three  $Fe^{2+}$  ions by two  $Fe^{3+}$  ions, leaving a hole or vacancy but keeping the overall electroneutrality (Figure 8.8). Because most of the *d*-block metals have cations differing by only one unit of charge, there are many nonstoichiometric *d*-block metal oxides, including (for example) those of ideal composition TiO, VO, MnO, FeO, CoO, and NiO. If the +2 and +3 oxidation states are of comparable stability, a wide range of nonstoichiometry can exist: Vanadium(II) oxide can range from an actual composition of  $V_{0.77}O$  to  $V_{1.27}O$ , while nickel(II) oxide ranges only from Ni<sub>0.999</sub>O to Ni<sub>1.000</sub>O. You should be able to verify that the structural segment shown in Figure 8.8 is neutral, and that its stoichiometry is  $M_{0.917}O$ .



**Figure 8.8.** Planar segment of the structure of a nonstoichiometric oxide  $M_{0.917}$ O. **Brown** = oxide ions, **gray** = 2+ ions, and black = 3+ ions.

#### 8.3. CLOSE PACKING OF ANIONS: ISOMORPHOUS SUBSTITUTION IN MIXED-METAL OXIDES 469

**Electrical Conductivity of Solid Oxides.** An electrical current consists of moving charged particles. In molten or dissolved ionic salts, the ions are free to move and to conduct an electrical current. In most *solid* metal oxides (and other salts) the ions are immobilized by the crystal lattice, so solid ionic compounds are generally not good conductors of electricity. Some metal oxides,<sup>11</sup> such as the nonstoichiometric early *d*-block metal ions of the fourth period,  $Ti_xO$  and  $V_xO$  ( $x \approx 1.0$ ), have metal-like conductivity due to the easy transfer of *electrons* between titanium or vanadium ions differing by one unit of charge.

In certain types of lattices and under certain conditions, *ions* can move in solids, hence conduct an electric current: There are materials in which the smaller type of ion can move readily, while the larger counterions maintain the rigidity of the solid-state lattice as a whole. Such materials are variously known as solid electrolytes, super-ionic conductors, and fast-ion conductors.<sup>12</sup> They are important for their potential uses in high-energy-density batteries, fuel cells, and lasers.

Because anions are commonly larger than cations, most solid electrolytes involve rapid cation motion. For example, some solid *iodides* allow super-ionic conduction of electronegative cations into tetrahedral holes in the iodide lattice. The structures of copper(I) and silver(I) tetraiodomercurates, Cu<sub>2</sub>HgI<sub>4</sub> and Ag<sub>2</sub>HgI<sub>4</sub>, feature fourcoordinate metal ions but only three-coordinate iodide ions; one-fourth of the tetrahedral holes about the large (approximately cubic close-packed) iodide ions are vacant. At low temperatures the vacant holes are ordered and the cations cannot move into them; the compounds have low conductivity and light colors (red for the Cu<sup>+</sup> and yellow for the Ag<sup>+</sup> salt). At a specific temperature (50°C for the Ag<sup>+</sup> salt), a phase transition occurs in which the lattice opens up enough for the cations to move between the iodide ions. The cations and vacant holes are then disordered, the motion increases the electrical conductivity dramatically, and the color darkens (to black in the Cu<sup>+</sup> salt and orange in the Ag<sup>+</sup> salt). Similar types of phenomena are found in solid AgI. At room temperature AgI adopts the zinc blende structure (Figure 4.2), with Ag<sup>+</sup> ions filling half the tetrahedral holes in an orderly pattern. Above 145.8°C the Ag<sup>+</sup> ions become mobilized to move easily between the easily deformed (soft) I<sup>-</sup> ions.





#### 470 CHAPTER 8. OXIDES AND SILICATES AS MATERIALS

## A CONNECTION TO MATERIALS SCIENCE

## **Conduction in Lithium-Ion Batteries**

Of particular importance for modern lightweight electronic devices such as laptop computers and cell phones are the rechargeable lithium-ion batteries (Sections 1.2C and 6.3A), in which the very light, relatively small Li<sup>+</sup> ion is mobile. The most common solid electrolyte<sup>13</sup> in these batteries is the mixed-metal oxide LiCoO<sub>2</sub>, which has a distorted NaCl type of structure in which layers of Li<sup>+</sup> and Co<sup>3+</sup> cations alternate.<sup>14</sup> The lithium ions are free to move within the two dimensions of its layer (Figure 8.9). When these batteries are charged, Li<sup>+</sup> ions are reduced to Li<sup>0</sup>, which migrates out of the lattice (for safety reasons, Li<sup>0</sup> is absorbed between graphite layers as the compound of approximate composition LiC<sub>6</sub>), and the cobalt is oxidized to Co(IV) oxide. During discharge the Li<sup>0</sup> releases its electron (producing a voltage of about 3.6 V) and migrates back into the solid, regenerating LiCoO<sub>2</sub>.

Two of the technologies for renewable energy generation, capturing wind power and solar energy, suffer from intermittency: The wind does not always blow and the sun does not always shine. Hence, if these are to be relied on, the energy must be stored during times of peak production and released during times of excess demand; much larger lithium-ion batteries are being investigated for this use.

#### **A CONNECTION TO MATERIALS SCIENCE**

## **Oxide-Ion Conductors in Automobile Catalytic Converters**

Oxide ions can be the mobile phase if the cations are large enough that oxide ions can move between them. This is the case between 500°C and 1000°C in zirconia (ZrO<sub>2</sub>) doped with CaO or with  $Y_2O_3$ . When a Ca<sup>2+</sup> ion or an  $Y^{3+}$  ion replaces a Zr<sup>4+</sup> ion in the zirconia lattice, charge neutrality of the lattice is maintained by deleting oxide ions as well. The resulting vacancies in the fluorite-type lattice act as holes into which other oxide ions can move (and hence carry current) if enough thermal energy is available. Oxygen detectors for pollution control in automobile exhaust employ solid oxide-ion conductors.

**8.3C. The First and Second Principles of Isomorphous Substitution.** Often in nature or the laboratory we have more than one metal ion present, and when we form a metal oxide or other salt, some of the metal ions of the second metal replace the same number of the first metal ion with the same positive charge, without changing the lattice type. This is **isomorphous substitution** (Figure 8.10) for the first ion and gives a type of solid solution. Dissolving a small percentage of  $Cr_2O_3$  into the lattice of



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**Figure 8.10.** Isomorphous substitution in the perovskite unit cell ABO<sub>3</sub>. Oxide (or halide) ions are shown encircled in **brown**, the large A cations are shown in black, and the smaller B cations are shown in **gray**. (a) The structure of CaTiO<sub>3</sub>. (b) Isomorphous substitution of Sr<sup>2+</sup> for Ca<sup>2+</sup>. (c) Isomorphous substitution of Na<sup>+</sup> for Ca<sup>2+</sup> and of Nb<sup>5+</sup> for Ti<sup>4+</sup>. (d) Isomorphous substitution of all ions: A<sup>+</sup> (= RNH<sub>3</sub><sup>+</sup>) for Ca<sup>2+</sup>, Pb<sup>2+</sup> for Ti<sup>4+</sup>, and I<sup>-</sup> for O<sup>2+</sup>.

colorless alumina (Al<sub>2</sub>O<sub>3</sub>) puts some colored Cr<sup>3+</sup> ions in sites normally occupied by Al<sup>3+</sup> ions. This gives the pink gemstone *ruby*. Similarly, dissolving some Ti<sub>2</sub>O<sub>3</sub> (with colored Ti<sup>3+</sup> ions) in Al<sub>2</sub>O<sub>3</sub> results in blue *sapphires*.

The type of cations that can substitute isomorphously for other cations in a metal oxide (or other type of salt) depends on (1) the size of those cations and (2) the charge of those cations. The **first principle of isomorphous substitution** states that *one ion may substitute for another in a lattice if the two ions have identical charges and differ in radii by not more than 10 to 20%*.

Examination of Table C shows that quite a few sets of cations can be found that have the same charge and very similar ionic radii. If we limit ourselves to ions

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commonly found in Earth's crust, the sets found in the columns of Table 8.5 result. As a salt or mineral is formed by crystallization or the cooling of molten magma, there is little reason for one of these matched types of ions to be preferred over another. Naturally occurring minerals often have a mixture of cations present, which vary depending on the composition of the melt or solution from which the mineral grew. For example,  $Mg^{2+}$  and  $Fe^{2+}$  not only have identical charges but also have very similar radii (86 and 92 pm, respectively). The mineral olivine, with an ideal composition of  $Mg_2SiO_4$ , is often "impure" and can contain varying percentages of the  $Fe^{2+}$  ion in place of an equal number of  $Mg^{2+}$  ions. Thus, the formula of olivine is often written  $(Mg,Fe)_2SiO_4$  to indicate that there are two magnesium or iron(II) cations present per mole of silicate ion, although there is no definite relationship between the number of magnesium and the number of iron(II) cations. Note how different this process is from what normally happens in synthesizing molecular (e.g., organic) compounds!

The substitution may be done more than once and may also be of anions for anions. In the latter case, polyatomic anions are likely involved, because there are more of them than there are simple anions. For example, the most important mineral in bones and teeth is *hydroxyapatite*,  $Ca_5(OH)(PO_4)_3$ . Because this compound contains a very strongly basic hydroxide anion, it is prone to reacting with acids generated in the mouth by bacterial action. The utility of adding trace amounts of fluoride to drinking water or toothpaste occurs when F<sup>-</sup> (radius 119 pm) substitutes isomorphously for OH<sup>-</sup> (no precise radius, but dominated by oxygen of ionic radius 126 pm) to give the mineral *fluorapatite*. Another set of hexagonal (six-sided) minerals arises by isomorphous substitution of polyatomic anions in minerals having the same stoichiometry as apatite. These minerals are lead minerals of stoichiometry Pb<sub>5</sub>Cl(EO<sub>4</sub>)<sub>3</sub>. When the EO<sub>4</sub> polyatomic anion is vanadate, the mineral is known as vanadinite; when the anion is arsenate, the mineral is called mimetite; when it is phosphate, the mineral is pyromorphite.

Range of Radii (pm)	+1 Charge <sup>a</sup>	+2 Charge <sup>a</sup>	+3 Charge <sup>a,b</sup>	+4 Charge <sup>a</sup>
54-67			Al <sup>3+</sup> (67)	Si <sup>4+</sup> (54)
74-92	Li <sup>+</sup> (90)	Mg <sup>2+</sup> (86)	Fe <sup>3+</sup> (78)	Ti <sup>4+</sup> (74)
		Fe <sup>2+</sup> (92)		
100–117	Na <sup>+</sup> (116)	Ca <sup>2+</sup> (114)	Ln <sup>3+</sup> (100–117)	
149–152	K+ (152)	Ba <sup>2+</sup> (149)		

## TABLE 8.5 Sets of Common lons Suitable for Isomorphous Substitution

<sup>*a*</sup> Radii listed in parentheses are in picometers (pm).

<sup>*b*</sup> Lanthanide ions =  $Ln^{3+}$ .

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## A CONNECTION TO RADIOCHEMISTRY

## **Co-Precipitation**

Isomorphous substitution is often deliberately used in radiochemistry to isolate exceedingly tiny quantities of radioactive elements. Thus, to isolate a tiny amount of radium ion from a large amount of uranium ore, we could (using the solubility principles of Section 4.3) add sulfate ion to precipitate radium sulfate while leaving uranium and most other cations in solution. But this would pose two problems: (1) only a tiny amount of precipitate would be formed, which would be difficult to handle without losing it; and (2) there might be so much solution present that even the low solubility product of radium sulfate would not be exceeded, so no precipitate would form. Marie Curie overcame these problems by adding not only sulfate ion but also barium ion. A large amount of barium sulfate then precipitated, in which the radium substituted isomorphously for the barium. This technique is known as **co-precipitation**; the barium ion is said to act as a *carrier* for the Ra<sup>2+</sup>. Curie was then confronted with the formidable problem of separating the very similar barium and radium ions, but at least she was working with a much smaller volume of material.

#### A CONNECTION TO PHYSICAL CHEMISTRY

## **Doping Crystals by Isomorphous Substitution**

Another illustration of this process occurs in a familiar experiment of growing crystals of ionic compounds. For example, large, beautiful octahedral crystals of *alum*, KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, are readily grown from solution. But there exist a whole series of similar compounds that also form large, beautiful octahedral crystals having the same lattice types and the same shapes (these compounds are said to be isomorphous). In the formula for alum, the K<sup>+</sup> ion can be replaced by other +1 cations of similar radius, such as Rb<sup>+</sup> and NH<sub>4</sub><sup>+</sup>. The Al<sup>3+</sup> ion can be replaced by numerous other +3 ions of similar radius, such as Cr<sup>3+</sup> (giving purple crystals of *chrome alum*) or Fe<sup>3+</sup> (giving pale violet crystals of *ferric alum*). The sulfate anion can even be replaced by the selenate anion. If nearly any combination of these three ingredients is mixed and crystallized, large crystals of an alum are formed; if a mixture, say, including both Al<sup>3+</sup> and Cr<sup>3+</sup> is used, crystals can be grown containing both ions, having whatever shade of light purple you desire! Such a crystal is sometimes said to be *doped* with a certain percentage of the less abundant ion.

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The separation of the *f*-block cations involves quite a complex process of ion exchange. The most troublesome case of isomorphous substitution, however, is that of the elements Zr (Pauling electronegativity 1.3; ionic radius 86 pm) and Hf (Pauling electronegativity 1.3; ionic radius 85 pm). Hf occurs isomorphously substituted in all zirconium compounds to the same extent (about 2%), so there were no chemical discrepancies in the "pure" samples of zirconium prepared in 1825 and thereafter. As a result, the presence of Hf went undetected for a whole century!

### CHEMICAL TRIVIA

## What City Has the Greatest Number of Elements Named After It?

Perhaps the most extensive case of isomorphous substitution occurs in the minerals monazite and xenotime (MPO<sub>4</sub>) and bastnaesite (MFCO<sub>3</sub>). In 1794 J. Gadolin investigated a mineral obtained from the village of Ytterby, Sweden; from this mineral he extracted a metal oxide that he named *yttria*. But other chemists, in working with this material, kept getting slightly different properties; eventually it was realized that this oxide was a mixture. So, the mixture was separated, but the "pure" components also turned out to be mixtures. Eventually all of the *f*-block elements of the sixth period (except Pm), plus La and Y, turned out to be present in these minerals, isomorphously substituted for each other. (Refer to Tables A through C to note the extreme similarities of these elements to each other.) As element after element was discovered, the chemists were harder and harder pressed to come up with new names for them. Thus, it came to pass that the humble village of Ytterby has more elements named after it than any of the great cities of the world: yttrium, ytterbium, terbium, and erbium.

## **A CONNECTION TO BIOCHEMISTRY**

#### Substituting NMR-Active Nuclei in Enzymes

There are often very practical reasons for substituting one metal ion for another in an ionic lattice (or even in compounds such as metalloenzymes). The *s*- and *p*-block metal ions are all colorless. If they can be isomorphously substituted with *d*- and *f*-block ions, the spectra of these ions will give us information on the crystal field environment of the ions in the lattice or enzyme (Section 7.3). Metal ions also have other properties that tell us about their environment: Some are fluorescent; some have unpaired electrons with magnetic properties that can be studied; others with appropriate nuclei can be studied by nuclear magnetic resonance (NMR) or Mössbauer spectroscopy. Some of the geologically and biochemically most important metal ions, such as K<sup>+</sup> and Zn<sup>2+</sup>, however, are "silent metals" that lack most or all of these properties. Silent K<sup>+</sup> (radius = 152 pm) can often usefully be substituted with fluorescent and NMR-active Tl<sup>+</sup> (radius = 164 pm). Colorless Zn<sup>2+</sup> (radius = 88 pm) is usefully replaced by colored Co<sup>2+</sup> (radius = 88 pm). Silent Ca<sup>2+</sup> (radius = 114 pm) can be replaced by NMR-active Eu<sup>2+</sup> (radius = 131 pm), with seven unpaired electrons.

#### 8.3. CLOSE PACKING OF ANIONS: ISOMORPHOUS SUBSTITUTION IN MIXED-METAL OXIDES 475

**The Second Principle of Isomorphous Substitution.** There are a number of other perovskites that can be generated from the structure of CaTiO<sub>3</sub> through the application of either the first or the **second principle of isomorphous substitution**. The second principle allows more versatility: Although substituting ions must still be about the same size as the ions replaced in order not to change the lattice type, within certain strict limits the *charge* of the entering ion need not be identical to the charge of the departing ion. The basic principle is that the *total* charge of the pair of replacing ions must equal the total charge of the pair of replaced ions. This means that isomorphous substitution can occur even if the new ions C have a charge one greater than the old ions A, if there is *simultaneous* substitution by new ions D with a charge one *less* than the old ions B. This conserves the electroneutrality of the salt, because the sum of charges of the new ions C and D equals the sum of charges of the old ions A and B. Table 8.5 shows sets of common ions that frequently substitute for one another; to use the second principle, the substituting ions should be from the same row of this table and from adjacent columns.

We illustrate this process starting with the prototype perovskite,  $(Ca^{2+})(Ti^{4+})(O^{2-})_3$ , in Figure 8.7. The perovskite shown in Figure 8.7c is  $(Na^+)(Ta^{5+})(O^{2-})_3$ , obtained by the simultaneous substitution of Na<sup>+</sup> (r = 116 pm) for Ca<sup>2+</sup> (r = 114 pm) and of Ta<sup>5+</sup> (r =78 pm) for Ti<sup>4+</sup> (r = 74 pm). The substituted ions have nearly the same size as those in the prototype perovskite, so radius ratios in the lattice are not appreciably altered. The

## EXAMPLE 8.11

Which of the following minerals could arise by isomorphous substitution processes in leucite, KAlSi<sub>2</sub>O<sub>6</sub>? (a) KYSi<sub>2</sub>O<sub>6</sub>; (b) RbAlSi<sub>2</sub>O<sub>6</sub>; (c) BaBeSi<sub>2</sub>O<sub>6</sub>; (d) BaAlSi<sub>2</sub>O<sub>6</sub>.

**SOLUTION:** First, note that *the total charge of all the cations must equal the total charge of all the anions.* This requirement is implicit in the two principles of isomorphous substitution, but also gives a separate simple test in this example: If the total charge of all cations going into the structure is not the same as the total charge of all cations coming out, the new compound cannot exist, let alone be isomorphous. In (a) Y<sup>3+</sup> replaces Al<sup>3+</sup>; in (b) Rb<sup>+</sup> replaces K<sup>+</sup>; in (c) Ba<sup>2+</sup> and Be<sup>2+</sup> replace K<sup>+</sup> and Al<sup>3+</sup>; in (d) Ba<sup>2+</sup> replaces K<sup>+</sup>. Substitution product (d) cannot exist.

Note, too, that in order for the substitution to be isomorphous, *the total number of cations going in must be nearly equal to the total number coming out*. (If the two numbers are slightly unequal, a nonstoichiometric compound is formed, as was discussed on page 468.) All four possible substitution products given above obey this principle.

Once these two principles are satisfied, the two principles of isomorphous substitution are satisfied if the cations going into the replacement structures are within 10–20% of the radii of the cations coming out. In (a)  $Y^{3+}$  has a radius of 104 pm, which is too much bigger than  $Al^{3+}$  (67 pm) for the substitution to be isomorphous. However, (b) and (c) are satisfactory, since in (b) Rb<sup>+</sup> (166 pm) is close in size to K<sup>+</sup> (152 pm), and in (c) Ba<sup>2+</sup> (149 pm) is close to K<sup>+</sup> (152 pm), and Be<sup>2+</sup> (59 pm) is close to Al<sup>3+</sup> (67 pm).

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new ions have the same total charge (+6) as the old ions, and the opposite total charge to the three oxide ions, so the stoichiometry keeps the crystal neutral overall, as is also required. Among the suitable large A ions are  $Ca^{2+}$  (r = 114 pm),  $Y^{3+}$  (r = 104 pm),  $Ba^{2+}$  (r = 149 pm), and K<sup>+</sup> (r = 152 pm). Among the suitable small B ions are  $Cu^{3+}$  (r < 87 pm),  $Ti^{4+}$  (r = 74 pm), and Nb<sup>5+</sup> (r = 78 pm).

It is even possible to substitute *all* of the ions, provided that the sizes are proportional and the total charges add up to zero for the neutral salt. In a Connection in Section 6.4B, we mentioned how the ability of white  $\text{TiO}_2$  to absorb sunlight is enhanced by absorption of "perovskites" (RNH<sub>3</sub><sup>+</sup>)(Pb<sup>2+</sup>)(I<sup>-</sup>)<sub>3</sub>. These also have the ABO<sub>3</sub> stoichiometry with charges adding up to zero. But because all ions have half the charge of the charges in CaTiO<sub>3</sub>, the total lattice energy is *much* lower, so the physical properties of (RNH<sub>3</sub><sup>+</sup>)(Pb<sup>2+</sup>)(I<sup>-</sup>)<sub>3</sub> are quite different than those of CaTiO<sub>3</sub>.

## 8.4. Ferromagnetic, Antiferromagnetic, and Superconducting Solid Ionic Oxides

**OVERVIEW.** Paramagnetism found in simple ions (Section 7.2) can be modified by direct or indirect interaction with neighboring ions in solids such as some oxides to produce more complex magnetic properties: ferromagnetism, antiferromagnetism, ferrimagnetism, and superconductivity. The uses and difficulties of working with high-temperature superconducting oxides illustrate the challenges and potentials of materials science. Superconductors are identified and characterized in Exercises 8.51–8.55.

Section 8.4 includes two Connections to materials science. It builds upon the fundamental types of magnetic properties from Section 7.2, valence electron configurations from Section 1.3, and overlap of orbitals from Section 3.3. Ferromagnetism and superconductivity will appear again in elements and alloys in Sections 12.3B and 12.4C.

In materials such as oxides in which paramagnetic ions (those of the *d*- and *f*-block metals) lie close together, their magnetic moments can align in cooperation with each other throughout large domains of the solid sample. In **ferromagnets** all of the individual magnets (metal ions) in the domain are aligned in the same direction; in **antiferromagnets** every other metal atom or ion has its magnetic field oriented in the opposite direction (Figure 8.11).

**Ferromagnetism** is found in materials in which unpaired electrons in *d* or *f* orbitals interact with unpaired electrons in similar orbitals in neighboring atoms or ions, so as to align their spins parallel to each other (Figure 8.11a). This interaction must be weak, however; otherwise the electrons pair up in the same bonding orbital, and no magnetism results. **Antiferromagnetism** is also found in oxides and other compounds when the two metal ions interact indirectly, through a ligand whose paired electrons couple weakly and in opposite directions with the unpaired electrons of neighboring metal ions (Figure 8.11b, c), so as to align their spins antiparallel to each other. **Ferrimagnetism** is a property found in some mixed-metal oxides in which the two types of ions are each ferromagnetic—but one type of ferromagnetism is stronger than the other. Although the spins for each set of ions are opposed, the effects do not cancel out.



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**Figure 8.11.** Schematic two-dimensional representation of the parallel and antiparallel orientations of the magnetic fields and electron spins of neighboring metal ions in (a) ferromagnets and (b) antiferromagnets, respectively. (c) The antiferromagnetic coupling of electron spins between the paired electrons of a ligand and the unpaired electrons of two neighboring metal ions, resulting in the two metal ions having antiparallel spins. [(a) and (b) Adapted from I. S. Butler and J. F. Harrod, *Inorganic Chemistry: Principles and Applications*, Benjamin/Cummings: Redwood City, CA, 1989, p. 434. (c) Adapted from D. F. Shriver, P. W. Atkins, and C. H. Langford, *Inorganic Chemistry*, W. H. Freeman: New York, 1990, p. 586.]

Figure 8.12a first shows the case of simple *paramagnetism*: The magnetic susceptibility  $\chi_{\rm M}$  as a function of temperature is as predicted by Equation 7.3. Figure 8.12b shows the enhanced magnetic susceptibility of *ferromagnets* at low temperature. The weak tendency of ferromagnetism to order electrons is readily overcome by the entropic tendency to disorder. Ferromagnetism fades out at higher temperatures and finally disappears at the **Curie temperature**  $T_{\rm Curie}$ , above which paramagnetic behavior prevails. At low temperatures, *antiferromagnetic* materials show very low magnetic susceptibility,



which increases (Figure 8.12c) with temperature up to the **Néel temperature**  $T_N$ , above which entropy prevails and normal paramagnetic behavior is found.

**Figure 8.12.** Plots of the temperature dependence of magnetic susceptibility  $\chi_{\rm M}$  of an idealized substance acting (a) as a paramagnetic substance (\_\_\_\_\_); (b) as a ferromagnetic substance (\_\_\_\_\_) below its Curie temperature,  $T_{\rm Curie}$ ; and (c) as an antiferromagnetic substance (\_\_\_\_\_) below its Néel temperature,  $T_{\rm N}$ .

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**Figure 8.13.** Levitation of a magnet above a pellet of a high-temperature superconductor cooled below its  $T_{\rm C}$ .

Among the mixed-oxidation state spinels of Mn, Fe, and Co,  $Mn_3O_4$  and  $Co_3O_4$  are antiferromagnetic, while Fe<sub>3</sub>O<sub>4</sub> (the mineral *magnetite* or *lodestone*) is ferrimagnetic. Microscopic crystals of magnetite have been found in a number of different living organisms, including bacteria, pigeons, salmon, and (perhaps) in human brain tissue. These crystals might confer sensitivity to magnetic fields similar to Earth's.<sup>15</sup> Similarly, among the simple *d*-block dioxides, VO<sub>2</sub> and  $MnO_2$  are antiferromagnetic, while ferromagnetic CrO<sub>2</sub> is used in magnetic storage devices.

**Superconductivity** was first observed in metals (Section 12.4C). Superconductors have two outstanding characteristics below their **critical temperature**,  $T_{\rm C}$ , which is the highest temperature at which the superconducting state can be maintained. First, they are capable of excluding a magnetic field, a type of perfect diamagnetism known as the **Meissner effect**. This effect allows a superconductor to levitate a magnet above it (Figure 8.13). Second, the electrical resistance of superconductors drops to zero.

#### Molecular Magnetism in Prussian Blues

Prussian blues (Section 5.3) can be thought of as resembling oxides in which oxide-ion bridges are replaced with cyanide-ion bridges. The cyanide ion coordinated via its C donor atom is high on the spectrochemical series (Eq. 7.6), so the metal ion coordinated to the C donor atom is low spin. Furthermore, the  $e_g^*$  orbitals of the metal ion are so high in energy that they are not occupied. Hence, this metal ion must have six or fewer valence *d* electrons. In a  $d^6$  complex such as  $[Fe(CN)_6]^{4-}$  there are no unpaired electrons and the ion is diamagnetic, giving no possibility for ferromagnetism in salts of this ion. But earlier 4d-block complex cyanides such as  $[Cr(CN)_6]^{3-}$  can be paramagnetic and participate in ferromagnetic interactions as illustrated in Figure 8.11.

The N donor atom of the bridging  $CN^-$  ion has a moderate position in the spectrochemical series, so the metal ion(s) coordinated to it can be low spin, but are more often high spin and can go beyond a  $d^6$  electron configuration. This metal ion usually has unpaired electrons, is paramagnetic, and *may* have a ferromagnetic interaction with the metal ion coordinated to the C donor atom. As an example,  ${}^3_{\infty}{\{(Fe^{3+})[Fe(CN)_6]^{3-}\}}$  has unpaired electrons on each type of Fe<sup>3+</sup> ion and is ferromagnetic, but has a low Curie temperature.

Electrons in the *d* orbitals of early *d*-block metal ions extend further from the metalion nucleus (Section 9.4), so they can interact more strongly with the electrons in *d* orbitals of a  $[M(CN)_6]^{n-}$  ion. With early *d*-block ions such as V<sup>2+</sup>, Cr<sup>2+</sup>, and Cr<sup>3+</sup>, ferromagnetism may persist at or near room temperature.<sup>16</sup> A  $T_{Curie}$  of  $-3^{\circ}C$  is found in a mixed-valence chromium(II,III) hexacyanochromate(II,III),  $\frac{3}{\infty}[(Cr)_{2.12}(CN)_6]$ .<sup>17</sup> An even higher  $T_{Curie}$  of 42°C is found when vanadium is incorporated in  $\frac{3}{\infty}\{(V^{2+})_{0.49}(V^{3+})_{0.67}[Cr^{III}(CN)_6]\}$ .<sup>18</sup> Such materials are of interest as *molecular magnets*.

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In 1987<sup>19</sup> the scientific world was very much surprised to learn that mixedmetal oxides can show the property of superconductivity. The first of these oxides,  $La_{1.85}Sr_{0.15}CuO_4$ , showed a higher  $T_C$ , 30 K, than any of the metals or alloys (Section 12.4C). Very soon a mixed-metal oxide with a  $T_C$  of about 90 K was discovered,  $YBa_2Cu_3O_7$  (which is familiarly known as "123" for the ratios of the metal ions in the formula). With this high a  $T_C$ , the cheap and abundant coolant, liquid nitrogen, can be used to cool the superconductor below  $T_C$ . (Above  $T_C$  superconductors show the antiferromagnetic properties that are common in metal oxides.)

The structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (Figure 8.14) is related to that of perovskite (Figure 8.7). This relationship can be seen if we take three adjacent A-centered unit cells (Figure 8.14) and allow Y<sup>3+</sup> to occupy the A position in the central cell and Ba<sup>2+</sup> to occupy the A positions in the outer cells. The other alteration is that three perovskite unit cells would contain a total of nine, not seven, oxide ions, and would require an impossibly high oxidation number for at least one of the metals. The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> structure deletes oxide ions from each of the three cells: along the front and back outer edges in the two Ba-centered cells, and along the middle edges in the Y-centered cell. In addition, the superconductor is slightly nonstoichiometric, so it has a formula of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>.

Removing oxide ions changes the polyhedra of the copper ions. The  $d^8$  Cu<sup>3+</sup> ions found on the top and bottom surfaces of the new, larger unit cell of Figure 8.14 (those closer to Ba than to Y) show square planar coordination; bridging oxide ions link these squares into polymeric *chains*, as shown by the arrows in Figure 8.14. In contrast, the  $d^9$  Cu<sup>2+</sup> ions found in the center of the new unit cell (sandwiched between Ba and Y) lose only one oxide neighbor, so they show square pyramidal coordination; the square pyramids are also linked by bridging oxide ions, but this time in two dimensions to form *planes* of Cu<sup>2+</sup> polyhedra.

Experiments in isomorphous substitution have helped decide which parts of the structure in Figure 8.14 are crucial for superconductivity. The diamagnetic  $Y^{3+}$  ions can be replaced with most of the lanthanide ions without altering the superconductivity (even though these ions are mostly paramagnetic!). Slight replacement (doping) of the Cu<sup>3+</sup> ions from the chains of CuO<sub>4</sub> square planes with other +3-charged ions such as Ga<sup>3+</sup> lowers  $T_C$ , but not as severely as does slight replacement of the Cu<sup>2+</sup> ions from the planes of CuO<sub>5</sub> square pyramids with divalent ions such as Zn<sup>2+</sup>.

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-8</sub> is prepared by sintering the solid oxides Y<sub>2</sub>O<sub>3</sub>, CuO, and the oxide precursor BaCO<sub>3</sub> at 950°C for an extended time, followed by a slow cooling and exposure to O<sub>2</sub> at 500–600°C, whereupon one-third of the Cu<sup>2+</sup> ions are oxidized to Cu<sup>3+</sup> ions. Materials scientists continue to be challenged by the basic physical properties of such oxides. Synthesis by sintering requires high temperatures and long reaction times. It is difficult to insure that only one product is produced when so many mixed-metal oxides are possible; with such nonvolatile, insoluble products, normal methods of purification after synthesis are impossible. The brittleness of the products makes it very difficult to draw the superconductor into wires or to deposit it as films. In addition, with the presence of the high Cu<sup>3+</sup> oxidation state, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is air- and moisture-sensitive.
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**Figure 8.14.** The structure of the hightemperature superconductor  $YBa_2Cu_3O_7$ as it relates to three A-centered unit cells of the perovskite structure. At the top the oxide ions from neighboring unit cells have been added in to show the  $CuO_4$ square planar units, which are linked into chains by shared bridging oxide ions in the direction shown by the top arrows. Similarly, nearer to the center the square pyramidal coordination of another copper ion is completed; again sharing of oxide bridges gives rise to sheets extending in the two dimensions indicated by the four arrows in the center.

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# A CONNECTION TO MATERIALS SCIENCE

# Newer High-Temperature Superconductors

A variety of related "cuprate" high-temperature superconductors have since been discovered. YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> and Y<sub>2</sub>Ba<sub>4</sub>Cu<sub>7</sub>O<sub>15</sub> add additional chains of CuO<sub>4</sub> squares, but the most dramatic improvements in  $T_{\rm C}$  result from incorporating heavy *p*-block metal ions of mercury, thallium, and bismuth, resulting in idealized formulas including HgBa<sub>2</sub>CuO<sub>4</sub>, Bi<sub>2</sub>Sr<sub>2</sub>CuO<sub>6</sub>, Tl<sub>2</sub>Ba<sub>2</sub>CuO<sub>6</sub>, and TlBa<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>. The highest  $T_{\rm C}$  yet found, 125 K and 133 K, belong to superconductors having three layers of Cu ions, Tl<sub>2</sub>Ba<sub>2</sub>CaCu<sub>3</sub>O<sub>10</sub> and HgBa<sub>2</sub>CaCu<sub>3</sub>O<sub>8</sub>, respectively. These structures lack chains of CuO<sub>4</sub> squares but still have the planes of cuprate units, confirming their importance in superconductivity. The production of the thallium- and mercury-containing cuprates is limited by the toxicity and high-temperature volatility of Tl<sub>2</sub>O and HgO, which have low lattice energies and hence relatively high vapor pressures at temperatures at which the other oxides react to give superconductors.

Since these discoveries, superconductivity has been found in other classes of materials. One recent new class of high-temperature superconductors are based on a more complex lattice that has alternating oxide and arsenide layers,  $^2_{\infty}$  [LaO]<sup>+</sup>  $^2_{\infty}$  [FeAs]<sup>-.20,21</sup> With about 10% of the oxide ions replaced by fluoride ions, the material showed a critical temperature of 26 K. By utilizing a high-pressure synthesis, the temperature was raised to 43 K.<sup>22</sup> Still more recently, a record-high  $T_{\rm C}$  of 203 K was achieved in H<sub>2</sub>S compressed to such high pressure that it decomposes to other species—perhaps H<sub>3</sub>S.<sup>23</sup>

#### **CONNECTIONS TO MATERIALS SCIENCE**

# **SQUIDs and Maglev Trains**

Limited commercialization of high-temperature superconductors has occurred.<sup>24,25</sup> A superconducting tape in which filaments of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> are sheathed with metallic silver is now produced, and superconducting power cables are now available, but they are expensive. Some applications involving low magnetic fields and electric current density and using liquid nitrogen cooling include microwave filters and superconducting quantum interference devices (SQUIDs). The application that most catches the public fancy is the construction of **maglev trains**, in which the train floats 8 mm above the track; despite formidable costs and difficulties, such a train is now operating on a 19-mile track between Shanghai and its international airport. With zero friction between the train and the tracks, speeds of 260 miles per hour have been reached.

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# 8.5. Acidity, Solubility, and Atmospheric Chemistry of Oxides

**OVERVIEW.** Oxides of elements show periodic gradations in acid-base properties. They range from the soluble basic oxides containing the nonacidic and feebly acidic cations, through the insoluble basic oxides of other metals in moderate oxidation states, to the insoluble acidic oxides of metals in moderate oxidation states and metalloids, to the soluble acidic oxides of metals in high oxidation states and most nonmetals (Sections 8.5A). You can practice applying these classification schemes by trying Exercises 8.56-8.63. Acidic and basic oxides can react with each other without the involvement of water, in what is called a Lux-Flood acid-base reaction (Section 8.5B). You can practice predicting products of such reactants by trying Exercises 8.64-8.69. The acidic volatile oxides of the nonmetals, most of which are acidic or can be oxidized to forms that are acidic, are involved in environmental problems such as the formation of acid rain (Section 8.5C). This subsection does not introduce new principles, but Exercises 8.70-8.73 develop your practical knowledge of the atmospheric chemistry of these oxides, while applying principles from this text to understanding this chemistry.

Section 8.5 includes Connections to agricultural chemistry, atmospheric chemistry, environmental chemistry, and industrial chemistry. It will be helpful in applying these concepts to review the acidity classifications of cations (Section 2.2), the solubilities of metal oxides and hydroxides (Section 2.5), the drawing of Lewis structures of molecules (Section 3.1), and the formulas, acid–base properties, and speciation of oxo anions and acids (Sections 3.5–3.8).

**8.5A Acidic and Basic Oxides.** To a first approximation, the acid-base properties of oxides of the elements can be thought of as a composite of the very strongly basic properties of the oxide ion and the acidic properties of the element "cation," which can range from nonacidic to very strongly acidic. Many metal oxides are **basic oxides**: the basic properties of the oxide ions, which are very strong, prevail over the lesser acidic properties of most metal cations. We may further subdivide the basic oxides into those that are soluble and those that are insoluble.

The **soluble basic oxides** are the oxides of the nonacidic and feebly acidic metal cations in the lower left part of the periodic table: They dissolve sufficiently in water to give hydroxides of these metal ions in solutions of high pH.

$$BaO(s) + H_2O \rightarrow Ba^{2+}(aq) + 2OH^{-}(aq)$$
(8.3)

The **insoluble basic oxides** are oxides of the weakly acidic and yet more acidic metal cations. By Solubility Rule I these are insoluble in water, so they do not give solutions of elevated pH values. Nonetheless, they do dissolve in, and partially neutralize, strong acids, so they show basic properties.

$$Fe_2O_3(s) + 6H^+(aq) \rightarrow 2Fe^{3+}(aq) + 3H_2O$$
 (8.4)

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Often, however, the acidity of a very strongly acidic "cation" can prevail over the basicity of the oxide ion, so many oxides of the nonmetals at the right of the periodic table, or of metals in very high oxidation states, are **acidic oxides**. They can be categorized as soluble and insoluble, too.

Acidic Oxides. The process of dissolving an acidic oxide in water can be envisioned as involving at least two equilibria that influence each other. We may suppose that a soluble acidic oxide first reacts reversibly with water to give an oxo acid:

$${}_{\infty}^{1}[\text{SeO}_{2}] + \text{H}_{2}\text{O} \implies \text{H}_{2}\text{SeO}_{3}(aq)$$

$$(8.5)$$

If the resulting oxo acid is very strongly acidic, strongly acidic, or moderately acidic (Section 3.7), a second equilibrium then proceeds appreciably to the right:

$$H_2SeO_3(aq) + H_2O(aq) \implies H_3O^+(aq) + HSeO_3^-(aq)$$
(8.6)

For these three categories of oxo acids this equilibrium then shifts the position of the previous equilibrium far enough to the right to allow the original metal oxide to dissolve in neutral water and to lower its pH. Oxides that can dissolve to give very strongly acidic, strongly acidic, or moderately acidic oxo acids generally are **soluble acidic oxides**.

As an example, the soluble acidic oxide  $P_4O_{10}$  reacts very completely with water and hence is used as a drying agent. But it is dangerous to use it to dry organic liquids, because it releases so much heat via Equation 8.7 that it can set the organic liquid on fire:

$$P_4O_{10}(s) + 6H_2O(l) → 4H_3PO_4(aq)$$
 ΔH = -428.5 kJ (8.7)

The reaction with water is involved in the production of high-purity "syrupy" (85% or 15 M concentrated) phosphoric acid, which is used in making detergents, tooth-paste, and in foods such as colas (about 0.05%  $H_3PO_4$ , pH = 2.3).

Most other nonmetal oxides, and a significant number of metal oxides, do not undergo sufficient ionization analogous to Equation 8.6 to allow them to dissolve in neutral water, but they dissolve in strong bases, partially neutralizing them. These may be termed **insoluble acidic oxides**. Major soluble and insoluble acidic oxides, and the products they form on dissolving in water, are indicated in Table 8.6.

Table 8.7 summarizes, in a general way, the locations in the periodic table of the four principal acid–base classes of oxides. Soluble basic oxides and soluble acidic oxides occupy opposite edges of the periodic table, except that metals in very high oxidation states can also give rise to soluble acidic oxides. In between we find insoluble basic oxides (more to the left) and insoluble acidic oxides (more to the right).

**Amphoteric and Neutral Oxides.** The realms of insoluble acidic oxides and insoluble basic oxides overlap extensively, however. There are many insoluble oxides such as Al<sub>2</sub>O<sub>3</sub> that do not dissolve in water, but dissolve in strong acids *and* (in separate experiments) in strong bases:

$$Al_2O_3(s) + 6H^+ \implies 2Al^{3+}(aq) + 3H_2O$$
 (8.8)

$$Al_2O_3(s) + 2OH^- + 3H_2O \implies 2[Al(OH)_4]^-$$
 (8.9)

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$\begin{array}{c} B_2O_3 \rightarrow \\ H_3BO_3(w) \end{array}$	$\begin{array}{c} \mathrm{CO}_2 \rightarrow \\ \mathrm{H}_2 \mathrm{CO}_3(m) \end{array}$	$ \begin{array}{c} N_2O_5 \rightarrow \\ HNO_3(s) \end{array} $			
		$ \begin{array}{c} N_2O_3 \to \\ HNO_2(m) \end{array} $			
$\begin{array}{c} \operatorname{Al}_2\operatorname{O}_3 \to \\ \operatorname{AlO}_4^{5-} \end{array}$	$\begin{array}{c} {\rm SiO_2} \rightarrow \\ {\rm SiO_4^{4-}} \end{array}$	$\begin{array}{c} P_4O_{10} \rightarrow \\ H_3PO_4(m) \end{array}$	$SO_3 \rightarrow H_2SO_4(s)$	$\begin{array}{c} \text{Cl}_2\text{O}_7 \rightarrow \\ \text{HClO}_4(\textit{vs}) \end{array}$	
		$\begin{array}{c} P_4O_6 \rightarrow \\ H_3PO_3(m) \end{array}$	$SO_{2} \rightarrow H_{2}SO_{3}(m)$	$\begin{array}{l} Cl_2O \to \\ HClO(w) \end{array}$	
$Ga_2O_3 \rightarrow GaO_4^{5-}$	$GeO_2 \rightarrow GeO_4^{-4-}$	$\begin{array}{c} As_2O_5 \rightarrow \\ H_3AsO_4(m) \end{array}$	$\begin{array}{c} {\sf SeO}_3 \rightarrow \\ {\sf H}_2 {\sf SeO}_4(s) \end{array}$		
		$\begin{array}{c} As_4O_6 \rightarrow \\ AsO_3^{3-} \end{array}$	$ \begin{array}{c} \operatorname{SeO}_2 \to \\ \operatorname{H}_2 \operatorname{SeO}_3(m) \end{array} $	$Br_2O \rightarrow HBrO(w)$	
	$SnO_2 \rightarrow SnO_6^{8-}$	$\begin{array}{c} \mathrm{Sb_2O_5} \rightarrow \\ \mathrm{SbO_6}^{7-} \end{array}$	$TeO_3 \rightarrow TeO_6^{6-}$		$XeO_4 \rightarrow H_4XeO_6(s)$
	$SnO \rightarrow SnO_3^{4-}$	$\begin{array}{c} {\operatorname{Sb}}_2{\operatorname{O}}_3 \to \\ {\operatorname{Sb}}{\operatorname{O}}_3^{3-} \end{array}$	$TeO_2 \rightarrow TeO_3^{2-}$	$ \begin{array}{c} I_2O_5 \rightarrow \\ HIO_3(s) \end{array} $	$\begin{array}{c} {\sf XeO}_3 \rightarrow \\ {\sf H}_2 {\sf XeO}_4(s) \end{array}$
	$PbO_2 \rightarrow PbO_6^{4-}$				
		$\begin{array}{c} V_2O_5 \rightarrow \\ VO_4^{3-} \end{array}$	$CrO_3 \rightarrow H_2CrO_4(s)$	$\begin{array}{c} Mn_2O_7 \rightarrow \\ HMnO_4(\mathit{vs}) \end{array}$	
			$MoO_3 \rightarrow MoO_4^{2-}$	$ \begin{array}{c} {\rm Tc}_2{\rm O}_7 \rightarrow \\ {\rm HTcO}_4(vs) \end{array} $	RuO <sub>4</sub>
			$WO_3 \rightarrow WO_4^{2-}$	$\frac{\text{Re}_{2}\text{O}_{7}}{\text{HReO}_{4}(vs)}$	OsO <sub>4</sub>

# TABLE 8.6 Major Acidic Oxides of the *p*- and *d*-Block Elements<sup>a-c</sup>

<sup>*a*</sup> Oxides above and to the right of the lines (in **brown** boxes) are *soluble* acidic oxides; the acids they form on dissolving, and their strengths, are also shown.

<sup>b</sup> Oxides within the lines (in light brown boxes) are *insoluble* acidic oxides; the corresponding nonprotonated oxo anions are also shown. (Normally the anions formed are then partially protonated—for example,  $Sb_2O_5(s)$ +  $5H_2O(s) + 2OH^-(aq)$ 2[Sb(OH)<sub>6</sub>]<sup>-</sup>(aq).

<sup>c</sup> Amphoteric oxides and their oxo anions are shown in the white region (for the *p*-block elements only).

# TABLE 8.7. Soluble and Insoluble Acidic and Basic Oxides<sup>a</sup>

Li	Be				Soli acidic	uble oxides						В	С	N	a	Solut cidic o	ole kides
Na	Mg				(in h oxid.: on	igher states IV)	Insoluble ←— acidic oxides ——				AI	Si	Ρ	S	Cl		
к	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Pd	Rh	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po		
Fr	Ra	Insoluble acidic oxides $$								_	– Solu basi	ble c oxide	s				
Solu basic	oluble ic oxides											(in lower oxid. states only)					

<sup>*a*</sup> Elements forming soluble acidic oxides are shaded in **brown**. Elements forming soluble basic oxides are shaded in **gray**. The elements in the unshaded region vary from insoluble basic oxides on the left to insoluble acidic oxides on the right, with no strong boundary between them.

Such oxides are known as **amphoteric oxides**. These are scattered somewhat unsystematically in the center part of the periodic table (Table 8.7). Some insoluble basic oxides derived from even weakly acidic cations (e.g., ZnO) do dissolve in strong bases, so they are amphoteric; some derived from moderately or even strongly acidic cations (e.g., Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) do not, so they are insoluble basic oxides.

Because the acidity of a cation rises rapidly with its charge, there are several *d*-block elements possessing several oxidation states (such as chromium) that have one or more oxides that show only basic properties [e.g., chromium(II) oxide, CrO], one or more oxides that are amphoteric [e.g., chromium(III) oxide,  $Cr_2O_3$ ], and one or more oxides that possess only acidic properties [chromium(VI) oxide,  $CrO_3$ ]. Thus, the higher the oxidation number of a given element, the more acidic the corresponding oxide is.

# **EXAMPLE 8.12**

Consider the following oxo acids: (a)  $H_3VO_4$ ; (b)  $H_2XeO_4$ ; (c)  $HTcO_4$ ; (d)  $H_4SnO_3$ ; (e)  $H_6MoO_6$ . For each oxo acid, give (1) its category of acidity; (2) its name; (3) the formula of the acidic oxide from which it might be prepared by the addition of water only (i.e., no redox chemistry); (4) whether it will be soluble or insoluble in water.

**SOLUTION**: Acidity categories of oxo acids are covered in Section 3.7, and they are based on the number of oxo groups. The nomenclature of oxo acids is covered in Section 3.9 and is based on the oxidation state of the central atom.

(a)  $H_3VO_4$  has one oxo group and the vanadium has an oxidation number equal to the group number of +5, so this is vanadic acid, which is moderately acidic. The oxide of V<sup>5+</sup> is  $V_2O_5$ , which should be soluble because it gives a moderately acidic oxo acid. (In fact, it is only slightly soluble.)

(b)  $H_2XeO_4$  has two oxo groups and the xenon has an oxidation number equal to the group number 8 - 2 = +6, so this is xenic acid, which is strongly acidic. The oxide of Xe<sup>6+</sup> is XeO<sub>3</sub>, which should be soluble because it gives a strongly acidic oxo acid.

(c)  $\text{HTcO}_4$  has three oxo groups and the technetium has an oxidation number equal to the group number of +7, so this is pertechnetic acid, which is very strongly acidic. The oxide of  $\text{Tc}^{7+}$  is  $\text{Tc}_2\text{O}_7$ , which should be soluble because it gives a very strongly acidic oxo acid.

(d)  $H_4SnO_3$  has no oxo groups (arguably it has -1 oxo group!) and the tin has an oxidation number equal to the group number 4 - 2 = +2, so this is stannous acid, which is weakly acidic at best. The oxide of  $Sn^{2+}$  is SnO, which should be insoluble because it gives (at best) a weakly acidic oxo acid.

(e) Although the oxo anion of Mo is  $MoO_4^{2-}$ , the oxo acid, anomalously, is  $H_6MoO_6$ , which has no oxo groups and is weakly acidic. Hence,  $MoO_3$  is relatively insoluble.

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# **EXAMPLE 8.13**

Classify each of the following oxides as acidic, basic, or amphoteric or neutral, and decide whether it will be soluble in water: (a)  $P_4O_{10}$ ; (b) RaO; (c)  $Tl_2O$ ; (d)  $SO_2$ ; (e)  $Al_2O_3$ .

**SOLUTION**: (a)  $P_4O_{10}$  is a nonmetal oxide (so it is likely acidic) built from a  $P^{5+}$  "cation" in Period 3. Therefore, the oxo anion and oxo acid should show the penultimate TCN of four:  $PO_4^{3-}$ and  $H_3PO_4$ , a moderately acidic oxo acid.  $P_4O_{10}$  is therefore soluble. (b) RaO is a metal oxide built from a feebly acidic  $Ra^{2+}$  cation, so it is basic and soluble. (c)  $T1_2O$  is a metal oxide built from a nonacidic or feebly acidic  $T1^+$  cation, so it is basic and soluble. (d)  $SO_2$  is a nonmetal oxide (so it is likely acidic) built from a : $S^{4+}$  "cation" in Period 3. Therefore, the oxo anion and oxo acid hould show the penultimate TCN of four: : $SO_3^{2-}$  and  $H_2SO_3$ , a moderately acidic oxo acid.  $SO_2$ is therefore soluble. (e)  $Al_2O_3$  is the oxide of moderately acidic  $Al^{3+}$ , so this oxide will be insoluble. It could be an insoluble basic oxide or an insoluble acidic oxide, or both, in which case it is amphoteric. (This is actually the case.)

# Oddball Oxides

Three monomeric nonmetal oxides from the upper-right portion of the *p* block have such low oxidation numbers for the nonmetal atom that they lack any acidic properties namely, CO, N<sub>2</sub>O, and NO; because these certainly don't have basic properties, they are neutral oxides. In addition, there are a few oxides, such as the free radicals NO<sub>2</sub> and ClO<sub>2</sub>, which do not correspond in oxidation state to stable or known oxo acids or anions. These can give rise to a mixture of oxo acids or anions by disproportionation:

$$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O$$
 (8.10)

**8.5B.** Lux–Flood Acid–Base Reactions. Because basic oxides can react with the hydronium ion, a strong aqueous acid, and acidic oxides can react with the hydroxide ion, a strong aqueous base, basic oxides such as SrO and acidic oxides such as SiO<sub>2</sub> can react directly with each other:

$$2\text{SrO}(s) + \text{SiO}_2(s) \rightarrow \text{Sr}_2\text{SiO}_4(s) \qquad \Delta H = -209.8 \text{ kJ}$$
(8.11)

$$\operatorname{ZrO}_2(s) + \operatorname{SiO}_2(s) \rightarrow \operatorname{ZrSiO}_4(s)$$
  $\Delta H = -32.1 \text{ kJ}$  (8.12)

In such a reaction there is a transfer of *oxide ions*. In the Lux–Flood acid–base classification system an oxide-ion donor is a base and an oxide-ion acceptor is an acid. The products of these reactions are salts of oxo acids and, because water is not involved in the reaction, can be prepared even though oxides such as  $ZrO_2$  and  $SiO_2$  are insoluble in water, and the oxo anion  $SiO_4^{4-}$  is too basic to exist in water. Equation 8.12 produces

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the mineral zircon (ZrSiO<sub>4</sub>) and can be carried out by sintering the two oxides at 1500°C for 4–6 hours. Direct reactions of acidic and basic oxides are important in such areas as control of pollution by gaseous acidic oxides and in the production of materials such as cement, glass, and ceramics. The  $\Delta H$  of a Lux–Flood acid–base reaction can be approximately predicted from the  $Z^2/r$  ratios of the elements in the reacting acidic and basic oxides.<sup>26</sup>

# **EXAMPLE 8.14**

Identify the Lux–Flood acid and base, then complete and balance the equations for their reactions, if any: (a)  $N_2O_3 + Tl_2O \Rightarrow$ ; (b)  $BaO + OsO_4 \Rightarrow$ ; (c)  $SrO + ZrO_2 \Rightarrow$ ; (d)  $Fe_3O_4 + H^+ \Rightarrow$ .

**SOLUTION**: (a)  $N_2O_3$  is a nonmetal oxide, so it is most likely an acidic oxide. With its oxidation state of +3 and penultimate TCN of +3, its corresponding oxo anion is : $NO_2^-$ . Tl<sub>2</sub>O is a basic oxide, so the two can react to give TlNO<sub>2</sub>, the salt of Tl<sup>+</sup> with NO<sub>2</sub><sup>-</sup>:

$$N_2O_3 + Tl_2O \rightarrow 2TlNO_2$$

(b) Because  $Ba^{2+}$  is a feebly acidic cation, BaO is a basic oxide. Because the hypothetical  $Os^{8+}$  cation is very strongly acidic,  $OsO_4$  is an acidic oxide. Os would probably show its penultimate TCN of six and form the  $OsO_6^{4-}$  anion (Table 3.5). Balancing the -4 charge of this anion with two  $Ba^{2+}$  cations, we predict the following reaction:

$$2BaO + OsO_4 \rightarrow Ba_2OsO_6$$

(c) Because  $Sr^{2+}$  is a feebly acidic cation, its oxide SrO is a basic oxide.  $Zr^{4+}$  in  $ZrO_2$  is strongly acidic, so its oxide is (unpredictably) either basic or amphoteric. If  $ZrO_2$  is also a basic oxide (as it is, in fact), there can be no acid–base reaction between these oxides. (They might form a mixed-metal oxide.)

(d)  $Fe_3O_4$  is a mixed-metal oxide in which the average oxidation state of iron is +2.67, which means that two-thirds of the iron ions are moderately acidic  $Fe^{3+}$  and one-third are weakly acidic  $Fe^{2+}$  ions. The oxides of such ions are insoluble in water, but they do dissolve in acids. Therefore,  $Fe_3O_4$  is a basic oxide:

 $Fe_{3}O_{4} + 8H^{+} \rightarrow Fe^{2+} + 2Fe^{3+} + 4H_{2}O$ 

#### A CONNECTION TO AGRICULTURAL CHEMISTRY

# **Fertilizer Composition**

The three main nutrient elements provided in fertilizers are K, P, and N; the potassium and phosphorus are provided in the form of K<sup>+</sup> and PO<sub>4</sub><sup>3-</sup> and the nitrogen either as the NH<sub>4</sub><sup>+</sup> ion or the NO<sub>3</sub><sup>-</sup> ion. Interestingly, the K and P compositions of fertilizers are often expressed in terms of the masses of K<sub>2</sub>O and P<sub>4</sub>O<sub>10</sub> or P<sub>2</sub>O<sub>5</sub> needed to give the 100 g of the fertilizer via Lux–Flood acid–base reactions. Because the nitrogen may be present as NH<sub>4</sub><sup>+</sup>, which cannot arise from a Lux–Flood acid–base reaction, its content is given simply as %N. A fertilizer labeled 16-48-0 contains 16% N, 48% P<sub>2</sub>O<sub>5</sub>, and 0% K<sub>2</sub>O.

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#### A CONNECTION TO INDUSTRIAL CHEMISTRY

# **Concrete and Cement Chemistry**

Concrete has been made since Roman times; it physically mixes sand with  $Ca(OH)_2$  (hydrated or slaked lime). To make calcium hydroxide,  $CaCO_3$  (limestone) is first heated above 800°C:

 $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$   $\Delta H = +178.3 \text{ kJ}$  (8.13)

This is followed by the exothermic reaction of the basic oxide CaO with water to generate  $Ca(OH)_2$ . The strongly basic  $Ca(OH)_2$  supported on the grains of sand reacts slowly with the acidic oxide  $CO_2$  from the air to form interlocking strong crystals of  $CaCO_3$ .

Discovered in the early 1800s, Portland cement is generated by the high-temperature reaction of limestone (CaCO<sub>3</sub>) with aluminosilicate clays. The firing (thermal decomposition) generates the basic oxide CaO (and some MgO from the clay), and the acidic oxides  $CO_2(g)$ ,  $SiO_2$ , and  $Al_2O_3$  (also from the clay). After firing, the dry cement contains principally the minerals  $(Ca^{2+})_3(SiO_4^{4-})(O^{2-})$ ,  $Ca_2SiO_4$ , calcium aluminate, and some free CaO and MgO (from the clay). When water is added to Portland cement to cause it to set, reactions such as the following occur:

 $4(Ca^{2+})_{3}(SiO_{4}^{4-})(O^{2-}) + 12H_{2}O \rightarrow Ca_{6}(OH)_{8}[Si_{4}O_{10}] \cdot 2H_{2}O + 6Ca(OH)_{2} \quad (8.14)$ 

As a result, both concrete and Portland cement are strongly basic and much more reactive than people commonly realize, continuing to react with acidic  $CO_2$  from the air for years to form CaCO<sub>3</sub>. The reactivity of the cement used in its construction is what caused the failure of Biosphere II—a self-contained, sealed-off ecosystem—in Arizona in the early 1990s.  $CO_2$  in its atmosphere was supposed to undergo photosynthesis to generate food for the inhabitants to eat and  $O_2$  for them to breathe, but the  $CO_2$  ended up reacting with the cement instead. As a result, the  $O_2$  content of the atmosphere of Biosphere II fell from the normal 21% down to 14%, barely enough to sustain human life. Most species in the Biosphere became "extinct," with the few remaining species (cockroaches, ants, katydids, and morning glories) overrunning the environment.<sup>27</sup>

Recent research in cement chemistry has focused on its environmental impact: Equation 8.13 in the manufacture of Portland cement produces 5% of the total atmospheric load of the greenhouse gas CO<sub>2</sub>. Among the changes being tried are to replace up to half of the Portland cement with blast-furnace slag and fly ash left over from coal-fired power plants.<sup>28</sup>

**8.5C. Production, Uses, and Atmospheric Chemistry of Volatile Acidic Oxides**— **Connections with Environmental Chemistry.** A number of the volatile (and usually acidic) oxides, and some of the oxo acids formed from them, are of immense significance in our technological civilization. These include some of the chemicals produced in the greatest total tonnage in the world. We can anticipate that the large quantities of these oxides in the atmosphere will result in air-pollution problems such as the production of acid rain. In the remainder of this section we deal with the uses and environmental chemistry of the most important of these oxides; there are many useful

sources of this information that should be consulted for more details.<sup>29,30</sup> We should also be able to predict some uses and environmental chemistry for other volatile oxides, should they come into widespread use.

Carbon monoxide is produced industrially on a huge scale in the process of **coal** gasification as a mixture with  $H_2$ , by the reaction of steam with hot coal:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
  $\Delta H = +131.3 \text{ kJ}$  (8.15)

This mixture of carbon monoxide and hydrogen is known as **water gas**; after adjustment of its hydrogen content it is known as **synthesis gas**, because it is used in the industrial production of a number of important organic chemicals. Intensive research is currently focused on the chemistry of carbon monoxide, because this mixture could be a source of organic chemicals from coal when our present source of many organic chemicals, petroleum, is exhausted. For example, synthesis gas can be converted to hydrocarbons via the Fischer–Tropsch process:

$$nCO + (2n + 1)H_2 \rightarrow C_n H_{2n+2} + nH_2O$$
 (8.16)

Environmentally, the main anthropogenic (human-created) source of carbon monoxide is the incomplete combustion of fuel in automobile engines (197 million tons per year). In urban environments this is a problem due to the high toxicity of this odorless soft base (Section 5.7B). In terms of the global atmospheric environment, however, carbon monoxide is not considered a serious pollutant, because natural production of CO [i.e., by the oxidation of CH<sub>4</sub> produced in swamps and in the tropics (Section 6.5B)] far outweighs human production, and because natural processes continuously remove CO from the atmosphere. These processes include microbial degradation in the soil and reactions in the atmosphere with reactive free radicals such as hydroxyl ( $\cdot$ OH) and hydroperoxyl (HO<sub>2</sub> $\cdot$ ).

Carbon dioxide is produced industrially by a number of reactions, such as the combustion of carbonaceous fuels, and by the **water-gas shift reaction**:

$$CO(g) + H_2O(g) \implies CO_2(g) + H_2(g) \qquad \Delta H = -41.2 \text{ kJ}$$
 (8.17)

Because of its physical properties,  $CO_2$  is widely used as a refrigerant. The solid form, dry ice, sublimes at -78°C, thus cooling its environment without generating any messy liquids or toxic gases. It is also used on a large scale in fire extinguishers and to carbonate beverages.

Although of very low toxicity, carbon dioxide *is* considered to be a potentially serious global atmospheric pollutant. It is removed from the atmosphere by plant photosynthesis and put into the atmosphere by plant and animal respiration; presumably these processes have reached a balance over time. However, the atmospheric concentration of  $CO_2$ , as measured in such remote locations as Antarctica and the top of Mauna Loa, Hawaii, has been increasing 0.2% a year since about 1870. This is thought to be the result of the combustion of fossil fuels and the cutting and burning of many of the tropical forests of the world. This is of concern because of the vital role of  $CO_2$  in the atmosphere: It absorbs infrared light (heat) emitted by Earth and returns some

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of it to the surface of Earth, thereby warming it; this process is popularly known as the **greenhouse effect**. An increase of only 2°C or 3°C would have profound effects on the climate of Earth; between 1880 and 1940 the mean temperature of Earth rose 0.4°C. Warmer air stores more water vapor, and it is predicted to result in a new climate with greater extreme variation between periods of drought and quick deluges of rain.\*

At low temperature and high pressures (conditions under which  $CO_2$  is a liquid),  $CO_2$  absorbs water to form a clathrate compound,  $CO_2 \cdot 5.75H_2O$  (clathrates were mentioned in Section 5.3B). This process has been filmed at a depth of 3600 meters;<sup>31</sup> a lake of liquid  $CO_2$  with associated microbes has been seen at a hydrothermal vent.<sup>32</sup> Methods of disposing of  $CO_2$  that has been removed from stationary sources such as smokestacks or cement kilns include injection in the deep ocean as well as in depleted oil and gas fields.

**Nitrogen Oxides.** Only three nitrogen oxides are stable enough to be of practical use or environmental importance. One of these,  $N_2O$  (commonly called **nitrous oxide**), is used as an anesthetic and as a propellant (to provide pressure to expel ingredients) in aerosol cans. It is involved in reactions in the upper atmosphere that could deplete the ozone layer.

**Nitric oxide** (NO) has two common sources. One is the catalytic oxidation of ammonia (which comes ultimately from petroleum and air):

$$4NH_3 + 5O_2 \implies 4NO + 6H_2O$$
 (8.18)

The other is the direct combination of nitrogen and oxygen of the air in an electrical discharge (lightning) or at around 2000°C (e.g., in a power plant during the burning of coal or in an automobile engine):

$$N_2 + O_2 \implies 2NO$$
 (8.19)

Nitric oxide is known to catalyze the destruction of vital ozone ( $O_3$ ; Section 12.1) in the upper atmosphere:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{8.20}$$

$$O_3 \implies O_2 + O$$
 (8.21)

$$O + NO_2 \rightarrow NO + O_2 \tag{8.22}$$

Overall, the reactions add up to

#### $2O_3 \rightarrow 3O_2$

**Nitrogen Dioxide.** After a few days in the atmosphere, NO is oxidized by oxygen to NO<sub>2</sub>; hence in air-pollution work these two are often collectively referred to as NO<sub>x</sub>. **Nitrogen dioxide** and its dimer, **dinitrogen tetroxide**, are readily interconverted in an equilibrium that is visible due to the brown color of nitrogen dioxide:

$$N_2O_4 \implies 2NO_2 \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$
(8.23)

\* The author is personally sensitive to this: His hometown, Cedar Rapids, IA, was massively flooded after an unprecedented rainfall of 15 inches in 2008, and he barely escaped a similar event in Nashville, TN, in 2010. Each event resulted in \$2 billion in damages. In the solid state this system is colorless, because it is completely in the form of  $N_2O_4$ . At its boiling point (21°C), the liquid is deep brown due to a 0.1% content of  $NO_2$ . The vapor becomes steadily darker with increasing temperature due to the increasing dissociation of the dimer, which is nearly complete at 140°C.

NO<sub>2</sub> reacts with water by disproportionation to produce nitric acid:

 $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$  (8.24)

This reaction occurs in the atmosphere and is one of the sources of acid rain and of nitrate as a plant nutrient. It is also carried out in industry in the manufacture of nitric acid, which is used on a large scale in the manufacture of ammonium nitrate fertilizer, nylon, steel, and in rockets (as the oxidizer of the rocket fuel).

In the lower atmosphere,  $NO_2$  is involved in a complex series of **photochemical** reactions in air that is also contaminated with unburned hydrocarbons (from automobile exhaust) and in the presence of the ultraviolet component of bright sunlight (e.g., in Los Angeles). These reactions produce ozone, aldehydes, and organic nitrates such as peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN), which are powerful eye irritants and are quite damaging to vegetation.

**Sulfur dioxide** is made commercially by the combustion of sulfur,  $H_2S$ , or sulfide ores such as FeS<sub>2</sub>. It is a colorless, poisonous gas with a choking odor and a relatively high boiling point (-10°C). Sulfur dioxide is useful as a solvent, refrigerant, food preservative, and (mainly) in the manufacture of sulfuric acid. In this process the SO<sub>2</sub> must first be oxidized by air to SO<sub>3</sub>, which is a kinetically slow process, so a catalyst of platinum sponge,  $V_2O_5$ , or NO is required. The **sulfur trioxide** resulting from this oxidation reacts very exothermically with water to give  $H_2SO_4$ .

Sulfuric acid is the leading industrial chemical in terms of the number of tons produced per year. Concentrated sulfuric acid is 98%  $H_2SO_4$  by weight, making it about 18 M. It boils at 338°C. It has a very strong affinity with water and releases a great deal of heat on absorbing water. Contact with the skin causes dehydration and chemical burns; should a spill occur, the acid should immediately be flushed away with large quantities of water for *at least 15 minutes*. The dilution of concentrated sulfuric acid should be carried out *cautiously*—the acid should be poured slowly into water with good stirring to dissipate the heat. Adding water to the acid can cause dangerous spattering of concentrated acid. Sulfuric acid even removes water from many organic molecules, converting carbohydrates to carbon, for example.

The uses of sulfuric acid are so many and varied that the figures for production of sulfuric acid in a given country have been used as a reliable indicator of that country's industrial capacity. The largest usage is in the production of fertilizer (Section 4.3); other major uses are in the refining of petroleum, in metallurgy, and in the manufacture of chemicals. For example, nitration of organic molecules to produce explosives (Section 6.3B) typically use a mixture of HNO<sub>3</sub> and  $H_2SO_4$ , the latter to remove water. This reaction not only generates toxic nitrogen oxides, but also produces waste dilute sulfuric acids. Clean  $H_2SO_4$ -free nitrating reagents are now being advocated, using the oxide  $N_2O_5$  by itself.

Natural sources produce large amounts of  $SO_2$  via decay of organic matter to  $H_2S$ , which is rapidly oxidized to  $SO_2$  in the atmosphere. Anthropogenic  $SO_2$  is produced

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in comparable quantities during the roasting of sulfide ores and the burning of oil and coal (which often contains substantial amounts of  $FeS_2$ ). In the atmosphere,  $SO_2$  is also oxidized to  $H_2SO_4$ . The resulting acid mist, which once prevailed in London fog (as opposed to Los Angeles or photochemical smog), has been found in many cities of the world in which homes were heated by burning soft coal. Breathing in droplets of sulfuric acid strains the lungs and heart, and has shortened the lives of many people during such episodes of smog.

In the vicinity of smelters in which sulfide ores are oxidized (roasted), the concentration of sulfuric acid and sulfur oxides has been so great that artificial deserts have been created. This problem has been alleviated by the construction of very high smokestacks ("the solution to pollution is dilution"). Unfortunately this spreads the sulfur oxides and sulfuric acid over whole continents and has helped cause the current problem of acid rain (Section 3.8B). This acid rain is corroding away many historic monuments and statues made of susceptible salts of basic oxo anions (marble and limestone are largely CaCO<sub>3</sub>). Lakes that are in contact with limestone deposits are protected by the same reaction, which neutralizes the acid rain. Lakes that are not so fortunate become quite acidic, with harmful consequences already discussed in Section 3.8B. Effects on trees and vegetation are now also being discovered.

Due to these problems, a considerable amount of research has been done on methods of control of sulfur dioxide emissions from smelters and power plants. This would seem to be a simple matter, because acidic oxides such as  $SO_2$  and  $SO_3$  would be expected to react readily with inexpensive basic oxides or hydroxides. Thus, a solution of  $Ca(OH)_2$  can be sprayed down the smokestack of the plant in a *scrubber* to react with the sulfur oxides according to the reaction in Equation 8.25:

$$Ca(OH)_2 + SO_2 + (1/2)O_2 \rightarrow CaSO_4 + H_2O$$
(8.25)

Finding a suitable chemical reaction is only the first step. A coal-fired power plant emits much more  $CO_2$  than  $SO_2$ ;  $CO_2$  is also a weakly acidic oxide that would use up much of the Ca(OH)<sub>2</sub>. As a consequence, for each ton of coal burned, up to 0.2 tons of limestone would be required, and an enormous quantity of wet CaSO<sub>4</sub> would be generated. This would convert an air-pollution problem into a solid-waste problem, because there are not enough uses of CaSO<sub>4</sub> to be able to market such quantities. A second problem is that the lime solution cools the exhaust gases so much that they no longer rise up out of the smokestack, so the stack gases have to be reheated!

A number of other alternative processes have been studied. For example, using  $Mg(OH)_2$  or MgO instead of Ca(OH)\_2 has advantages. The adsorption of SO<sub>2</sub> (as well as other acidic and even organic pollutants) by MgO(*s*) is greatly improved if the MgO consists of tiny nanocrystals, because the nanocrystals have high surface areas with more coordinatively unsaturated surface sites.<sup>33</sup> After the SO<sub>2</sub> reacts with the slurry of Mg(OH)<sub>2</sub>, the resulting MgSO<sub>3</sub> can be heated (in another location) to regenerate the SO<sub>2</sub>:

$$MgSO_3 \implies MgO + SO_2$$
 (8.26)

The MgO can be recycled to form  $Mg(OH)_2$ ; thus, there would be no solid-waste problem and no great investment in  $Mg(OH)_2$ . The SO<sub>2</sub> is formed at a concentration

great enough to allow the manufacture of sulfuric acid, which could be sold. However, sulfuric acid is the cheapest acid, and the sale of this acid would not pay for the heat used to decompose the MgSO<sub>3</sub>.

Although many other alternatives exist, each has its own drawbacks. It was estimated that equipping the power plants of the United States with devices to remove most of the  $SO_2$  would cost about \$32 billion. Unless subsidized by the government, this amount would be added to consumers' electric power bills.

# **EXAMPLE 8.15**

As you read Section 8.5C, (a) what are the seven volatile oxides discussed? (b) Which of these are acidic? (c) Which of these seven oxides are represented in the redox predominance diagram of Figure 6.7? How are they represented? (d) Of the oxides represented in Figure 6.7, which should be oxidized by  $O_2$ ? (e) The presence of these oxides in the atmosphere suggests that their oxidation may not be rapid. Why might this be?

**SOLUTION:** (a) CO, CO<sub>2</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>.

(b)  $CO_2$ ,  $SO_2$ ,  $SO_3$ , and  $NO_2$  (by disproportionation).

(c) CO as unstable (to the right of the diagram),  $CO_2$  as stable, NO as unstable, NO<sub>2</sub> as unstable, SO<sub>2</sub> as unstable H<sub>2</sub>SO<sub>3</sub>, and SO<sub>3</sub> as stable HSO<sub>4</sub><sup>-</sup>.

(d) There are positive  $E^{\circ}$  gaps between O<sub>2</sub> at +1.23 V and the following oxides: CO at -0.11 V, NO at +1.03 V, NO<sub>2</sub> at +0.80 V, and H<sub>2</sub>SO<sub>3</sub> at -0.16 V, so these oxides should be oxidized.

(e) One factor is that redox predominance diagrams are for 1 M aqueous solutions, not for gaseous oxides; water can play an important role in stabilizing reactants or products. Another factor is that redox predominance diagrams do not predict kinetics—whether the reaction will be fast or slow. (The two half-reactions of the oxide with  $O_2$  would generally involve different numbers of electrons.)

# 8.6. Polysilicates: Basic Structural Types, Uses, and Chemistry

**OVERVIEW.** The various types of silicate and polysilicate ions in nature illustrate the different degrees of polymerization of oxo anions. The complex structures of many of the polysilicate ions are often represented with polyhedra, which you should be able to interpret. Some of the properties of these polysilicates follow from the degree of anion polymerization. You may practice taking the formula of a silicate mineral, determining which class of silicate ion it contains, and analyzing the structural unit from which it is built. From the charge densities per structural unit of different polysilicate ions, you can estimate their relative basicities (Section 8.6A; Exercises 8.74–8.80). Silicate minerals are subject to changes in polymerization isomerism with pressure, as they move to deeper layers of Earth and as simple silicates are subject to weathering to forms such as oxides and clays; you may apply the concepts of relative weathering rates (Section 8.6B) in Exercises 8.81–8.86.

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Section 8.6 includes a Connection to the chemistry of art and five Connections to geochemistry. In Sections 8.6 and 8.7 you will use charge balance from Sections 1.4 and 3.2 to deduce the charges of silicate ions, the principles of Section 3.1 for assembling/disassembling the Lewis structure of a polyatomic anion, and the basicity classification of oxo anions from Section 3.7. The effects of pressure on the degree of polymerization was covered earlier in Section 4.1C.

**8.6A.** Classes of Silicate Anions. Of overwhelming importance in the geochemistry of Earth's crust are the silicates and polysilicates. These contain definite silicon oxo anions, with covalent Si–O single bonds and a TCN = 4 for Si. Most of them do not have the simple silicate ion  $SiO_4^{4-}$  that we discussed in Chapter 3, but rather have two-coordinate oxygen atoms covalently linking different silicon atoms into oligomeric or one-, two-, or three-dimensional polysilicate ions. We will see differences in physical properties caused by the different degrees of polymerization of the covalent bonding in the polysilicate ions. (Regardless of the degree of polymerization of the polysilicate ions, these are finally linked into three-dimensional ionic lattices by counterions.)

Simple Silicates (Nesosilicates). The simple silicate ion  $SiO_4^{4-}$  (also called *orthosilicate* ion, to distinguish it from the polysilicate ions, or called *nesosilicate* by geochemists) is not found in a wide variety of minerals: It is a very strong base that cannot persist in aqueous solution, but it does occur in nature as insoluble salts of acidic cations. Some of the mineral forms containing the orthosilicate ion are phenacite,  $Be_2SiO_4$ ; willemite,  $Zn_2SiO_4$ ; zircon,  $ZrSiO_4$ ; thorite,  $ThSiO_4$ ; the garnets,  $(M^{2+})_3(M^{3+})_2(SiO_4)_3$  ( $M^{2+} = Ca$ , Mg, Fe, Mn;  $M^{3+} = Al$ , Cr, Fe); and olivine,  $(M^{2+})_2SiO_4$  ( $M^{2+} = Mg$ , Fe)\*. Although with these relatively acidic cations there is doubtless some covalent character to the M–O bonds, we will treat these as salts. Isomorphous substitution is very common in minerals such as these, so the formula of olivine, for example, is often written as (Fe,Mg)\_2SiO\_4, with commas separating ions that can and do substitute for each other in any proportion.

**Oligosilicates: Disilicates (Sorosilicates).** The basic structural unit of the disilicate ion,  $[O_3Si-O-SiO_3]^{6-}$  or  $[Si_2O_7]^{6-}$ , is ()<sub>0.5</sub>SiO<sub>3.5</sub><sup>3-</sup>, with one-half VCS per structural unit. The disilicate ion is found in hemimorphite,  $Zn_4(OH)_2(Si_2O_7)\cdot H_2O$ , and the rare mineral thortveitite,  $Sc_2Si_2O_7$ .

As we start building more polymeric silicate ions, their structural formulas become larger. In Figure 8.15 we show a more compact representation of these structures, in which tetrahedra are drawn to symbolize the silicon atom and its four coordinated oxides.



**Figure 8.15.** Tetrahedral models of the simple silicate and disilicate ions. The small black circles represent Si, the large **brown** circles represent terminal O, and the large **light brown** circles represent bridging O atoms. The point at the center of each tetrahedron is a terminal oxygen atom (**brown**) directly above a silicon atom (black); the point of view is directly down this O–Si bond.

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**Figure 8.16.** Tetrahedral and ball-and-stick models of two cyclic silicate ions: (a)  $Si_3O_9^{6-}$ ; (b)  $Si_6O_{18}^{12-}$ . The drawings are color-coded as described for Figure 8.15. In the ball-and-stick models on the right, the structural units,  $[()SiO_3]^{2-}$ , are enclosed in circles.

Conceptually, we can suppose that this ion is constructed by linking simple silicate ions in an acid–base neutralization reaction. To make room for a link to a bridging oxygen from one  $SiO_4^{4-}$ , an oxide ion must be removed from another:

$$SiO_{4}^{4-} + 2H^{+} \rightarrow [()SiO_{3}]^{2-} + H_{2}O$$
  
[()SiO\_{3}]^{2-} + SiO\_{4}^{4-} \rightarrow [O\_{3}Si-O-SiO\_{3}]^{6-}
(8.27)

The disilicate ion has a lower *charge density* (three negative charges per Si structural unit or "nucleus") than does the orthosilicate ion; it is consequently less basic than  $SiO_4^{4-}$ .

**Oligosilicates:** Cyclic Silicates (Cyclosilicates). The structural unit of the cyclic silicate ions is ()<sub>1</sub>SiO<sub>3</sub><sup>2-</sup>. Cyclic trimers,  $[SiO_3]_3^{6-}$ , and hexamers,  $[SiO_3]_6^{12-}$  (Figure 8.16) are most common and are found in such minerals as benitoite, BaTi(Si<sub>3</sub>O<sub>9</sub>); beryl/ emerald, Be<sub>3</sub>Al<sub>2</sub>(Si<sub>6</sub>O<sub>18</sub>)\*; and the more complex tourmaline (which also contains borate anions). Cyclic silicates have a still lower charge density of -2 per silicon nucleus, so they are less basic than disilicates.

**Chain Polysilicates: Single-Chain Polysilicates (Inosilicates).** These chain polysilicates have the same structural unit as the cyclic silicates,  $[()SiO_3]^{2-}$ . In chain silicates, the bridging oxygens are linked instead to form chain polymers,  ${}^{1}_{\infty}[SiO_3^{2-}]$  or  $[SiO_3]_n^{2n-}$ , rather than oligomers (Figure 8.17). Chain polymers are more common than cyclic oligosilicates and result in the important class of minerals known as the pyroxenes, which includes enstatite, MgSiO<sub>3</sub>; diopside, CaMgSi<sub>2</sub>O<sub>6</sub>\*; spudomene, LiAlSi<sub>2</sub>O<sub>6</sub>; and pollucite, CsAlSi<sub>2</sub>O<sub>6</sub>. The negative charge remains at –2 per structural unit.

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# EXAMPLE 8.16

(a) The tetrahedral drawing of the  $Si_6O_{18}^{12-}$  ion in Figure 8.16b has not been colorized to distinguish atoms (including bridging and terminal oxygen atoms); do this. (b) Write the formula of the structural unit in this ion. Tell how many charges and how many VCS it has.

**SOLUTION:** (a) The colorized version of this ion is:

(b) The structural unit of this ion includes only one tetrahedron, and it looks like the following:

It has one silicon atom, two terminal oxygen atom (one at the peak of the tetrahedron

and one at the top) and two bridging oxygen atoms (shown cut in half). So, the formula of the tetrahedral unit can be written as  $[SiO_2(O_{1/2})_2]$ . We can rewrite this as  $[()SiO_3]$  (showing one VCS to give silicon a coordination number of four). Its charge can be calculated from oxidation numbers: +4 for Si + 3(-2) for O = -2. Therefore, the structural unit is  $[()SiO_3]^{2-}$ .



**Figure 8.17.** Tetrahedral models of chain and double chain polysilicate ions. The drawings are color-coded as described for Figure 8.15.

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**Chain Polysilicates: Double-Chain Polysilicates.** Further reduction in anion basicity is achieved by expulsion of one oxide ion from every fourth  $\text{SiO}_3^{2-}$  structural unit found in chains. Then each chain is linked to its neighbor chain, giving rise to the *double-chain polysilicates* such as tremolite,  $\text{Ca}_2\text{Fe}_5(\text{OH})_2[\text{Si}_4\text{O}_{11}]_2^*$ . These contain the polymerized  $\frac{1}{\infty}[\text{Si}_4\text{O}_{11}]_6^{--}]$  or  $[\text{Si}_4\text{O}_{11}]_n^{6n-}$  anion (Figure 8.17). We can envision the structural unit as ( $)_{1.25}\text{SiO}_{2.75}^{1.5-}$ . Figure 8.18 represents the steps by which we can imagine the ( $)_{1.25}\text{SiO}_{2.75}^{1.5-}$  structural unit polymerizing to give the final double chain.

The double-chain amphibole asbestos minerals such as crocidolite,  $Na_2Fe_5(OH)_2$ -[Si<sub>4</sub>O<sub>11</sub>]<sub>2</sub>, and amosite, (Mg,Fe)<sub>7</sub>(OH)<sub>2</sub>[Si<sub>4</sub>O<sub>11</sub>]<sub>2</sub>, have long been prized for their fireand heat-resistance and for their fibrous nature (undoubtedly rooted in the long chain structure of the anion), which allows the weaving of insulating, nonflammable garments, as well as the fabrication of more than 3000 other products. Now these minerals are feared, though, because it has been found that the inhalation of the tiny fibers of asbestos often leads, after 20 or 30 years, to asbestosis (nonmalignant scarring of the lungs) or rare cancers such as mesothelioma. Finding materials to



**Figure 8.18.** Hypothetical steps in the polymerization of an ( )<sub>1.25</sub>SiO<sub>2.75</sub><sup>1.5-</sup> structural unit to give: (a) a [( )<sub>2</sub>Si<sub>4</sub>O<sub>11</sub><sup>6-</sup>] simplest formula unit; (b) chain polymerization of the simplest-formula unit to give chains of  $\frac{1}{\infty}$ [( )Si<sub>4</sub>O<sub>11</sub><sup>6-</sup>]; (c) side-to-side crosslinking of two chains to eliminate the final VCS and give the double-chain structure,  $\frac{1}{\infty}$ [Si<sub>4</sub>O<sub>11</sub><sup>6-</sup>].

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**Figure 8.19.** A sample of asbestos, showing its fibrous nature.

replace asbestos in its 3000 uses poses quite a challenge to the industrial inorganic chemist.

Layer Polysilicates (Phyllosilicates). If the side-to-side linking of chains is continued indefinitely, still further oxide ions are eliminated to give a structural unit of ()<sub>1.5</sub>SiO<sub>2.5</sub><sup>0.5-</sup> of still lower basicity with more VCS per Si nucleus (1.5) and a greater ability to link as in Figure 8.20 to give a layer silicate,  $\frac{2}{\infty}$ [Si<sub>4</sub>O<sub>10</sub><sup>4-</sup>] or [Si<sub>4</sub>O<sub>10</sub>]<sub>n</sub><sup>4n-</sup>. The layer polymeric silicates have been extremely important to humans for millennia, due in part to their ready cleavage into thin sheets and other properties that can be related to their layer structures. These minerals include clay minerals such as kaolinite or china clay, Al<sub>4</sub>(OH)<sub>8</sub>(Si<sub>4</sub>O<sub>10</sub>)\*; pyrophyllite\*, Al<sub>2</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>); talc or soapstone, Mg<sub>3</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>)\*; and serpentine, Mg<sub>6</sub>(OH)<sub>8</sub>(Si<sub>4</sub>O<sub>10</sub>). The contribution of the aluminum or magnesium hydroxide layers to the properties of these minerals is discussed in Section 8.7A. For now we note that the Mg<sub>6</sub>(OH)<sub>8</sub> layers in serpentine impart a curvature to the sheets of this mineral, which therefore wrap into fibrous tubules. In this form they are the chrysotile form of asbestos, which was 95% of the asbestos used in the United States and which is not as dangerous as the double-chain forms.



**Figure 8.20.** Tetrahedral model layer polysilicate ions. The drawings are color-coded as described for Figure 8.15.

Structure	Formula	Name	Total O/Si ratio	Vacant cordination sites per Si	Charges per Si
= SiO <sub>4</sub>	SiO4 <sup>4-</sup>	Orthosilicate	4	0	-4
	Si <sub>2</sub> O <sub>7</sub> <sup>6-</sup>	Disilicate	3.5	0.5	-3
V	Si <sub>3</sub> O <sub>9</sub> <sup>6–</sup>	Cyclic silicate	3	1	-2
	Si <sub>6</sub> O <sub>18</sub> <sup>12-</sup>	Cyclic silicate	3	1	-2
	"¹[SiO <sub>3</sub> ²−]	Pyroxene (chain silicate)	3	1	-2
	.₀[Si₄O <sub>11</sub> <sup>6–</sup> ]	Amphibole (double chain)	2.75	1.25	-1.5
	∞ <sup>2</sup> [Si <sub>4</sub> O <sub>10</sub> <sup>4–</sup> ]	Infinite sheet silicate	2.5	1.5	-1
	"³[SiO₂]	Silica	2	2	0

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**Figure 8.21.** Structures of some polysilicates and the resulting ratios of oxygen atoms and charge to the number of silicon-atom structural units present. [Adapted from J. E. Ferguson, *Inorganic Chemistry and the Earth: Chemical Resources, Their Extraction, Use, and Environmental Impact*, Pergamon: Oxford, UK, 1982.]

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#### A CONNECTION TO THE CHEMISTRY OF ART

# **Ancient Pigments**

Early artists such as those working in the Lascaux cave or in South Africa 100,000 years  $ago^{34}$  used naturally occurring inorganic pigments such as yellow hydrated iron(III) oxide (ocher) and red HgS (cinnabar), but stable blue pigments were unavailable in nature. Blue pigments based on layer polymeric polysilicate ions were invented in antiquity, however:<sup>35</sup> Egyptian blue, CaCu[Si<sub>4</sub>O<sub>10</sub>], was first produced around 3600 BC by the heating to 800–900°C of limestone, sand, some Na<sub>2</sub>CO<sub>3</sub>, and a copper mineral such as malachite:

$$Cu_2(CO_3)(OH)_2 + 8SiO_2 + 2CaCO_3 \rightarrow 2CaCu[Si_4O_{10}] + 3CO_2 + H_2O$$
 (8.28)

Later, in China, the related pigment Han blue,  $BaCu[Si_4O_{10}]$ , was produced at a slightly higher temperature by using  $BaCO_3$  (witherite) in place of the  $CaCO_3$ .

Other important pigments for paints include, above all, the extremely white  $TiO_2$ . Colored pigments include green  $Cr_2O_3$ , chrome yellow (PbCrO<sub>4</sub>), molybdate red [Pb(Cr,Mo,S)O<sub>4</sub>], and cobalt blue (CoAl<sub>2</sub>O<sub>4</sub>).

**Classifying Structures and Relative Basicities of Silicates.** As summarized in Figure 8.18, the successive steps of polymerization of the simple silicate ion have four results. (1) There is a successive reduction of the overall ratio of oxygen atoms to silicon atoms, from 4:1 in the orthosilicate ion to 2:1 in silica. (2) There is an increase in the number of VCS per silicon nucleus, which increases the number of possibilities for linkage. (3) There is a decrease in the charge per silicon nucleus in the anion. Hence, (4) the charge density per silicon tetrahedron decreases, and there is a decrease in basicity of the anion.

These changes are mathematically related, because (at atmospheric pressure) the silicon atoms always obey the octet rule (have a TCN of four). Thus, the total of (1) the number of oxygen atoms per silicon atom and (2) the number of VCS, must be *four*. Also, (3) the charge per silicon nucleus must be -2 for each oxygen atom in excess of two (because SiO<sub>2</sub> is uncharged). Hence, the charge density per silicon structural unit (charges per Si) is as shown in the right column of Figure 8.21. It decreases going down the figure, except that the charges per Si are the same, -2, for the third, fourth, and fifth entries. Hence, with the exception of these three polysilicates, the basicity decreases from top to bottom,

The chemical formulas of minerals are often written to set off the polysilicate ions from other anions, such as hydroxide, that may also be present. If this is done it is relatively easy to interpret the formula to tell what kind of polysilicate ion is present.

**Framework Silicates (Tectosilicates).** If the elimination of oxide ions is continued and sheets are linked into three-dimensional polymers, *all* of the oxide ions are ultimately eliminated, *all* of the remaining oxygens are converted into bridging oxygens, and the uncharged oxide silica,  $^{3}_{\infty}$ [SiO<sub>2</sub>], is produced (Figure 4.7). Having no negative charge, it is no longer basic at all; it is an acidic oxide.

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# EXAMPLE 8.17

Identify the degree of polymerization of the polysilicate ions found in the following minerals: (a) pyrophyllite,  $Al_2(Si_4O_{10})(OH)_2$ ; (b) grunerite,  $Fe_7(Si_4O_{11})_2(OH)_2$ ; (c) spessartite,  $Mn_3Al_2(SiO_4)_3$ ; and (d) bustamite,  $CaMn(SiO_3)_2$ .

**SOLUTION**: Calculation of the ratio of oxygen to silicon atoms allows a choice among the structures shown in Figure 8.21 (or more generally in Figure 8.1), with the exception of the choice between chain and cyclic structures. The O:Si ratio in these minerals is 10:4 or 2.5 in pyrophyllite, 22:8 or 2.75 in grunerite, 4.0 in spessartite, and 3.0 in bustamite. Hence, the number of VCS per silicon nucleus are 1.5, 1.25, 0, and 1.0, respectively. Thus, the simple orthosilicate ion is present in spessartite (a type of garnet), and the degree of polymerization increases in the sequence bustamite < grunerite < pyrophyllite. Reference to Figure 8.21 identifies grunerite as a double-chain polysilicate and pyrophyllite as a layer silicate. Bustamite could be either a ring or a chain silicate; it happens to be the latter.

# Aluminophosphates

Isomorphous substitution of two Si<sup>4+</sup> in an Si<sub>2</sub>O<sub>4</sub> fragment by one Al<sup>3+</sup> ion and one P<sup>5+</sup> ion gives rise to the first of a family of *aluminophosphates*,  ${}^{3}_{\infty}$ [AlPO<sub>4</sub>]. Polymorphs of  ${}^{3}_{\infty}$ [AlPO<sub>4</sub>] are known with structures isomorphous to quartz (the mineral berlinite), tridymite, and cristobalite (Figure 4.7). Because Al<sup>3+</sup> readily exceeds coordination number four, however, most aluminophosphates have a more open-chain structure analogous to the zeolites discussed in Section 8.7B.<sup>36</sup>

**8.6B.** Planetary Transformations of Silicates. As noted above, increasingly polymerized polysilicate ions have decreasing charges per silicon nucleus, so these ions are less basic. This fact has important consequences in soil chemistry: The more basic the polysilicate anion of a mineral, the more readily it reacts with weak acids, changing the polysilicate structure in the process of **weathering**. Rainwater is acidic even in the absence of sulfur and nitrogen oxides (Section 8.5C) due to dissolved carbon dioxide. This solution of carbonic acid is weakly acidic, and over the ages it reacts with the less polymerized silicate anions to remove oxide ions (as water). This results in replacement of the oxide ion with bridging oxygen to produce a more highly polymerized silicate:

$$Mg_2SiO_4 + 2H^+ \rightarrow Mg^{2+}(aq) + H_2O + Mg(SiO_3)$$
(8.29)

$$4Mg_{2}SiO_{4} + 6H_{2}O \rightarrow Mg_{6}(OH)_{8}[Si_{4}O_{10}] + 2Mg(OH)_{2}$$
(8.30)
Serpentine

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Soils containing large amounts of simple silicates such as olivine are characterized as "youthful" soils. These soils may have crystallized from volcanic magma recently. Or they may be present in a desert region or the "dry valleys" of Antarctica, in which the liquid water necessary to weather the soil is absent. Volcanic soils, and desert soils when first irrigated, are often very fertile, because olivine has high concentrations of the nutrient ions  $Fe^{2+}$  and  $Mg^{2+}$ .

The cyclic and chain polysilicates weather somewhat more slowly; these are followed by the double-chain silicates, while layer polysilicates are quite persistent. Even SiO<sub>2</sub> may dissolve: SiO<sub>2</sub> is substantially more soluble in water than we might have expected. Its total solubility at pH values up to 9 is about  $2 \times 10^{-3}$  M. (It dissolves as  $H_3SiO_4^-$  and as oligomeric silicic acids such as  $H_6Si_2O_7$ .) At the intermediate stage of weathering, such as is found in the temperate regions under a cover of grass or trees, layer silicates such as serpentine tend to predominate, along with some quartz. As can be seen from Equations 8.29 and 8.30, this weathering process is accompanied by a loss of soil cations, which is especially prominent for nonacidic and feebly acidic cations. Thus, the soil is less fertile than it was, due to the loss of the nonacidic plant nutrient potassium ion. The layer silicates present in the intermediate soils can still hold cations on their negatively charged surfaces, however. These cations can readily be exchanged for other ions (such as H<sup>+</sup>), and are thus released as plants need them. Such soils are found in the still-quite-fertile corn and wheat belts of the world.

In the tropics, however, when the trees are cut down and frequent rain and heat speed up the weathering process, the aging process becomes quite advanced. Such soils have high levels of oxides of the most acidic cations, such as anatase and rutile ( $TiO_2$ ), zirconia ( $ZrO_2$ ), hematite ( $Fe_2O_3$ ), and gibbsite [ $Al(OH)_3$ ]. These soils can no longer hold the less acidic nutrient metal ions and are quite infertile. When tropical rain forests are removed in "slash and burn" agriculture, the soil can be used for agriculture for only a few years; after that it becomes infertile (and rock-hard).

# EXAMPLE 8.18

Rank the order of weathering (from most quickly weathered to most persistent) of the silicate structure types shown in Figure 8.21.

**SOLUTION:** Generally, the more basic the silicate anion, the more rapidly its salts will be weathered (assuming constant acidities of the cation). As discussed above, the basicities fall in the order oligosilicates > disilicates > cyclic silicates = chain silicates > double-chain silicates > sheet silicates > silica. Therefore, this is the order of weathering as well. The exception, however, is that silica (SiO<sub>2</sub>) is more soluble than expected, so it weathers before sheet silicates. Sheet silicates (clays, etc.) are the most long-lived in aqueous environments.

#### **A CONNECTION TO GEOCHEMISTRY**

# The Chemistry of Mars

The concepts of weathering have been put to use in exploring the surface of Mars for evidence of its history. Mars has long been noted to have channels that suggest water erosion. The data from probes of Mars, including the two roving robots named *Spirit* and *Opportunity*, have provided a wealth of clues. The abundant presence of olivine was noted, suggesting rock that had not been weathered by contact with water. However, further sampling also revealed a number of minerals that are only formed on Earth in the presence of water. These include hydrated hydroxide-containing clays, magnetite ( $Fe_3O_4$ ), goethite (FeOOH), and most remarkably the sulfate-containing mineral jarosite  $[KFe_3(SO_4)_2(OH)_6]$ . The current interpretation of the clues is that Mars may have had oceans for perhaps its first billion years of history (so may have had life!). After this period, water was largely absent, so more recent volcanically produced olivine would not have weathered.<sup>37</sup> Unlike Earth, Mars does not currently have a magnetic field, so it is bombarded heavily by cosmic rays, which can break water down to  $H_2$  (which easily escapes the atmosphere) and  $O_2$ . It is speculated that Mars' core, being smaller than Earth's, may have solidified and lost its magnetism, with disastrous impacts on Mars' environment.

More recently the rover *Curiosity* landed in the ancient 96-mile-wide Gale Crater. At the center of this crater is a three-mile-high mountain, Aeolis Mons, which *Curiosity* ascended very slowly. Aeolis Mons is composed of layer after layer of sedimentary rock—layer silicates (clays) that can form only in water of near-neutral pH! This suggested a long history of (continuous or intermittent) immersion in water.<sup>38</sup>

In view of the low temperature and low atmospheric pressures on Mars, it was very unexpected when transient liquid water was detected flowing down the sides of Gale crater.<sup>39</sup> In contrast to Earth, the nonbasic but strongly oxidizing perchlorate ion (Section 6.3A) was detected on Mars by the *Phoenix* landing craft,<sup>40</sup> and is widespread. Although perchlorates of large nonacidic cations such as K<sup>+</sup> are insoluble (Section 4.3), those of feebly or weakly acidic cations are soluble and are deliquescent, so they can retain water even under the conditions on Mars. The spectra obtained from the *Mars Reconnaissance Orbiter* show clear evidence for the presence of hydrated magnesium perchlorate, magnesium chlorate, and sodium perchlorate.<sup>41</sup>

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#### A CONNECTION TO GEOCHEMISTRY

# The Mantle of Earth

The mantle of Earth constitutes 85% of Earth's volume, and consists mainly of silicon, oxygen, magnesium, and iron. Deeper in the mantle, however, pressures increase and different silicate minerals predominate. The upper mantle, at typical depths of 35 to 660 km, has as a dominant mineral olivine,  $(Mg,Fe)_2SiO_4$  (surface density 3.55 g cm<sup>-3</sup>). Below a depth of about 410 km, the olivine then undergoes two phase transitions, to polymerization isomers that have close-packed spinel structures with higher densities and about 6% lower volume. At these depths the mineral ringwoodite has also been detected, which incorporates up to ~2.6% water as hydroxide ions. Ringwoodite would have formed during the planet's formation, so it could be the source of Earth's oceans.<sup>42</sup>

Below about 660 km, the lower mantle begins. The  $(Mg,Fe)_2SiO_4$  decomposes to MgO (density 3.6 g cm<sup>-3</sup>) and a form of  $(Mg,Fe)SiO_3$  that has a perovskite structure ABO<sub>3</sub> with six-coordinate silicon atoms in the B sites and 12-coordinate Mg atoms in the A sites; this transformation results in a further loss of volume of about 8%.

Recently it has been discovered that below 2600 km (at a pressure exceeding 3 million atmospheres) the perovskite structure of  $(Mg,Fe)SiO_3$  is transformed into an even more compressed structure.<sup>43,44</sup> This structure has silicate layers, but these differ from all previously discussed silicate structures in that each silicon is *six*-coordinated (and each oxygen is two-coordinate) in  $_{\infty}^2$ [SiO<sub>3</sub><sup>2-</sup>] anions. Between these layers lie eight-coordinated Mg<sup>2+</sup> and Fe<sup>2+</sup> ions. In this structure the Fe<sup>2+</sup> ions can be so close to each other as to result in greatly enhanced electrical conductivity and conduction of heat from the core. Reaction of this *post-perovskite* mineral with iron in the core below 2900 km generates stishovite (SiO<sub>2</sub>, Table 4.2), the iron silicide FeSi, and FeO.<sup>45</sup> The heat generated by this violent oxidation–reduction reaction may be involved in the thermal currents that drive continental drift.

# **A CONNECTION TO GEOCHEMISTRY**

#### The Chemistry of Earthquakes

Olivine, as noted above, is relatively reactive, and does not persist for long periods in contact with water. It is the most common mineral, however, in the upper mantle of Earth. Where it is exposed to water near the crust, it is readily transformed to the less-basic mineral serpentine by Equation 8.30. As serpentine-containing crust is subducted into the mantle at higher pressures as a result of plate tectonics where two plates are colliding, the serpentine  $[Mg_c(Si_4O_{10})(OH)_{8}; density 2.55 \text{ g cm}^{-3}]$  decomposes to olivine  $(Mg_2SiO_4; density 3.21 \text{ g cm}^{-3})$ .

As the subduction continues (below a depth of about 410 km), the olivine then undergoes the changes discussed in the previous Connection to even more dense perovskite, then post-perovskite (Mg,Fe)SiO<sub>3</sub>. The losses of volumes can, at least under some circumstances, result in the sudden shifting of layers to fill the voids, leading to deep earthquakes.<sup>46</sup>

#### 8.7. ALUMINOSILICATES 505

# A CONNECTION TO GEOCHEMISTRY

# The Most Stable Mineral

In contrast to olivine, zircon ( $ZrSiO_4$ ) may be the most stable mineral on Earth. As the salt of a strongly acidic cation and a very strongly basic anion, it is very insoluble and undergoes no phase transitions to other polymorphs at temperatures found on the crust of Earth or during plate-tectonic subduction, so zircon crystals can last for the entire history of Earth. Furthermore, isomorphous substitution of U<sup>4+</sup> for Zr<sup>4+</sup> occurs when the zircon crystallizes initially from molten material. This U<sup>4+</sup> is then essentially trapped forever, until it undergoes radioactive decay to isotopes of lead. Recent dating of tiny zircon crystals from Western Australia indicate that they crystallized 4.4 billion years ago—that is, only 100 million years after the formation of Earth.<sup>47,48</sup> However, these zircons may not have formed in rocks at the surface. Surface rock from 4.4 billion years ago may or may not have been found at Nuvvuagittuq in northern Canada.<sup>49</sup>

#### 8.7. Aluminosilicates

**OVERVIEW.** The aluminum ion can readily replace the silicon ion in polysilicate ions to produce aluminosilicate ions. When this substitution occurs in layer polysilicates, aluminosilicate clays are produced (Sec. 8.7A). The charges of the aluminosilicate layer anions are neutralized in clays by, first of all, additional polymeric layer cations containing Al<sup>3+</sup> and Mg<sup>2+</sup> ions bridged by hydroxide ions. In some clays negative charge still remains, and is charge-balanced with layers of Group 1 or 2 cations or even hydronium ions that easily engage in ion exchange with hydrated cations in water. You may practice identifying and classifying the acid–base properties of layer aluminosilicate clays by trying Exercises 8.87–8.90.

When Al<sup>3+</sup> replaces Si<sup>4+</sup> in silica itself, framework aluminosilicates result (Section 8.7B). Negative charge is produced by this substitution, so the silica structure must open up to make room for additional cations (this substitution is non-isomorphous). This results in the feldspars and the more open-structure zeolites, which are of use in catalysis. Zeolites occur with a wide variety of structures and open connected channels. Because the anion charge is altered by this substitution, so is the anion basicity. You may practice identifying layer and framework aluminosilicates and their properties such as resistance to weathering by trying Exercises 8.91–8.96.

Section 8.7 contains Connections to agricultural chemistry, environmental chemistry, industrial chemistry, and organic chemistry.

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**8.7A.** Aluminosilicate Clays. Aluminosilicates can be imagined as arising from the *non-isomorphous* replacement of part of the Si<sup>4+</sup> by Al<sup>3+</sup> within the structure of a polysilicate polymer such as a sheet polysilicate. To maintain charge neutrality we must also add a +l ion that is *not* part of the polysilicate layer. This substitution is best indicated by writing the formula of the aluminosilicate ion in brackets, enclosing the framework aluminum ions inside the brackets but keeping the +1 or other counterions outside of the brackets.

Weathering reactions such as that of Equation 8.30 give rise not only to layer polysilicates such as serpentine but also layer aluminosilicates. Clays are characteristic of moderately weathered soils in the temperate zones of Earth.

Besides having layer polysilicate or polyaluminosilicate ions such as  ${}^{2}_{\infty}$ [Si<sub>4</sub>O<sub>10</sub><sup>4-</sup>] containing *tetrahedrally coordinated* Al<sup>3+</sup> or Mg<sup>2+</sup> ions (shown in Figure 8.22 in **brown**), clays are characterized by having additional parallel layers of *octahedrally coordinated* Al<sup>3+</sup> or Mg<sup>2+</sup> ions such as  ${}^{2}_{\infty}$ [Al<sub>4</sub>(OH)<sub>8</sub><sup>4+</sup>] bridged by OH<sup>-</sup> ions (shown in Figure 8.22 in **light brown**). These are the only two layers in the simplest clay, kaolinite (Figure 8.22a); the bilayer "sandwiches" are bound to neighboring sandwiches only by comparatively weak hydrogen bonds. When kaolinite,  ${}^{2}_{\infty}$ ([Al<sub>4</sub>(OH)<sub>8</sub>][Si<sub>4</sub>O<sub>10</sub>]), is heated in an oven, its hydroxide groups are dehydrated, and it is converted to a mixture including (the otherwise-rare mineral) mullite (Al<sub>2</sub>Si<sub>6</sub>O<sub>13</sub>). This mixture is a chemical precursor to the ceramic that is the basis of brick, pottery, china, porcelain, and enamels.



**Figure 8.22.** Layer structures of selected clays and their interrelationships via isomorphous or non-isomorphous substitution. (a) Kaolinite,  $_{\infty}^{2}([Al_{4}(OH)_{8}][Si_{4}O_{10}])^{*}$ ; (b) pyrophyllite,  $_{\infty}^{2}([Al_{4}(OH)_{4}][Si_{4}O_{10}]_{2})^{*}$ ; (c) montmorillonite,  $_{\infty}^{2}(M_{\delta}[Mg_{\delta}Al(_{4-\delta})(OH)_{4}][Si_{4}O_{10}]_{2})^{*}$  (illustrated for  $\delta = 2$ ); (d) muscovite,  $_{\infty}^{2}(K_{2}[Al_{4}(OH)_{4}][AlSi_{3}O_{10}]_{2})^{*}$ ; and (e) vermiculite,  $_{\infty}^{2}\{(Ca,Mg)_{2}[Al_{2}Mg_{2}(OH)_{4}][AlSi_{3}O_{10}]_{2}\}^{*}$ . Aluminosilicate layers with tetrahedral coordination are shown in **brown**; hydroxide-bridged Al<sup>3+</sup>–Mg<sup>2+</sup> layers with octahedral coordination are shown in **light brown**.

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Other important clays involve three layers, two of which are anionic tetrahedral polysilicate or polyaluminosilicate layers (shown in **brown**) sandwiching a central cationic octahedral aluminum hydroxide or magnesium aluminum hydroxide layer (shown in **light brown**). In pyrophyllite (Figure 8.22b), the central  $^{2}_{\infty}$ [Al<sub>4</sub>(OH)<sub>4</sub><sup>8+</sup>] layer exactly neutralizes the two outer layers. Only hydrogen bonds link one triple layer to another, so cleavage into layers is very easy.

In muscovite (mica; Figure 8.22d), the two outer layers are each -5-charged aluminosilicate layers, so their total charge exceeds that of the central octahedral layer. Charge balance thus requires a fourth layer of cations such as K<sup>+</sup> (shown uncolored). Two other clays, montmorillonite (Figure 8.22c) and vermiculite (the familiar packing material; Figure 8.22e) are derived from the structure of muscovite by different isomorphous substitution processes of the second kind.

A shorthand way of writing the simplest formula of the mineral muscovite,  $^{2}_{\infty}(K_{2}[Al_{4}(OH)_{4}][AlSi_{3}O_{10}]_{2})$ , is  $KAl_{2}[AlSi_{3}O_{10}](OH)_{2}$ , showing that only one-third of the  $Al^{3+}$  ions enter into the layer polysilicate ions. To determine the layer structure of this material from its formula, we can calculate the ratio of oxygens to silicon plus *nuclear aluminum atoms*: 10/(3 + 1) = 2.5; thus, it is a layer structure with 1.5 VCS in the structural unit.

# **EXAMPLE 8.19**

(a) Predict the formula of the anion of montmorillonite,  ${}^{2}_{\infty} \{M_{\delta}[Mg_{\delta}Al(_{4-\delta})(OH)_{4}]$ - $[Si_{4}O_{10}]_{2}\}$ , if only one-fourth of the cations in the central layer are magnesium ions and three-fourths are aluminum ions (i.e., if  $\delta = 1$ ). (b) Predict the  $pK_{b}$  and the basicity classification of the anion, based on the (untested) hypothesis that this can be estimated from the formula of the mononuclear structural unit obtained by depolymerizing the anion, then counting the number of oxo groups and units of negative charge in the structural unit. (c) Predict the acidity classification of this montmorillonite.

**SOLUTION**: (a) In Figure 8.22c, one-half of the cations in the central layer are  $Mg^{2+}$  and one-half are  $Al^{3+}$ . Making an isomorphous substitution of another  $Al^{3+}$ , the anion formula becomes  $MgAl_3(OH)_4[Si_4O_{10}]_2^{-}$ , containing 12 metal cations (which we combine as E) and one fewer negative charges. Dividing by 12, the structural unit is  $EO_{1.67}(OH)_{0.33}^{0.083-}$ .

(b) We can then apply Equation 3.14 to obtain  $pK_{b1} = 10.0 + 5.7(1.67) - 10.2(0.083) = 18.4$ . Therefore, this anion is presumably nonbasic.

(c) Neutralizing the negative charge of the structural unit by adding 0.083 H<sup>+</sup>, the oxo acid structural unit becomes (HO)<sub>0.413</sub>EO<sub>1.587</sub>. Applying Equation 3.18, the presumed  $pK_{a1}$  of this acid is 8.5 – 5.7(1.587) = –0.55, so the acidic form of montmorillonite is presumably strongly acidic.

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# CONNECTIONS TO AGRICULTURAL CHEMISTRY, INDUSTRIAL CHEMISTRY, AND ORGANIC CHEMISTRY

# **Montmorillonite Chemistry**

Montmorillonite,  ${}_{\infty}^{2}$  {M<sub>δ</sub>[Mg<sub>δ</sub>Al(<sub>4-δ</sub>)(OH)<sub>4</sub>][Si<sub>4</sub>O<sub>10</sub>]<sub>2</sub>}, is formed in large quantities on Earth from the weathering of volcanic ash, and it has been detected on Mars. As calculated in Example 8.19, its layer anion is nonbasic. The cations absorbed on the surfaces of the charged clays (muscovite, vermiculite, montmorillonite) are weakly attracted to the clay and are easily exchanged with ions from solution. Clays perform this function naturally in the soil. Enormous quantities of hydrated cations can be held to the negatively charged surfaces of clays; these cations include many nutrient ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>. As slightly acidic rainwater percolates over these clays, these nutrient ions are slowly released by ion exchange with the hydronium ion in the water and made available for plants to use (Figure 8.23). The largest and the least charged of these hydrated ions are held most loosely and are released first (and become depleted first). Recalling that smaller ions have larger secondary hydration spheres (Section 4.5B), we find that the order of release is Na<sup>+</sup> before K<sup>+</sup> before Mg<sup>2+</sup> before Ca<sup>2+</sup>. Because plants make little use of Na<sup>+</sup>, the first deficiency that occurs among cationic nutrients is of K<sup>+</sup>. Anionic nutrients such as NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> cannot be bound to clays at all, so they are rapidly lost from soils. Thus, we see the need of fertilizers containing (especially) potassium, nitrogen, and phosphorus.





The cations on the surface of montmorillonite readily adsorb additional water (to form secondary hydration spheres) when montmorillonite is placed in water; these hydration spheres then hydrogen-bond to each other, thickening the suspension in water—at least until the suspension is stirred, which breaks up the hydrogen bonds and thins the suspension. Montmorillonite is thus a useful *thixotropic agent* and is used in paints to keep them from flowing while wet, and in drilling muds in the oil industry.

As also calculated in Example 8.19, the acidic form of montmorillonite is very strongly acidic (calculated  $pK_a = -0.55$ ; observed pH after acid washing = -5.6 to -8). As an *insoluble strong acid*, it is much more easily handled than sulfuric or other strong acids. Montmorillonite is finding use in catalyzing typical organic reactions requiring acid catalysis, such as the Friedel–Crafts reaction.<sup>50</sup> Montmorillonite absorbs RNA nucleotide monomers by van der Waals attractions of the montmorillonite silicate layers to the purine and pyrimidine bases of the nucleotide. It then efficiently and (somewhat) selectively catalyzes the condensation of the bases into larger oligomers resembling RNA and containing 30–50 monomer units.

**8.7B. Framework Aluminosilicates.** To date we have discussed only one threedimensional (framework) silicate,  ${}^{3}_{\infty}$ [SiO<sub>2</sub>] itself (Section 4.1C; Table 4.2). **Framework aluminosilicates** can be imagined as arising from the *non-isomorphous* replacement of part of the Si<sup>4+</sup> by Al<sup>3+</sup> within the  ${}^{3}_{\infty}$ [SiO<sub>2</sub>] network and by a +l ion that is *not* part of the network. The extra +1 ion then goes into holes in expanded  ${}^{3}_{\infty}$ [Si<sub>x</sub>Al<sub>2-x</sub>O<sub>2</sub>] structures having larger ring sizes. Notice in Figure 8.24 that quartz (on the left) has smaller rings than the framework aluminosilicate albite, Na[AlSi<sub>3</sub>O<sub>8</sub>], on the right.





(b)

**Figure 8.24.** Structure of (a) quartz compared with the structure of (b) albite. Clear = oxygen, black = aluminum or silicon. Sodium ions are not shown in (b); they sit at the centers of the large rings. [Based upon materials developed by the Materials Research Science and Engineering Center on Structured Interfaces at the University of Wisconsin-Madison with funding from the National Science Foundation under award numbers DMR-1121288, DMR-0520527, DMR-0079983, and EEC-0908782.]

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**Feldspars.** The most abundant of all minerals (about 60% of Earth's crust) are the **feldspars**, which include K[AlSi<sub>3</sub>O<sub>8</sub>] (orthoclase), Ba[Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>] (celsian), Na[AlSi<sub>3</sub>O<sub>8</sub>] (albite)\*, and Ca[Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>] (anorthite). The feldspars themselves fall into two groups. One group includes orthoclase and celsian, and incorporates 150-pm ions such as K<sup>+</sup> and Ba<sup>2+</sup>. Note that orthoclase and celsian are related to each other by isomorphous substitution of the second type. The other group, the plagioclase feldspars, involve the smaller 115-pm Na<sup>+</sup> and Ca<sup>2+</sup> ions; compositions range continuously from Na[AlSi<sub>3</sub>O<sub>8</sub>] (albite) through Na<sub>0.33</sub>Ca<sub>0.67</sub>[Al<sub>1.67</sub>Si<sub>2.33</sub>O<sub>8</sub>] (labradorite) to Na<sub>0</sub>Ca<sub>1</sub>[Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>] (anorthite).

**Zeolites.** Perhaps the best known of the framework aluminosilicates are the **zeo-lites**, <sup>51</sup> with anions of general formula  $[Al_xSi_yO_{2x+2y}]^{x-}$  with  $x \le y$  and an oxygen-to-(aluminum plus silicon) ratio of 2. The fundamental structural unit of zeolite structures is the **sodalite cage**  $[(Si,Al)_{24}O_{48}]$  (Figure 8.25a). In Figure 8.25b the sodalite cage is drawn omitting all oxygen atoms and showing the 24 (Si,Al) nuclei at the intersections of the lines (which represent bridging oxygen atoms). Figure 8.25b shows how the zeolite cage structure consists of interlinked six-nucleus  $[(Si,Al)O_2]_6$  rings (as in SiO<sub>2</sub> itself) and four-nucleus  $[(Si,Al)O_2]_4$  rings.



**Figure 8.25.** Structural representations of the zeolite structure. (a) Connection of aluminosilicate nuclei to form an open basket-like cluster known as the sodalite cage  $[(Si,Al)_{24}O_{48}]$  (**brown** = oxygen; black circles = silicon or aluminum); (b) line representation of the sodalite cage in (a), in which black vertices represent silicon/aluminum nuclei and **brown** bridging oxygens lie along the edges; (c–e) connection of sodalite cages to give (c) sodalite,  $^{3}_{\infty}(Na_{6}[Al_{6}Si_{6}O_{24}]\cdot 2H_{2}O)^{*}$ ; (d) Linde A,  $^{3}_{\infty}(Na_{8}[Al_{8}Si_{40}O_{96}]\cdot 24H_{2}O)$ ; and (e) faujasite,  $^{3}_{\infty}(Na_{58}[Al_{58}Si_{134}O_{384}]\cdot 240H_{2}O)^{*}$ . [Adapted from G. T. Kerr, *Sci. Amer.* 261, 100 (1989).]

In zeolites, sodalite cages are linked to each other to give rise to large, three-dimensional structures that feature open channels (Figure 8.26). For example, in Figure 8.25c each square face of each sodalite cage is used twice (shared) between two adjacent sodalite cages to give the smallest possible network polymer, the mineral sodalite,  ${}_{\infty}^{3}$ (Na<sub>6</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>]·2H<sub>2</sub>O)\*, which has a central four-sided channel of 220 pm diameter.

In Figures 8.25d and 8.25e, the sodalite cages are instead linked to adjacent complete cages by converting terminal oxygen atoms of the original sodalite cage (Figure 8.25a) to bridging oxygens. In Figure 8.25d, square faces are linked to give an eight-sided channel with a diameter of 410 pm in the zeolite Linde A,  $^{3}_{\infty}$ (Na<sub>8</sub>Al<sub>8</sub>Si<sub>40</sub>O<sub>96</sub>]·24H<sub>2</sub>O).



**Figure 8.26.** A larger view of the three-dimensional channels in the zeolite ZSM-11.

In Figure 8.25e, hexagonal faces are linked to give a 12-sided channel with a diameter of about 850 pm in the zeolite faujasite,  ${}^{3}_{\infty}(Na_{58}[Al_{58}Si_{134}O_{384}]\cdot 240H_2O)^*$ . Many other natural and artificial zeolites are known involving other channel sizes, which can have up to 14 sides.<sup>52</sup>

# AN AMPLIFICATION

# Syntheses of Zeolites

The syntheses<sup>53</sup> of zeolites is a craft that involves the reaction of sodium silicate, sodium aluminate, and aluminum sulfate solutions in various ratios for extended times (e.g., 20–30 hours) at carefully controlled temperatures (e.g., 92  $\pm$  2°C). Reactions are carried out in the presence of appropriate quaternary ammonium (R<sub>4</sub>N<sup>+</sup>) or other organic cations that act as templates to help determine the shape and size of the holes and channels in the aluminosilicate structures. After the synthesis is completed, the product is heated to a high temperature to vaporize or burn off the organic template, leaving behind voids where the organic cations had been.

In nature, the cations in the holes and cavities are normally hydrated nonacidic and feebly acidic cations; the water of hydration can be driven off by heating to leave a structure with enlarged channels. If the cation of the zeolite is the relatively large K<sup>+</sup> (in Zeolite 3A), a small channel of 300-pm (3-Å) diameter is available. If the cation is Na<sup>+</sup> (in Zeolite 4A), a larger channel of 400-pm diameter is present. If the cation is Ca<sup>2+</sup> (in Zeolite 5A), a still larger channel of 500-pm diameter is present, because only half as many cations are present alongside the channel. The resulting zeolites have cavities of tailored sizes that are used as Molecular Sieves<sup>TM</sup> to adsorb molecules of different sizes from liquids. Among the small molecules most readily adsorbed are water molecules, which re-form the hydrated metal ions. Thus, these zeolites are very effective drying agents.

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#### A CONNECTION TO ENVIRONMENTAL CHEMISTRY

# Water Softening and Decontaminating Radioactive Waste

Hydrated metal cations in such a structure, being large cations in a lattice with very large insoluble anions, are loosely bound and can readily be exchanged with other cations. Zeolites are used for *water softening*: the removal of ions of +2 charge found in tap water that would precipitate the anions used in detergents. A concentrated solution of NaCl is first percolated through the solid (insoluble) zeolite ion-exchanger, replacing whatever hydrated ions are present with hydrated Na<sup>+</sup> ions. Then the tap water is run through the zeolite; Ca<sup>2+</sup> and other +2 ions become associated with the anion in the solid phase, while Na<sup>+</sup> ions go into solution. When the Na<sup>+</sup> ions in the zeolite are depleted, the solid is again "recharged" by running concentrated NaCl solution through it. With appropriate-sized cavities, zeolites can be made that selectively remove Cs<sup>+</sup> from water. Because <sup>134</sup>Cs<sup>+</sup> and <sup>137</sup>Cs<sup>+</sup> are among the most dangerous byproducts of nuclear power generation, bags of zeolites were immersed in the sea offshore from the earthquake- and tsunami-damaged Fukushima Daiichi power plant in April 2011.

#### A CONNECTION TO ORGANIC CHEMISTRY

# **Gasoline from Petroleum**

Channels may penetrate through the zeolite in one dimension, or they may intersect other channels that go off in the other two directions. The channels thus may be tailored to be of such a size as to admit only molecules below a certain size, or only straight-chain but not branched-chain hydrocarbons, and so on. In combination with these possibilities of selectivity, the dehydrated zeolites have semi-bare dehydrated metal cations with Lewis acid properties. In addition, the metal ions can be ion-exchanged for hydrogen ions, which, if driven off by heat, leave behind positively charged silicon atoms with VCS that are powerfully acidic sites (Figure 8.27). The combination of powerful Lewis acidity with site selectivity makes these of great importance as catalysts. For example, ZSM-5\* is used to catalyze the rearrangement of two moles of toluene to give one of benzene and one of *para*-xylene (*ortho*-xylene does not fit the cavity), to catalyze the alkylation of benzene with ethylene to give ethyl benzene, to catalyze the conversion of methanol (which can be made from coal and water) into gasoline plus water, and in the cracking of petroleum to form gasoline. Analogies have been drawn between the action of zeolites and the actions of enzymes, because both depend on the availability of reactive (e.g., Lewis-acidic) sites along with shape selectivity. And the easily recovered and regenerated zeolite and other solid acid catalysts are far more "environmentally friendly" than concentrated sulfuric acid.

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**Figure 8.27.** Dehydration of the surface of an acidexchanged zeolite to leave coordinately unsaturated, hence strongly acidic, silicon cationic sites. Formal charges of atoms are shown in circles.

The cavities within zeolites also provide environments in which unstable chemical species can be protected. An ancient naturally occurring blue pigment is *lapis lazuli* or lazurite, a zeolite mineral the blue color of which is due to unstable polyatomic sulfur *radical anions* such as  $S_3^-$ . Correspondingly, zeolites such as anhydrous sodium zeolite X,  $Na_{92}[Si_{100}Al_{92}O_{384}]$ , in vacuum absorb 14 additional sodium atoms to form unstable polyatomic  $Na_3^{2+}$  cations,<sup>54</sup> and the all-silica zeolite ITQ-4 (Figure 4.7g) can encapsulate Cs<sup>+</sup> cations and *electride* ions (Section 6.4A).<sup>55</sup>

# **EXAMPLE 8.20**

Consider the following mineral pairs. Classify each as related to the other by (1) isomorphous substitution of the first kind; (2) isomorphous substitution of the second kind; (3) non-isomorphous substitution; or (4) a pair that is completely unrelated in structure. (a) Rb[AlSi<sub>3</sub>O<sub>8</sub>] and K[AlSi<sub>3</sub>O<sub>8</sub>]; (b) Rb[AlSi<sub>3</sub>O<sub>8</sub>] and Li[AlSi<sub>3</sub>O<sub>8</sub>]; (c) Na[AlSi<sub>3</sub>O<sub>8</sub>] and Na<sub>12</sub>[Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub>]; (d) Rb[AlSi<sub>3</sub>O<sub>8</sub>] and Ba[Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>]; (e)  $\frac{3}{2}$ {[SiO<sub>2</sub>]<sub>24</sub>} and  $\frac{3}{2}$ {Na<sub>12</sub>[Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub>]}

**SOLUTION**: All of these have ratios of oxygen to (silicon + aluminum) = 2:1, so they are framework silicates or aluminosilicates. Zeolites, however, have much larger ring sizes than feldspars, and the plagioclase feldspars have the larger cations. Hence, in (a) both are plagioclase feldspars with large cations, which differ by isomorphous substitution of the first kind. In (b), Li<sup>+</sup> is much smaller than Rb<sup>+</sup>, so these two feldspars are different types—they are related by non-isomorphous substitution. In (c), the first salt is a feldspar and the second, with the larger rings, is a zeolite, so these are unrelated structures. In (d), we substitute Ba<sup>2+</sup> and Al<sup>3+</sup> for Rb<sup>+</sup> and Si<sup>4+</sup>, which is isomorphous substitution of the second kind. In (e), the subscript 24 for both structures implies large rings of zeolite size, but replacement of 12 Si<sup>4+</sup> with 12 Al<sup>3+</sup> and 12 Na<sup>+</sup> is a non-isomorphous substitution.

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# 8.8. Background Reading for Chapter 8

Physical Properties of Materials and Oxides (Periodic Trends)

- R. J. Gillespie, "Covalent and Ionic Molecules: Why are BeF<sub>2</sub> and AlF<sub>3</sub> High Melting Point Solids whereas BF<sub>3</sub> and SiF<sub>4</sub> are Gases?" *J. Chem. Educ.* 75, 923–925 (1998).
- A. Muñoz-Páez, "Transition Metal Oxides: Geometric and Electronic Structures," *J. Chem. Educ.* 71, 381–388 (1994).
- J. D. Holbrey and R. D. Rogers, "Physicochemical Properties of Ionic Liquids: Melting Points and Phase Diagrams," in *Ionic Liquids in Synthesis*, 2nd ed., P. Wasserscheid and T. Welton, Eds., Wiley-VCH Verlag: Weinheim, 2008, Chapter 3.1, pp. 57–72.
- V. A. Cocallia, A. E. Visser, R. D. Rogers, and J. D. Holbrey, "Solubility and Solvation in Ionic Liquids," in *Ionic Liquids in Synthesis*, 2nd ed., P. Wasserscheid and T. Welton, Eds., Wiley-VCH Verlag: Weinheim, 2008, Chapter 3.3, pp. 89–102.

High-Temperature Superconductivity in Oxides

- A. Bussman-Holder and K. A. Müller, "The Route to High Temperature Superconductivity in Transition Metal Oxides," in 100 Years of Superconductivity, H. Rogalla and P. H. Kes, Eds., CRC Press: Boca Raton, FL, 2012, Chapter 4.2, pp. 233–239.
- D. Johnson, "Superconductivity above 10 K in Non-Cuprate Oxides," in *100 Years of Superconductivity*, H. Rogalla and P. H. Kes, Eds., CRC Press: Boca Raton, FL, 2012, Chapter 4.3, pp. 239–244.
- C. W. Chu, "Cuprates—Superconductors with a *T<sub>c</sub>* up to 164 K," in *100 Years of Superconductivity*, H. Rogalla and P. H. Kes, Eds., CRC Press: Boca Raton, FL, 2012, Chapter 4.4, pp. 244–255.

Chemistry of Cement and Concrete

F. A. Rodrigues and I. Joekes, "Cement Industry: Sustainability, Challenges, and Perspectives," *Environ. Chem. Lett.* 9, 151–166 (2011).

#### Environmental Chemistry of Volatile Acidic Oxides

S. Manahan, *Environmental Chemistry*, 9th ed., CRC Press: Boca Raton, FL, 2010, pp. 285–304 (Chapter 11: Gaseous Inorganic Air Pollutants).

Chemistry of Mars

P.R. Christensen, "The Many Faces of Mars," Sci. Amer. 293(1), 32–39 (2005).

J. Bell, "The Red Planet's Watery Past," Sci. Amer. 295(6), 62–69 (2006).

Chemistry of the Early and Deep Earth

- K. Hirose, "The Earth's Missing Ingredient," *Sci. Amer.* 302(6), 76–83 (2010). A new form of MgSiO<sub>3</sub> at the border of the mantle and the outer core.
- J. W. Valley, "A Cool Early Earth?" Sci. Amer. 293(4), 58-65 (2005).

C. Zimmer, "The Oldest Rocks on Earth," Sci. Amer. 310(3), 59-63 (2014).

Numbered references from this chapter may be viewed online at www.uscibooks.com/foundations.htm.

8.9. EXERCISES 515

# 8.9. Exercises

**8.1.** \*Sulfur trioxide exists in three forms, which have the molecular formulas SO<sub>3</sub>, S<sub>3</sub>O<sub>9</sub>, and  $\frac{1}{\infty}$ [SO<sub>3</sub>]. (a) Classify each of these into one of the structural classifications given in Figure 8.1. (b) Assuming (contrary to actual fact) that the three forms are not readily interconverted, rank these three forms in order of increasing melting point. Which of the three is most likely to be a gas at room temperature?

**8.2.** The oxide of a certain element E in its group oxidation state has the polymorphs and/or structural isomers (1), (2), and (3):



(a) Give the best description of each structure (e.g., as a monomer, a polyhedral oligomer, a layer polymer, etc.). (b) Which one of these three polymorphs and structural isomers would likely be most volatile? Which would most likely be a high-boiling liquid? (c) Which one of the elements C, Si, Pb, O, Se, Po, or Xe is element E most likely to be?

**8.3.** \*Below are sketched some structures of four structural types **A**, **B**, **C**, and **D** of a particular element or element oxide, in which the structural unit is represented by an "•" and the links by lines "—."



Which of these (**A**, **B**, **C**, **D**, or none) is (a) a viscous liquid, (b) a high-melting solid, (c) a monomer, and (d) a substance about as hard as diamond?

**8.4.** Below are sketched some structures of four structural types **A**, **B**, **C**, and **D** of a particular element or element oxide, in which the structural unit is represented by an "•" and the links by lines "—."



Which of these (**A**, **B**, **C**, **D**, or none) is (a) a layer polymer, (b) an oligomer, (c) a low-boiling gas, and (d) a chain polymer?

**8.5.** \*Select one of the materials  $C_{60}$ , He,  ${}^{3}_{\infty}[(Th^{4+})(O^{2-})_{2}]$ ,  ${}^{3}_{\infty}[C]$ ,  ${}^{2}_{\infty}[C]$ , or  ${}^{1}_{\infty}[S]$  as an example of a material likely to exhibit the following physical property at room temperature: (a) viscous liquid; (b) slippery solid; (c) low-boiling gas; (d) soft solid; (e) hard solid; (f) low-density solid; (g) high-density solid.
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**8.6.** For each of the room-temperature physical properties on the left, pick the one structure type on the right that is most likely to be associated with it.

Viscous liquid	Oligomer
Slippery solid	Molecular monomer
Low-boiling gas	Chain polymer
Soft solid	Layer polymer
Hard solid	Network polymer
Low-density solid	Ionic salt
High-density solid	

**8.7.** \*Boron nitride has two polymerization isomers, and both have melting points in the vicinity of 3000°C. Polymerization isomer A is almost as hard as diamond and has a density of 3.47 g cm<sup>-3</sup>; polymerization isomer B is slippery and has a density of 2.25 g cm<sup>-3</sup>. (a) Which formula is best applied to polymerization isomer A:  $B_{30}N_{30}$ ,  $^{2}_{\infty}$ [BN], or  $^{3}_{\infty}$ [BN]? (b) Which formula is best applied to polymerization isomer B? (c) Consider the formula you did *not* choose for isomer A or isomer B. Should this third polymerization isomer have a density that is greater than 3.47 g cm<sup>-3</sup> or less than 2.25 g cm<sup>-3</sup>? Should its melting point be less than 3000°C, equal to 3000°C, or greater than 3000°C?

**8.8.** Which of the following salts or complexes are good candidates to be ionic liquids: FeO,  $KClO_4$ ,  $(C_3H_7)_4NCl$ , and/or  $(C_3H_7)_4PF_6$ ?

**8.9.** \*Which of the following salts or complexes are good candidates to be ionic liquids:  $C_3H_3(NCH_3)(NR)^+[Al_2Cl_7^-]$ ,  $Ba(NO_3)_2$ ,  $[Cr(NH_3)_3Cl_3]$ , and/or  $[Cr(NH_2C_8H_{17})_3]Cl_3$ ?

**8.10.** (a) Consult Table C to find the eight cations with radii most nearly appropriate to having a TCN of 4 or less. (b) Considering only the *p* block, which ions expected to have penultimate total coordination numbers of 4 or less based on their period in the periodic table (i.e., on the ideas of Section 3.5) are *absent* from the list generated from Table C?

**8.11.** \*The "cations" Be<sup>2+</sup>, Si<sup>4+</sup>, and Se<sup>6+</sup> each have a radius of about 55 pm. Assuming this radius, predict the number of VCS in the structural units of the fluoride of each element.

**8.12**. Because the cations in all of the following structural units have radii  $\leq$  54 pm, it is reasonable to expect total coordination numbers of four for SiO<sub>2</sub>, PO<sub>2.5</sub>, SO<sub>3</sub>, and ClO<sub>3.5</sub>. (a) How many VCS are there for each structural unit? (b) Which one will form a dimeric molecule? What is its formula? (c) Which one is most likely to form two polymorphs, one of which is a cyclic oligomer? What would its other polymorph be? (d) In which one will *all* of the oxygen atoms donate electron pairs to VCS on other structural units?

**8.13.** \*Suppose that we have two new *p*-block cations with no tendency toward  $\pi$  bonding: *sixium* is found in Group 16/VI and forms the Sx<sup>6+</sup> cation, whereas *eightium* is found in Group 18/VIII and forms the Eg<sup>8+</sup> cation. Both cations have cationic radii of 52 pm, right on the boundary for different total coordination numbers. (a) What are the formulas of the structural units of these oxides? (b) Based on radius ratios, what are the two most likely total coordination numbers for each of these cations? (c) How many VCS would be found for the two possible structural units of sixium oxide? Of eightium oxide? (d) Write the formula (including prescripts such as  $\frac{1}{\infty}$ [] if appropriate) of the oxide that is most likely to be a gas. (e) Write the formula (including prescripts such as  $\frac{1}{\infty}$ [] if appropriate) of the oxide that is most likely to be a chain polymer.

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**8.14.** If possible, draw Lewis structures for the following (presumably covalent) molecules or formula units. Use your results to help classify the oxides as (1) monomeric or dimeric molecular, (2) oligomeric molecular, or (3) ionic or macromolecular substances. (a) Na<sub>2</sub>O; (b)  $Cr_2O_3$ ; (c)  $CO_2$ ; (d)  $SiO_2$ ; (e)  $NO_2$ .

**8.15.** \*If possible, draw Lewis structures for the following (presumably covalent) molecules or formula units. Use your results to help classify the oxides as (1) monomeric or dimeric molecular, (2) oligomeric molecular, or (3) ionic or macromolecular substances. (a)  $P_4O_{10}$ ; (b) BaO; (c)  $Tl_2O$ ; (d)  $SO_2$ ; (e)  $Al_2O_3$ .

8.16. Consider the following dioxides of fifth-period elements: SnO<sub>2</sub>, TeO<sub>2</sub>, and XeO<sub>2</sub>.
(a) Use their common penultimate TCN to determine the number of vacant coordination numbers for each oxide. (b) Which oxide should be the most highly polymerized? (c) Which oxide should be the least polymerized? (d) Which oxide should have the highest melting point?

**8.17.** \*Most of the oxygen-bridged dimeric and the polyhedral oxides in Figure 8.5 have great differences among the observed element–oxygen bond lengths. Compare these observed bond lengths with the sums of covalent radii (Table 1.11). Suggest one or more possible reasons for the differences.

**8.18.** Figure 8.5 compares the observed element–oxygen bond lengths for  $OsO_4$  and  $XeO_4$  with the sums of covalent radii (Table 1.11). If the bonds are much shorter than the sums of single-bond covalent radii, suggest an explanation.

**8.19.** \*Assuming that each of the compounds is stable, predict whether melting points will increase or decrease in each of the following series of oxides. (If radius ratios are unavailable, use periodic trends in total coordination numbers.) (a)  $Cl_2O_5$ ,  $Br_2O_5$ ,  $I_2O_5$ ; (b) MnO,  $Mn_2O_3$ ,  $MnO_2$ ,  $Mn_2O_7$ .

**8.20.** The two-coordinate bridging oxygen atoms in the rhenium oxide of Figure 4.4 and in mercury(II) oxide have widely differing metal–oxygen–metal bond angles: In the rhenium oxide this angle is 180°, while in mercury(II) oxide this angle is 109°. (a) What might this difference in the bond angles signify? (b) What arguments can you offer against this interpretation of the bond angles?

**8.21.** \*(a) Predict the number of VCS for each of the following structural units: BaO, HfO<sub>2</sub>, WO<sub>3</sub>, and OsO<sub>4</sub>. (b) Which one of these oxides is least likely to have an ionic or network covalent structure? (c) Which one of these oxides is least likely to be a ceramic?

**8.22.** Which one of the following—an element tetroxide  $MO_4$ , an element trioxide  $MO_3$ , and an element dioxide  $MO_2$ —is most likely to (a) be volatile, (b) form a chain polymer, (c) form a monomeric molecule, and (d) be of use as a ceramic?

**8.23.** \*Put the following series of oxides in order of increasing melting points, and decide which are gases at room temperature: (a) Na<sub>2</sub>O,  $Cr_2O_3$ ,  $CO_2$ ,  $SiO_2$ ,  $P_4O_{10}$ ; (b)  $ZrO_2$ ,  $CO_2$ , SrO,  $Rb_2O$ ,  $Y_2O_3$ .

**8.24.** An element forms three dioxide polymerization isomers, which do not readily convert into the other isomers. Isomer A is monomeric molecular, isomer B is dimeric molecular, and isomer C is cyclic molecular. (a) Enthalpies of fusion (in kJ mol<sup>-1</sup>) for the three isomers are 20, 12, and 5. Which enthalpy of fusion is likely to belong to which isomer? (b) Boiling points for the three isomers are 90 K, 400 K, and 220 K. Which boiling point is likely to belong to which isomer?

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**8.25.** \*Which is more likely to have a higher enthalpy of fusion, and why? Is it (a) a Group 16/VI nonmetal trioxide or a Group 16/VI nonmetal hexafluoride, (b) a *d* block metal trioxide or a *d* block metal trifluoride, and (c) a Period 4 nonmetal dioxide or a Period 4 nonmetal tetrafluoride?

8.26. Why is it that many oxides but few if any fluorides can be considered to be ceramics?

**8.27.** \*Which of the following structural descriptions is/are inconsistent with the stoichiometry of the salt being described? (a)  $CdCl_2$  adopts an hcp lattice of chloride ions in which all of the octahedral holes are occupied by cadmium ions. (b)  $CdCl_2$  adopts a ccp lattice of chloride ions in which half of the octahedral holes are occupied by cadmium ions. (c)  $Li_2SO_4$  adopts an hcp lattice of sulfate ions in which all of the tetrahedral holes are occupied by lithium ions. (d)  $(CH_3)_4NF$  adopts a ccp lattice of tetramethylammonium ions in which all of the octahedral holes are occupied by fluoride ions.

**8.28.** Which of the following are true statements about octahedral holes in a (cubic or hexagonal) close-packed lattice of anions? (a) There is one octahedral hole per anion in the lattice. (b) All of the octahedral holes are occupied in the lattice of  $CdI_2$ . (c) A cation in an octahedral hole is surrounded by eight anions. (d) An octahedral hole is larger than a tetrahedral hole. (e) All of the octahedral holes are occupied in the lattice of NaCl.

**8.29.** \*Which of the following structural descriptions is/are inconsistent with the stoichiometry of the salt being described? (a)  $BiI_3$  adopts an hcp lattice of iodide ions in which one-third of the octahedral holes are occupied by bismuth ions. (b)  $Ga_2S_3$  adopts an hcp lattice of sulfide ions in which two-thirds of the tetrahedral holes are occupied by gallium ions. (c)  $Li_3N$  adopts a close-packed lattice in which all holes are occupied with  $Li^+$  ions.

**8.30.** Which of the following are true statements about tetrahedral holes in a (cubic or hexagonal) close-packed lattice of anions? (a) There is one tetrahedral hole per anion in the lattice. (b) All of the tetrahedral holes are occupied in the lattice of ZnS. (c) A cation in a tetrahedral hole is surrounded by four anions. (d) A tetrahedral hole is larger than an octahedral hole; (e) All of the tetrahedral holes are occupied in the lattice of NaCl.

**8.31.** \*The  $C_{60}^{3-}$  anion is nearly spherical, with a radius of roughly 500 pm. (a) Can it form a salt in which *all* holes are filled? Why? (b) If so, which salt is more likely:  $Rb_2CsC_{60}$  or  $RbCs_2C_{60}$ ? Why?

**8.32.** In the following list, (a) which oxides are likely to be spinels, and (b) which oxides could be perovskites? TiCo<sub>2</sub>O<sub>4</sub>, NaTaO<sub>3</sub>, SrTiO<sub>3</sub>, Zn<sub>2</sub>SiO<sub>4</sub>, ZnSeO<sub>3</sub>, CoFe<sub>2</sub>O<sub>4</sub>, and FeCo<sub>2</sub>O<sub>4</sub>.

**8.33.** \*In the following list, (a) which oxides are likely to be spinels, and (b) which oxides could be perovskites? NiFe<sub>2</sub>O<sub>4</sub>, BaFe<sub>2</sub>O<sub>4</sub>, BaTiO<sub>3</sub>, BeTiO<sub>3</sub>, BaSO<sub>3</sub>, TiZn<sub>2</sub>O<sub>4</sub>, Ni<sub>3</sub>O<sub>4</sub>, Pb<sub>3</sub>O<sub>4</sub>, and NaTaO<sub>3</sub>.

**8.34.** There are also sulfide-ion-based spinels, where the anions are sulfide ions rather than oxide ions. Write the probable formulas of the following spinels: (a) greigite, containing only Fe; (b) linnaeite, containing only Co; and (c) daubreeite, containing Fe and Cr.

**8.35.** \*Which of the following fluorides are likely to be perovskites?  $KMgF_3$ ,  $CaTiF_3$ ,  $LiBaF_3$ ,  $LiCF_3$ ,  $TlCoF_3$ ,  $Cu_2F_3$ , or none of these.

**8.36.** Which of the following formulas correspond to possible nonstoichiometric oxides?  $Sr_{0.95}O$ ,  $Fe_{0.95}O$ ,  $Ni_{0.95}O$ ,  $C_{0.95}O$ ,  $Cr_{0.95}O$ , and  $N_{0.95}O$ .

**8.37.** \*Which of the following formulas correspond to possible nonstoichiometric oxides?  $Ca_{0.95}O$ ,  $Fe_{0.95}O$ ,  $Co_{0.95}O$ ,  $C_{0.95}O$ ,  $Cr_{0.95}O_3$ , and  $Eu_{0.95}O$ .

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**8.38.** Why would you not expect very high-oxidation-number oxides such as  $Mn_2O_7$  and  $OsO_4$  to be nonstoichiometric (i.e.,  $Mn_{2,2}O_7$  or  $Os_{1,13}O_4$ )?

**8.39.** \*Which of the following are likely formulas for an isomorphously substituted salt: (Be,Ra)SO<sub>4</sub>, (Li,Mg)O, and (Zn,Fe)<sub>2</sub>SiO<sub>4</sub>?

**8.40.** The formula of the mineral tremolite is  $Ca_2(Mg,Fe)_5(OH)_2(Si_4O_{11})_2$ . Interpret the part of the formula which is written (Fe,Mg)<sub>5</sub>. What is the term for this phenomenon?

8.41. \*You are studying the mineral hornblende, Ca<sub>2</sub>Mg<sub>5</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>, and find samples in which isomorphous substitution of the magnesium and the calcium has occurred. Which of the following are possible minerals that could result from isomorphous substitution processes in hornblende? (a) Y<sub>2</sub>Mg<sub>5</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>; (b) Na<sub>2</sub>Mg<sub>5</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>; (c) Na<sub>2</sub>Mg<sub>3</sub>(Fe<sup>III</sup>)<sub>2</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>; (d) Y<sub>2</sub>Mg<sub>3</sub>Li<sub>2</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>; (e) Sr<sub>2</sub>Mg<sub>5</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>.

**8.42.** The formula of the common form of the mineral garnet, andradite, can be written as  $Ca_3Fe_2Si_3O_{12}$ ; there is a family of garnets, including (a)–(c). For each member of the family, tell whether the first or the second principle of isomorphous substitution (or both) is (or are) used to generate that member from common garnet (and confirm that it applies). Identify the oxidation state of any *d*-block metal ions. (a) Almandite,  $Fe_3Al_2Si_3O_{12}$ ; (b) grossularite,  $Ca_3Al_2Si_3O_{12}$ ; (c) spessartite,  $Mn_3Al_2Si_3O_{12}$ .

**8.43.** \*The formula of the common form of the mineral garnet, andradite, can be written as  $Ca_3Fe_2Si_3O_{12}$ ; there is a family of garnets, including (a)–(c). For each member of the family, tell whether the first or the second principle of isomorphous substitution (or both) is (or are) used to generate that member from common garnet (and confirm that it applies). Identify the oxidation state of any *d*-block metal ions. (a) Uvarovite,  $Ca_3Cr_2Si_3O_{12}$ ; (b) the synthetic "YAG," used in lasers:  $Y_3Al_5O_{12}$ ; (c) the synthetic  $Y_3Fe_5O_{12}$ , of importance for its magnetic properties.

**8.44.** The formula of one common form of feldspar, anorthite, can be written as  $Ca[Al_2Si_2O_8]$ . For the real or possible feldspars (a) and (b), tell which principle of isomorphous substitution—first or second—is used to generate this feldspar from anorthite. (a) Albite,  $Na[AlSi_3O_8]$ ; (b) the synthetic  $Sr[Ga_2Si_2O_8]$ .

**8.45.** \*Which principle of isomorphous substitution—the first or the second—is involved in converting (a)  ${}^{3}_{\infty}$ [Si<sub>2</sub>O<sub>4</sub>] to  ${}^{3}_{\infty}$ [AlPO<sub>4</sub>] with the same structure; (b)  ${}^{3}_{\infty}$ [LaPO<sub>4</sub>] to  ${}^{3}_{\infty}$ [CePO<sub>4</sub>] with the same structure?

**8.46.** Which one of the following could arise by isomorphous substitution of ions in leucite,  $KAlSi_2O_6$ ?  $KYSi_2O_6$ ,  $BaBeSi_2O_6$ ,  $BaAlSi_2O_6$ .

**8.47.** \*Some semiconductors are soft-base salts that can be generated by isomorphous substitution of the second type, starting from the four-coordinate semiconducting elements, silicon and germanium. (a) Thinking of elemental silicon as  ${}^{3}_{\infty}$ [Si<sup>4+</sup>Si<sup>4-</sup>] and estimating a radius for Si<sup>4-</sup>, give a product that is obtained by carrying out the substitution first once and then twice. (b) Thinking of elemental germanium as  ${}^{3}_{\infty}$ [Ge<sup>4+</sup>Ge<sup>4-</sup>] and estimating a radius for Ge<sup>4-</sup>, give a product that is obtained by carrying out the substitution first once and then twice.

**8.48.** The mineral jarosite,  $KFe_3(SO_4)_2(OH)_6$ , was recently in the news when it was found on Mars. Consider the possibility of isomorphous substitution for the metal ion(s) in jarosite, with the following cations being candidates for substituting into jarosite: Li<sup>+</sup>, Rb<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, and Cr<sup>3+</sup>. (a) Which charge does Fe have in jarosite? (b) Which of the cations is the best candidate for replacing the K<sup>+</sup> in jarosite by isomorphous substitution of the first kind? Write the formula of the resulting jarosite in which all of the K<sup>+</sup> has been replaced.

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(c) Which of the cations is the best candidate for replacing the iron in jarosite by isomorphous substitution of the first kind? Write the formula of the resulting jarosite in which all of the iron has been replaced. (d) Which two of the cations are the best candidates for replacing the  $K^+$  and one of the iron ions in jarosite by isomorphous substitution of the *second* kind? Write the formula of the resulting jarosite in which this has been done.

8.49. \*Consider mineral pairs (a)–(e). Classify each as related to the other by (1) isomorphous substitution of the first kind; (2) isomorphous substitution of the second kind; (3) non-isomorphous substitution; or (4) a pair that is completely unrelated in structure.
(a) KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and RbAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O; (b) KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and KCr(SO<sub>4</sub>)<sub>2</sub>; (c) Pb<sub>5</sub>Cl(PO<sub>4</sub>)<sub>3</sub> and Pb<sub>5</sub>Cl(VO<sub>4</sub>)<sub>3</sub>; (d) CO<sub>2</sub> and SiO<sub>2</sub>; (e) xenotime (YPO<sub>4</sub>) and zircon (ZrSiO<sub>4</sub>).

8.50. Use the specified principle of isomorphous substitution and Table C to convert
(a) wollastonite, Ca(SiO<sub>3</sub>), to another isomorphous mineral (first principle, replacing Ca);
(b) magnesioriebeckite, Na<sub>2</sub>Mg<sub>3</sub>Fe<sub>2</sub>[Si<sub>4</sub>O<sub>11</sub>]<sub>2</sub>(OH)<sub>2</sub>, second principle, replacing Na and Fe.

**8.51.** \*(a) Verify that the large unit cell of  $YBa_2Cu_3O_7$  shown in Figure 8.14 indeed shows the correct stoichiometry of ions. (b) If there were no mixing of  $Cu^{3+}$  and  $Cu^{2+}$  ions between the chains and sheets of copper ions, which type of copper ion would reside in the chains and which in the sheets in order to give the proper stoichiometry?

8.52. Choose the appropriate classifications(s)—perovskite, spinel, nonstoichiometric, defect perovskite, superconductor—for each of the following mixed-metal oxides: (a) BaTiO<sub>3</sub>;
(b) La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub>; (c) Fe<sub>0.95</sub>O; (d) Fe<sub>3</sub>O<sub>4</sub>; (e) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub>.

8.53. \*Choose the appropriate classifications(s)—perovskite, spinel, nonstoichiometric, superconductor, impossible—for each of the following mixed-metal oxides: (a) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>;
(b) Co<sub>3</sub>O<sub>4</sub>; (c) RbNbO<sub>3</sub>; (d) Os<sub>0.95</sub>O<sub>4</sub>.

8.54. Choose the appropriate classifications(s)—perovskite, spinel, nonstoichiometric, superconductor, or none of the above—for each of the following mixed-metal oxides:
(a) CsNbO<sub>3</sub>; (b) LiPaO<sub>3</sub>; (c) Mn<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>; (d) MgAl<sub>2</sub>O<sub>4</sub>; (e) Ba<sub>7</sub>SbO<sub>6</sub>; (e) ThO<sub>2</sub>.

**8.55.** \*Determine the coordination number and list the nearest neighbors of the oxide ions in (a) perovskite and (b)  $YBa_2Cu_3O_7$ . (c) Confirm that Equation 4.1 applies to these mixed-metal oxides if it is modified to read:  $\sum$ (Coord. No. of M)(No. of M in formula) = (Coord. No. of Anion)(No. of Anions in formula).

**8.56.** Classify each oxide as acidic, basic, or amphoteric or neutral, and decide whether it will be soluble in water: (a)  $Na_2O$ ; (b)  $Cr_2O_3$ ; (c)  $CO_2$ ; (d)  $SiO_2$ .

8.57. \*Arrange the following oxides in order of decreasing acidity/increasing basicity:
(a) Na<sub>2</sub>O, Cr<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>4</sub>O<sub>10</sub>; (b) ZrO<sub>2</sub>, CO<sub>2</sub>, SrO, Rb<sub>2</sub>O, Y<sub>2</sub>O<sub>3</sub>; (c) MnO, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>; (d) TiO<sub>2</sub>, TeO<sub>2</sub>, SO<sub>2</sub>, ThO<sub>2</sub>.

**8.58.** Consider oxo acids (a)–(e): (a)  $H_2SeO_3$ ; (b)  $H_6TeO_6$ ; (c)  $HMnO_4$ ; (d)  $H_3PO_4$ ; (e)  $H_4XeO_6$ . For each oxo acid, (1) determine whether it is soluble or insoluble in water, and (2) give the formula of the corresponding acidic oxide from which it might be prepared by the addition of water only (assuming solubility).

**8.59.** \*Suppose that five oxides of new elements have been discovered: hoffmon tetroxide, HmO<sub>4</sub> (Hm = fourth-period element); dimongium heptoxide, Mi<sub>2</sub>O<sub>7</sub> (Mi = sixth-period element); yangium dioxide, YaO<sub>2</sub> (Ya = second-period element with no unshared *sp* electron pairs); vermillium dioxide, VeO<sub>2</sub> (Ve = fifth-period element with one unshared *sp* electron pair); and luium dioxide, LmO<sub>2</sub> (Lm = fifth-period element with no unshared *sp* 

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electron pair). (a) Which two oxides are most likely to be gases at room temperature? (b) Which oxide is most likely to be strongly acidic? (c) Which oxide is most likely to be basic? Is it likely to be water soluble? (d) Which oxide is most likely to be useful for making ceramic plates to shield space shuttles from the heat of re-entry into the atmosphere?

**8.60.** Consider the following set of oxides: MnO<sub>2</sub>, OsO<sub>2</sub>, SnO<sub>2</sub>, CO<sub>2</sub>, OsO<sub>4</sub>, XeO<sub>4</sub>, and FeO<sub>4</sub>. (a) Which three of these oxides are high-melting solids? (b) Which four of these oxides are easily vaporized (are gases or at least volatile solids)? (c) Three of the four easily vaporized solids are in the same class of acid–base reactivity. Are these acidic or basic oxides? The fourth of these easily vaporized oxides is, in contrast to the others, a neutral oxide. Which one is this? Briefly explain why.

**8.61.** \*Consider the following set of oxides: SrO,  $ZrO_2$ , TeO<sub>3</sub>, and XeO<sub>4</sub>. (a) Which one of these oxides is a solid, insoluble in water, which reacts with the acidic oxide SiO<sub>2</sub> to give a simple silicate salt? Write an equation for this reaction. (b) Which one of these oxides is a solid that dissolves in water to give a basic solution? Write an equation for this process. (c) Which one of these oxides is a gas that dissolves in water to give an acidic solution? Write an equation for this process.

**8.62.** The elements V, Cr, Tc, and Os all form soluble acidic oxides. For each element, write the simplest formula of its soluble acidic oxide, then write the balanced chemical equation showing its reaction with water. (a) V; (b) Cr; (c) Tc; (d) Os.

**8.63.** \*You have produced minute quantities of radioactive element number 109, meitnerium, and are investigating its positive oxidation states. (a) Suppose that you have oxidized it very strongly in a hot acidic solution, and find the radioactivity coming from the vapors above the solution; you conclude that you have a volatile oxide. What oxidation state do you probably have? Give arguments why you chose that oxidation state and not some other. Draw a likely structure of the oxide. (b) Suppose that you subsequently obtain meitnerium in the +6 oxidation state in basic solution, and find that it gives a precipitate not only with Ba<sup>2+</sup> but also with most acidic cations. What does this lead you to suspect about the formula of the +6 species? (c) You have only a trace of Mt left, in the +7 oxidation state in basic solution. Outline a plan for precipitating it from solution.

**8.64**. Complete and balance the following chemical equations (or tell if no reaction will occur):

(a)  $N_2O_5 + H_2O \Rightarrow$ (b)  $Cl_2O_7 + H_2O \Rightarrow$ (c)  $Na_2O + H_2O \Rightarrow$ (d)  $Cr_2O_3 + H^+(aq) \Rightarrow$ (e)  $Cr_2O_3 + H_2O \Rightarrow$ (f)  $SiO_2 + OH^- \Rightarrow$ 

**8.65.** \*Complete and balance the following chemical equations (or tell if no reaction will occur):

(a)  $Tl_2O + H_2O \Rightarrow$ (b)  $I_2O_5 + H_2O \Rightarrow$ (c)  $Cl_2O(g) + H_2O \Rightarrow$ (d)  $La_2O_3 + H^+ \Rightarrow$ (e)  $B_2O_3 + OH^- + H_2O \Rightarrow$ (f)  $MnO + H^+(aq) \Rightarrow$ 

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**8.66.** Consider the oxides SrO,  $ZrO_2$ ,  $MoO_3$ , and  $RuO_4$ . If needed, take the radius of  $Ru^{8+}$  to be 52 pm. (a) Which of these oxides will be soluble in water to give a basic solution? Write a chemical equation for this process. (b) Which of these oxides will be soluble in water to give an acidic solution? Write an equation for this process. (c) Which of these oxides (if any) will be monomeric molecular substances? (d) Which of these oxides (if any) will most easily become a gas? (e) Which one of these oxides will most likely be a basic oxide that will be *insoluble* in water? Write an example of an equation for a chemical reaction that would justify classifying it as a basic oxide.

**8.67.** \*Classify each oxide below as acidic, basic, etc. Then complete and balance the following equations for Lux–Flood acid–base reactions, or note if no such reaction is to be expected.

(a)  $BaO(s) + P_4O_{10}(s) \rightarrow$ (b)  $TeO_3(s) + I_2O_5(s) \rightarrow$ (c)  $SrO(s) + MoO_3(s) \rightarrow$ (d)  $CaO(s) + TeO_3(s) \rightarrow$ (e)  $CaO(s) + MnO(s) \rightarrow$ 

**8.68.** Classify each oxide below as acidic, basic, etc. Then complete and balance the following equations for Lux–Flood acid–base reactions, or note if no such reaction is to be expected.

(a)  $Y_2O_3(s) + P_4O_{10}(s) \rightarrow$ (b)  $Na_2O(s) + V_2O_5(s) \rightarrow$ (c)  $Na_2O(s) + BaO(s) \rightarrow$ (d)  $Na_2O(s) + P_4O_{10}(s) \rightarrow$ (e)  $Fe_2O_3(s) + BaO(s) \rightarrow$ (f)  $FeO + P_4O_{10} \rightarrow$ 

**8.69.** \*(a) Would you expect a solid-state reaction between BaO and  $Sb_2O_5$ ? (b) If so, which would be the product:  $BaSbO_3$ ,  $Ba_3(SbO_4)_2$ ,  $Ba_7(SbO_6)_2$ , or  $BaSb_2O_6$ ?

**8.70.** Write three balanced chemical equations showing the three steps by which ammonia is converted industrially to nitric acid.

**8.71.** \*(a) Write three balanced chemical equations showing the three steps by which elemental sulfur in coal is converted to sulfuric acid in acid rain. (b) Sulfur dioxide can be removed from smokestack gases by reaction with (by "scrubbing" with) magnesium oxide. Write a chemical equation for this process. (c) Calculate the number of grams of magnesium oxide that would be needed to clean the smokestack gases from burning 1,000,000 g of coal that is 3.2% S by weight.

8.72. Which volatile oxides are associated with each of the environmental problems given in (a)–(d)? Why are the other volatile oxides discussed in this section not involved?(a) Acid rain; (b) the greenhouse effect; (c) the acidification of seawater; (d) London smog.

8.73. \*What methods are discussed for disposing of volatile acidic oxides from smokestacks?

**8.74.** Classify each of the silicates (a)–(e) as (1) a layer polysilicate, (2) a chain or cyclic polysilicate, (3) a simple silicate, or (4) a double-chain polysilicate: (a) bustamite =  $CaMn(SiO_3)_2$ ; (b) spudomene =  $LiAl(SiO_3)_2$ ; (c) tremolite =  $Ca_2Mg_5(OH)_2[Si_4O_{11}]_2$ ; (d) coffinite =  $U(SiO_4)$ ; (e) kaolinite =  $Al_2(OH)_4(Si_2O_5)$ .

8.75. \*Select one mineral—(1) wollastonite =  $CaSiO_3$ ; (2) talc =  $Mg_3(OH)_2[Si_4O_{10}]$ ; (3) grunerite =  $Fe_7(OH)_2[Si_4O_{11}]_2$ ; (4) monticellite =  $CaMgSiO_4$ ; (5) stishovite =  $SiO_2$ —as an

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example of each of the following: (a) contains a monomeric silicate ion; (b) contains a chain polysilicate ion; (c) contains a double-chain polysilicate ion; (d) contains a layer polysilicate ion.

**8.76.** Classify silicates (a)–(f) as (1) a simple silicate, (2) a disilicate, (3) a chain polysilicate or cyclic oligosilicate, (4) a layer polysilicate, or (5) a double-chain polysilicate: (a) acmite = NaFe(SiO<sub>3</sub>)<sub>2</sub>; (b) akermanite = Ca<sub>2</sub>Mg(Si<sub>2</sub>O<sub>7</sub>); (c) anthophyllite = Mg<sub>7</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub>; (d) fayalite = Fe<sub>2</sub>(SiO<sub>4</sub>); (e) pyrophyllite = Al<sub>2</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>); (f) zircon = Zr(SiO<sub>4</sub>); (g) talc = Mg<sub>3</sub>(OH)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>).

**8.77.** \*Classify silicates (a)–(d) as (1) a simple silicate, (2) a disilicate, (3) a chain polysilicate or cyclic oligosilicate, (4) a layer polysilicate, or (5) a double-chain polysilicate: (a) crocidolite,  $Na_2Fe_5(OH)_2[Si_4O_{11}]_2$ ; (b) enstasite,  $Mg(SiO_3)$ ;(c) olivine,  $(Mg,Fe)_2(SiO_4)$ ; (d) diopside,  $CaMg(SiO_3)_2$ .

**8.78.** Solutions of tetraalkylammonium silicates have been found to contain an anion of formula  $Si_8O_{20}^{8-}$ : M. Wiebke, M. Grube, H. Koller, G. Engelhardt, and J. Felsche, *Microporous Mater.* 2, 55 (1993). (a) Which class of polysilicate would this appear to be from its formula? (b) Check the literature article to see whether this is indeed the proper class. If not, would it be a member of a new class? In this case, suggest a new class based on the terminology of Figure 8.21.

**8.79.** \*Show that you understand the condensed drawings of the fragments of polysilicate structures shown in Figure 8.21 by redrawing them, using closed circles for Si atoms and open circles for O atoms. Redraw the following: (a)  $_{\infty}^{1}$ [SiO<sub>3</sub><sup>2–</sup>], (b)  $_{\infty}^{1}$ [Si<sub>4</sub>O<sub>11</sub><sup>6–</sup>], and (c)  $_{\infty}^{2}$ [Si<sub>4</sub>O<sub>10</sub><sup>4–</sup>].

**8.80.** A mineral proposed as an asbestos replacement called xonotlite,  $Ca_6(OH)_2[Si_6O_{17}]$ , is also a double-chain polysilicate, but it differs slightly in structure. Propose a structure for xonotlite.

**8.81.** \*Predict the basicity classification of the anion in polysilicates (a)–(d), based on the (untested) hypothesis that their  $pK_b$  values can be estimated from the formula of the structural unit of the polysilicate using Equation 3.14. (a) Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>; (b) Si<sub>3</sub>O<sub>9</sub><sup>6-</sup>; (c) Si<sub>4</sub>O<sub>11</sub><sup>6-</sup>; (d) Si<sub>4</sub>O<sub>10</sub><sup>4-</sup>. (e) Estimate the  $pK_a$  values of the corresponding conjugate acids of these silicate anions. If the hypothesis is valid, which of these polysilicates, when ion-exchanged into the H<sup>+</sup> forms, would be very strongly acidic?

**8.82.** Select one of the minerals mentioned in Exercise 8.75 as (a) the mineral that would weather the most rapidly; (b) the mineral that would weather the most slowly.

**8.83.** \*Select one of the minerals mentioned in Exercise 8.76 as (a) the mineral that would weather the most rapidly; (b) the mineral that would weather the most slowly.

**8.84.** Consider the following minerals and oxides: lime = CaO; ureyite = NaCr(SiO<sub>3</sub>)<sub>2</sub>; chabazite = Ca<sub>6</sub>[Al<sub>12</sub>Si<sub>24</sub>O<sub>72</sub>]; zirconia = ZrO<sub>2</sub>; tremolite = Ca<sub>2</sub>(Mg,Fe)<sub>5</sub>(OH)<sub>2</sub>[Si<sub>4</sub>O<sub>11</sub>]<sub>2</sub>; olivine = (Fe,Mg)<sub>2</sub>(SiO<sub>4</sub>); and kaolinite = Al<sub>4</sub>(OH)<sub>8</sub>[Si<sub>4</sub>O<sub>10</sub>]. (a) Which one would weather most quickly? (b) Which one would most characteristically be found on Earth's surface only in the youthful soil of a desert? (c) Which would be the last to weather away? (d) Which is abundant in the mantle and is converted to a spinel polymerization isomer deep in the mantle?

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8.85. \*Consider the following types of silicates or related soil minerals: layer aluminosilicates, layer polysilicates, chain or cyclic polysilicates, simple silicates, three-dimensional polymeric metal oxides (e.g., TiO<sub>2</sub>), and double-chain polysilicates.
(a) Which one would weather most quickly? (b) Which one would be most characteristically found in a desert soil? (c) Which one would be most characteristically found in the soil of a tropical region in which the forest has been cut down?

**8.86.** The atmosphere of Venus is very hot (~800°C) and dense, is composed mainly of  $CO_2$  with some  $N_2$ , and supports opaque clouds made of sulfuric acid. (a) How would you compare the acidity of this atmosphere to that of Earth? (b) How would you expect the rate of weathering of silicate minerals to be on Venus as compared to on Earth?

**8.87.** \*Which of the following minerals are layer aluminosilicates? (a) Hedenbergite =  $CaFe(SiO_3)_2$ ; (b) lepidolite =  $KAl_2[AlSi_3O_{10}](OH,F)_2$ ; (c) phenacite =  $Be_2(SiO_4)$ ; (d) petalite =  $Li[AlSi_4O_{10}]$ ; (e) mesolite =  $Na_2Ca_2[Al_2Si_3O_{10}]\cdot 8H_2O$ .

**8.88.** Which of minerals (a)–(d) is/are layer aluminosilicates? Which are clays? (a) Ureyite = NaCr(SiO<sub>3</sub>)<sub>2</sub>; (b) natrolite = Na<sub>2</sub>[Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>]·2H<sub>2</sub>O; (c) biotite = K(Mg,Fe)<sub>3</sub>[AlSi<sub>3</sub>O<sub>10</sub>](OH)<sub>2</sub>; (d) cummingtonite = Mg<sub>7</sub>(OH)<sub>2</sub>[Si<sub>4</sub>O<sub>11</sub>]<sub>2</sub>.

**8.89.** \*Devise a possible asbestos substitute that would be the aluminosilicate obtained from chrysotile (serpentine) asbestos  $Mg_6(OH)_8(Si_4O_{10})$  by isomorphous substitution of the second kind.

**8.90.** Figure 8.23 shows the relative availability of nutrient elements in soil as a function of soil pH. Using the principles in the book to date, explain why each element is available and unavailable at the pH values given.

**8.91.** You are studying the feldspar K[AlSi<sub>3</sub>O<sub>8</sub>] and find samples in which isomorphous substitution has occurred. Which of the following are possible minerals that could result from isomorphous substitution processes in this feldspar? (a) Ba[Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>]; (b) Rb[AlSi<sub>3</sub>O<sub>8</sub>]; (c) Na[AlSi<sub>3</sub>O<sub>8</sub>]; (d) Ba[AlSi<sub>3</sub>O<sub>8</sub>].

**8.92.** Select the proper structural type—framework aluminosilicate, layer polysilicate, chain or cyclic polysilicate, simple silicate, or double-chain polysilicate—for each of the following silicates: (a) ureyite =  $NaCr(SiO_3)_2$ ; (b) natrolite =  $Na_2[Al_2Si_3O_{10}] \cdot 2H_2O$ ; (c) cummingtonite =  $Mg_7(OH)_2[Si_4O_{11}]_2$ .

**8.93.** \*The formula of one common form of the mineral feldspar, anorthite, can be written as  $Ca[Al_2Si_2O_8]$ . Which principle(s) of isomorphous substitution (first and/or second) is(are) used to generate feldspars (a) and (b) from anorthite? (a) Albite,  $Na[AlSi_3O_8]$ ; (b) the synthetic  $Sr[Ga_2Si_2O_8]$ .

**8.94.** Select the proper structural type—framework aluminosilicate, layer polysilicate, chain or cyclic polysilicate, simple silicate, double-chain polysilicate, or layer aluminosilicate—for each of the following silicates: (a) willemite =  $Zn_2(SiO_4)$ ; (b) celsian =  $Ba[Al_2Si_2O_8]$ ; (c) chabazite =  $Ca_6[Al_{12}Si_{24}O_{72}]$ ; (d) tremolite =  $Ca_2(Mg,Fe)_5(OH)_2[Si_4O_{11}]_2$ ; (e) phenacite =  $Be_2(SiO_4)$ .

8.95. \*Consider the following silicates and aluminosilicates:

tremolite =  $Ca_2(Mg,Fe)_5(OH)_2[Si_4O_{11}]_2$ ; ureyite =  $NaCr(SiO_3)_2$ ; chabazite =  $Ca_6[Al_{12}Si_{24}O_{72}]$ ; kaolinite =  $Al_4(OH)_8[Si_4O_{10}]$ ; and phenacite =  $Be_2(SiO_4)$ . (a) Draw the structure of the simplest formula unit of each silicate or aluminosilicate anion except that of chabazite. (b) Write the formula of the (mononuclear) structural unit of each anion, along with its

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(possibly fractional) charge. (c) List the anions in order of increasing predicted basicity. (d) Briefly explain why aluminum is written inside the brackets in the formula of chabazite but outside the brackets in the formula of kaolinite,  $Al_4(OH)_8[Si_4O_{10}]$ .

**8.96.** Predict the basicity classification of the anion in each of the following polyaluminosilicates, based on the (untested) hypothesis that these can be estimated from the formula of the mononuclear structural unit obtained by depolymerizing the anion, then counting the number of oxo groups and units of negative charge in the structural unit: (a) anion of orthoclase; (b) anion of celsian; (c) anion of sodalite; (d) anion of ZSM-5. (e) Estimate the  $pK_a$  values of the corresponding conjugate acids of these aluminosilicate anions, assuming that the hypothesis in it has some validity. If so, which of these aluminosilicates, when ion-exchanged into the H<sup>+</sup> forms, would be very strongly acidic?