

The Oxides of the Elements

With Applications to Geochemistry, Environmental Chemistry, and Materials Science

13.1 The Physical States and Structures of the Fluorides and Oxides of the Elements

Like the elements themselves, the oxides of the elements include monomers, oligomers, and polymers with a vast variety of physical properties. As in Chapter 12, we will assemble the more complex oxides by linking together their fundamental *structural units*.¹ For most purposes, we will consider the basic structural unit of a *compound* as the unit represented by the simplest or empirical formula of the substance, but with the additional simplification that, if there are two or three atoms of the least abundant element in the simplest formula (e.g., Cl in Cl_2O_7), the structural unit will be reduced to include only one atom of this least abundant atom. Thus, the structural unit of Cl_2O_7 will be considered to be $\text{ClO}_{3.5}$.² The fractional number of oxygen atoms clearly indicates what we shall see later, that there is an oxygen atom common to two structural units and serving to *link* or *bridge* them. Note that in some applications such as silicate geochemistry (Sections 13.6 and 13.7) the structural unit is called a “nucleus” of the structure.

In contrast to the last two chapters, in this and subsequent chapters we will choose to link our structural units, not by sharing one electron from each unit, but rather by *coordinate covalent bonding*, in which the linking oxide (or other) ion provides the electron pair, while the central atom of the formula unit provides a vacant coordination site: a site of potential Lewis acidity. In terms used in Chapter 11, we will use the Lewis acid-base (LAB) approach to assembling our isolobal fragments (structural units), rather than the redox-radical (RR) approach. The LAB approach is justified on two grounds. First, the oxides and halides of the elements involve much more ionic bonds (due to greater electronegativity differences) than are present in the elements themselves or in most organometallic compounds. Second, using the RR approach and Table 11.6, we expect halide ions to form only one bond, and oxide ions to form only two. This will turn out not to be the case: Halide ions can act as bridging or linking ions, and oxide ions can link three central atoms. The “extra” bonds must be treated as

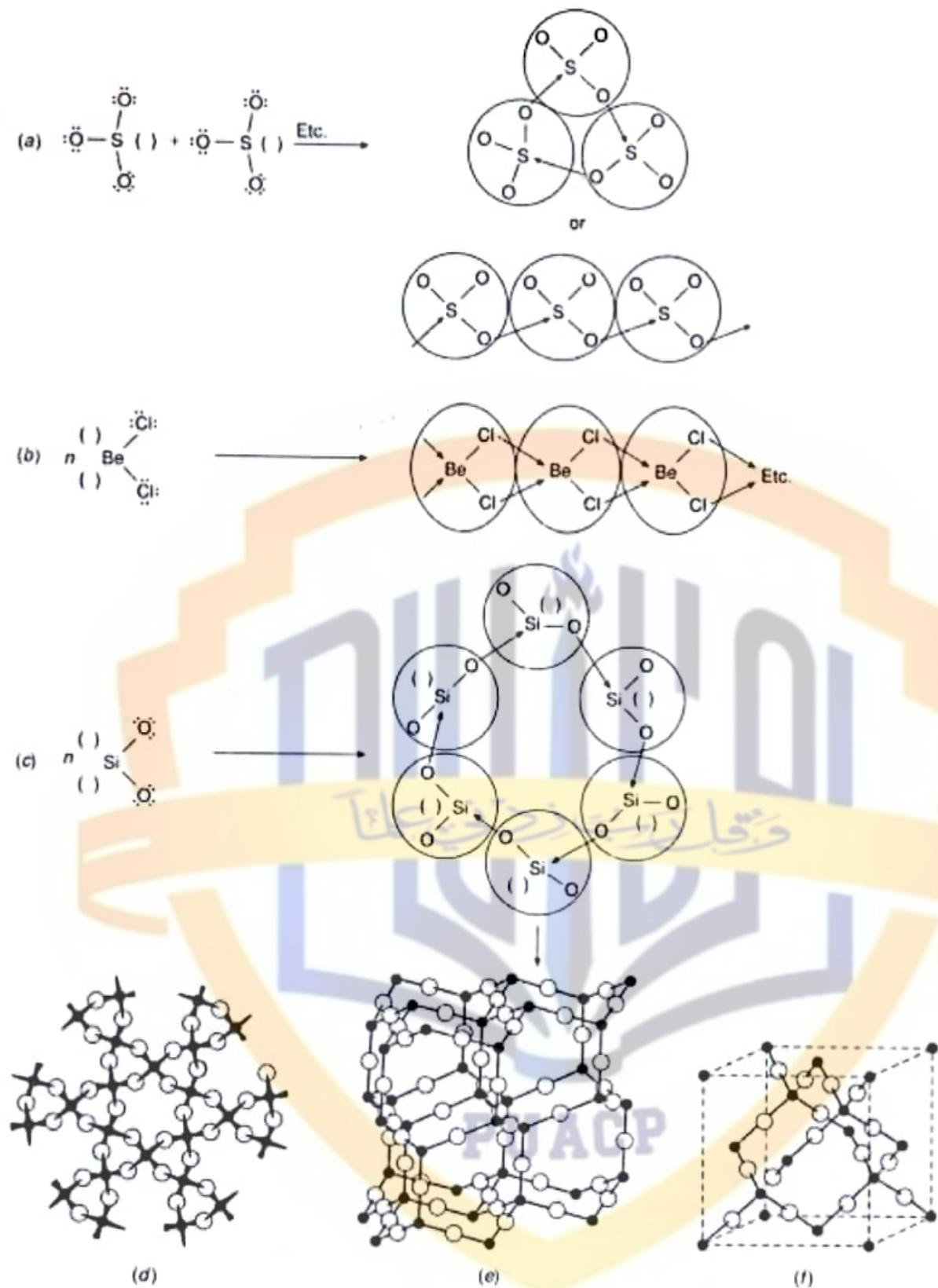
coordinate covalent bonds. It is simplest, then, to treat *all* of the bonds to the central atom as coordinate covalent bonds, and use the LAB approach; hence, we return to the approach emphasized in Chapters 2–5.

To a significant extent, the degree of polymerization of the structural units of an oxide or halide (and therefore many of the physical properties of that material) can be understood based on simple predictions of the *number of interunit links that the structural unit is likely to form*, given how close the structural unit actually comes to coordinative saturation, that is, on how close the coordination number of the central atom of the structural unit is to its expected maximum (or penultimate) coordination number. Let us begin by considering certain structural units from which real (or imaginary) oxides of third-period elements might be assembled by polymerization: MgO, SiO₂, SO₃, and “ArO₄.” If we simplistically assume a constant penultimate total coordination number of 4 for these central atoms, we see that this is achieved only in the hypothetical ArO₄, which is the only one of these oxides that we would certainly expect to be monomeric. In all other cases, the central atom falls short of its expected (penultimate) coordination number (and falls short of an octet of electrons). Thus the central atoms of these oxide structural units have vacant coordination sites—potential Lewis acid sites—which we might represent by empty parentheses: ()₃MgO; ()₂SiO₂; ()SO₃. The outer oxygen atoms or ions all have unshared electron pairs, and hence represent potential Lewis base sites.

Octets of electrons and coordinative saturation can then be completed for the central atoms in either of two ways: (1) by donation of a second pair of electrons from one oxygen atom to the central atom, forming a π bond; (2) by donation of an unshared electron pair from an oxygen atom or ion in a second structural unit, forming a linking coordinate covalent bond. As discussed earlier, only a few elements form good π bonds, so among the oxides in question only sulfur can utilize this option: SO₃ sometimes adopts a double-bonded, monomeric form, O=SO₂. Since σ bond linkage is normally stronger than π bond linkage, the remaining elements prefer to achieve octets and coordinative saturation by polymerization through bridging oxygen links, as sketched in Figure 13.1.

Even sulfur normally takes this second option; SO₃ is normally found as either an oligomer or a chain polymer, as shown in the figure. In either of these cases, the structure features *one interunit link* per structural unit. More than one structural form is possible for SO₃ (and many other linked materials), because the linking bonds to the two-coordinate oxygen atom may either be turned inward to give cyclic oligomers, or outward to give chain polymers. These different forms are often termed polymorphs of SO₃, since they have different crystal lattice types, but the difference between the oligomer and polymer is really more profound than this: Perhaps they should be called polymerization isomers.³ Because links can be formed at different angles, we generally cannot unambiguously predict the exact type of oligomerization or polymerization that will happen to a given coordinately unsaturated structural unit. Instead, we will follow periodic trends in the *degree* of oligomerization or polymerization as we cross periods or groups, and we will watch how physical properties change as a consequence.

Silicon in the SiO₂ structural unit has *two* vacant coordination sites, so we anticipate correctly that it is likely to polymerize to a greater extent than SO₃, forming two links per structural unit, and giving each bridging oxygen atom a coordination number of 2. We could conceive of these two bridging links turning sharply inward to give a double chain polymer, as shown in Figure 13.1(b) for the real case of $\frac{1}{x}$ [BeCl₂], but in fact the resulting bond angles at oxygen are too strained and the partial positively charged Si⁴⁺ “cations” are brought too close together. Therefore the SiO₂ structural

**Figure 13.1**

Lewis acid–base reactions between structural units (enclosed in circles in products) having vacant coordination sites (represented by parentheses), to generate different polymerization isomers. (Linkage by coordinate covalent bonds in the products is represented by arrows.) (a) Oligomerization or polymerization of SO_3 to give S_3O_9 or the one-dimensional polymer of SO_3 . (b) One-dimensional polymerization of BeCl_2 . (c) Cyclooligomerization of SiO_2 units to give $\text{cyclo-Si}_6\text{O}_{12}$ units, which are still coordinately unsaturated, and hence polymerize further to give various three-dimensional polymerization isomers (Si is represented by closed circles and O by large open circles): (d) β -quartz; (e) β -tridymite; (f) β -cristobalite. [(d)–(f) Adapted from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford, Clarendon Press, UK, 1984, pp. 1006–1007.]

unit polymerizes to give one of several network polymerization isomers, such as the three illustrated: β -quartz, β -tridymite, and β -cristobalite. Note that each of these contains large hexameric rings, $(\text{SiO}_2)_6$, of varying conformations; formation of the six links to give this ring take care of one vacant coordination site per SiO_2 unit. The other vacant site per unit leads to three-dimensional polymerization, but linkage in different directions result in the different coordination isomers shown, and gives each oxygen atom a coordination number of 2.

The MgO structural unit, with three vacant coordination sites, polymerizes to an ionic lattice; if it indeed had a maximum coordination number of 4, this would be a zinc blende or wurzite lattice (Fig. 4.8), and the oxygen ions would also have a coordination number of 4. In practice, MgO exhibits six coordination.

Hence, we see that increasing degrees of polymerization are foreshadowed by increasing numbers of vacant coordination sites at the central atom of the structural unit. The result is an increase in the average coordination number of the oxygen atoms or ions in the polymerized form of the material. If the central atom has no vacant coordination site, it is not a Lewis acid, and the structural unit remains as the monomeric molecular unit: the oxygens do not bridge, so they retain coordination numbers of 1.

The coordination numbers of cations or central atoms are more accurately predicted by carrying out ionic radius ratio calculations (Chapter 4) than by referring to maximum or penultimate total coordination numbers (Chapter 2), which are just the most common outcomes of radius ratio calculations for a given period. Radius ratio calculations, of course, are also not highly reliable, especially since many compounds are not ionic. These calculations do avoid having to prejudge the ionic or covalent nature of the bonding, and should be useful for predicting (and especially for understanding) periodic *trends* in structural types and physical properties such as melting and boiling points, as well as for understanding why dramatic changes occur approximately when they do in a period or a group. The appropriate calculations are outlined below.⁴

1. Calculate the radius ratio $r_{\text{cation}}/r_{\text{anion}}$. Referring to Table 4.4, use this ratio to predict the total coordination number (TCN) of the central (normally the metal) atom or ion. If the radius ratio is close to the cutoff points, there is a good deal of uncertainty in the result. Either total coordination number may prove correct: The compound may have one polymerization isomer with one coordination number and one with the other.⁵

2. The number of vacant coordination sites of the central atom in the structural unit is then obtained by subtracting the number of oxygen (or other outer) atoms in the structural unit from the expected total coordination number obtained in Step 1. Also, if the cation or metal is a *p*-block element with less than the maximum oxidation number, space must be reserved for the unshared pair of electrons⁶:

$$(\text{No. of vacant coordination sites around central atom}) = (\text{its expected TCN})$$

$$- (\text{No. of its outer atoms}) - (\text{No. of its unshared } sp \text{ electron pairs}) \quad (13.1)$$

Unless strong π bonding to outer oxygen atoms occurs instead (mainly for central C, N, or S atoms), each vacant coordination site leads to the formation of one bridging link, so Eq. 13.1 gives us the number of links expected per structural unit.

3. If the number of links expected per structural unit is zero, the species is predicted to occur as monomeric molecules, with relatively low melting or boiling points.

To predict whether it is a gas, liquid, or low-melting solid at room temperature, we need to look at the size of the molecule and whether or not it could engage in hydrogen bonding.

4. If the number of links expected per structural unit is *fractional* (< 1), we expect a small linear oligomer. As an example, the compound Cl_2O_7 has a structural unit of ClO_3 . The radius ratio prediction leads us to expect a coordination number of 4 for Cl, which therefore has 0.5 vacant coordination sites per chlorine. This is remedied by forming *one oxygen link between two structural units*, which produces $\text{O}_3\text{Cl}-\text{O}-\text{ClO}_3$ (Cl_2O_7).

5. If the number of links expected per structural unit is *one*, this can be achieved by forming either a cyclic oligomer or a chain polymer.

6. As the number of links increases above one per unit, greater degrees of polymerization are expected, but since the links can be arranged in several ways, various polymerization isomers may be possible. Eventually, network polymerization is generally to be anticipated, especially for more than three links per unit.

7. Occasionally, a *negative* number of vacant coordination sites may be computed: The N in “ NF_5 ” should have a coordination number of 4 from radius ratio calculations, which is exceeded in the structural unit NF_5 . In such cases, we expect the structural unit to *expel* an anion: as such, NF_5 is not known, but the ion NF_4^+ is known.

8. If it is desired, calculate the coordination number of the outer (oxygen) atom or ion, using Eq. (4.15); this can be useful in determining an ionic lattice type using Table 4.4.

We begin the illustration of these principles by considering the fluorides of some elements in their group oxidation states. As we discovered earlier (Chapter 3), fluorides serve as ideal illustrations of many phenomena of predominantly ionic compounds. The observed trends we find among many fluorides are simplified by the fact that, while fluoride *ion* readily serves to link units in ionic fluorides, covalently bonded fluorine does not readily serve as a bridging atom: Due to its high electronegativity it does not readily share a second pair of electrons. Hence, we shall see fewer than the expected number of oligomeric structures among fluorides, which allows very sharp contrast between the physical properties associated with monomeric molecular structures and those associated with network (ionic or covalent polymeric) structures (Table 13.1).

Example 13.1

Predict the coordination numbers, the physical states, and the relative melting and boiling points of the fluorides of the *sp*-block fourth-period elements in their group oxidation states. State whether each should have a monomeric, oligomeric, or polymeric or ionic structure.

SOLUTION:

The fluorides in question are KF , CaF_2 , GaF_3 , GeF_4 , AsF_5 , SeF_6 , and the (unknown) BrF_7 . The ionic radius of F^- is 119 pm; the radii of the “cations” of these compounds are also obtained from Table C. The radius ratios are 1.277, 0.958, 0.639, 0.563, 0.504, 0.471, and 0.445, respectively. Hence, the “cationic” coordination numbers are predicted to be 8 for K^+ and Ca^{2+} , and 6 for Ga^{3+} through Br^{7+} ; the last two values are close to the 0.414

cutoff radius ratio for a cationic coordination number of 4, so that this possibility remains open for Se^{6+} and Br^{7+} .

The number of vacant coordination sites per central atom are then calculated: this is $(8 - 1) = 7$ in KF , $(8 - 2) = 6$ in CaF_2 , $(6 - 3) = 3$ in GaF_3 , $(6 - 4) = 2$ in GeF_4 , $(6 - 5) = 1$ in AsF_5 , $(6 - 6) = 0$ (or negative) in SeF_6 , and $(6 - 7) = -1$ (or more negative) in BrF_7 .

We predict that BrF_7 should not exist; only BrF_6^+ forms for this oxidation state (in combination with large nonbasic fluoro anions). The SeF_6 molecule is coordinately saturated at Se, so it is a monomeric gas ($\text{mp} -40^\circ\text{C}$, Table 13.1). The AsF_5 unit would likely form a cyclic oligomer or chain polymer, except for the reluctance of covalent fluorides to bridge; it is actually a monomeric gas ($\text{mp} -63^\circ\text{C}$). The GeF_4 unit similarly does not form a low-dimensional polymer, but is in fact also a monomeric gas ($\text{mp} -37^\circ\text{C}$).

The remaining three compounds all show enough links per structural unit, and are ionic enough from their electronegativity differences, to make polymeric structures very likely. Hence, we predict that these will be ionic or macromolecular compounds, with high melting and boiling points, and we predict that these will all be solids at room temperature. Our predictions are verified: the melting point of KF is 857°C , and 1423°C for CaF_2 ; the sublimation temperature of GaF_3 is 800°C .

Example 13.2

Explain the trends in the physical states and boiling points of the Group 14(IVA) tetrafluorides.

SOLUTION:

From Table 13.1, we see that the top three fluorides (CF_4 through GeF_4) are gases with melting points below 0°C , while the bottom two fluorides are high-melting solids. The calculated radius ratios increase down the group (0.252, 0.454, 0.563, 0.697, and 0.765), as do the predicted central-atom coordination numbers (4, 4 or 6, 6, 6 or 8, 6 or 8) and central-atom vacant coordination sites (0, 0 or 2, 2, 2 or 4, 2 or 4). Our calculations predict that there will be a trend from monomeric gaseous fluorides at the top of the group to (probably) ionic network solids at the bottom, although the calculations are not trustworthy enough to predict exactly where the transitions will occur. The melting points correctly suggest that the top three fluorides are monomeric molecular substances (with increasing melting points due to increasing van der Waals forces); the tin and lead fluorides indeed have polymeric structures, with, in fact, average coordination numbers for Sn and Pb of 6. Two equatorial fluorines bridge adjacent Sn or Pb atoms to give a layer structure; the axial fluorines are terminal (have coordination numbers of 1), and hence are closer to the Sn atoms in SnF_4 (terminal Sn–F distance of 188 pm vs. bridging Sn–F distance of 212 pm).⁸

Among the structures of oxides, we find many more bridging covalent oxygen atoms and oligomeric structures, since a covalent oxygen atom following the octet rule readily forms two bonds to two different central atoms, without developing any formal charge. Oxygen, however, also forms π bonds that are relatively strong compared to its σ bonds (Section 3.1), so that if the bonding in the oxide is indeed covalent and the

Table 13.1
Melting Points of the Highest Fluoride of Each Element^a

HF																	
-83																	
LiF	BeF ₃																
848	535																
NaF	MgF ₂																
1012	1263																
KF	CaF ₂	ScF ₃	TiF ₄ (283)	VF ₃	CrF ₅ ^b	MnF ₄ dec.	FeF ₃ 1102	CoF ₃	NiF ₄ dec.	CuF ₂ 755	ZnF ₂ 927	GaF ₃ (800)	GeF ₄ -37	AsF ₅ -63	SeF ₆ -40	BrF ₃ -61	KrF ₂ dec.
657	1423	1227		110													
RbF	SrF ₂	YF ₃	ZrF ₄ (908)	NbF ₅	MoF ₆ 17	TcF ₆ 33	RuF ₆ 54	RhF ₆	PdF ₆	AgF ₃ dec.	CdF ₃ 1100	InF ₃ 1150	SnF ₄ 705	SbF ₅ -35	TeF ₆ 5	XeF ₆ 50	
775	1400	1152															
CsF	BaF ₂	LuF ₃	HfF ₄	TaF ₅ 97	WF ₆ 2	ReF ₇	OsF ₆ 32	IrF ₆ 44	PtF ₆ 57	AuF ₅	HgF ₃ 645	TlF ₃ 550	PtF ₆ 500	BiF ₅ dec.			
682	1290	1182															
				ThF ₄ 900	PaF ₅ (500)	UF ₆ 64	NpF ₆ 53	PuF ₆ 50									

SOURCES: Melting points in degrees Celsius taken from the *Handbook of Chemistry and Physics* and M. C. Ball and A. H. Norbury, *Physical Data for Inorganic Chemists*, Longman, London, 1974; pp. 70–91.

^aTemperatures enclosed in parentheses represent temperatures of sublimation.

^bIt is currently disputed whether the volatile highest fluoride of chromium is CrF₅ or CrF₆; J. Jacobs, H. S. P. Müller, H. Willner, E. Jacob, and H. Burger, *Inorg. Chem.*, 31, 5357 (1992).

central atom is relatively good at π bonding, the element may form two bonds to one oxygen in preference to one bond to two oxygen atoms, thus taking a lower total coordination number than our ionic model predicts. The good π bonding of oxygen was the reason why, in Chapter 3, we suggested the use of the penultimate rather than the maximum total coordination number for predicting the formulas of oxo anions; the same reasoning applies to oxides.

Example 13.3

Predict the coordination numbers, the physical states, and the relative melting 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 in an ionic lattice.

SOLUTION:

From Table B2, we see that these oxides are Li₂O, BeO, B₂O₃, CO₂, and N₂O₅. The ionic radius of the oxide ion is 126 pm (Table C); the radius ratios are 0.714, 0.464, 0.325, 0.238, and 0.214, respectively. The least abundant atom in Li₂O is oxygen; in the others it can be taken as the nonoxygen atom. Hence, the coordination numbers predicted are either 8 or 6 for O in Li₂O (hence, 4 or 3 for Li); either 6 or 4 for Be; 4 for B; 4 or 3 for C; and 3 for N.

We now compute the number of vacant coordination sites per structural unit: 3 or 2 for Li in LiO_{0.5}; 5 or 3 for Be in BeO; 2.5 for B in BO_{1.5}; 2 or 1 for C in CO₂; 0.5 for N in NO_{2.5}. The oxides of Li, Be, and B have enough vacant coordination sites for polymeric

(ionic) structures to be likely, so we predict that these will be ionic or polymeric covalent compounds, with high melting and boiling points, and we predict that these will all be solids at room temperature. Our predictions are verified: Li_2O has a melting point of 1427°C , BeO of 2530°C , and B_2O_3 of 450°C (but with a boiling point over 1860°C).⁹

For carbon dioxide, the prediction is uncertain but wrong in either case, since our calculations cannot predict the special stability of oxygen double-bonded to carbon. Carbon dioxide is actually a monomeric molecule and a gas at room temperature, which sublimes at -79°C at atmospheric pressure. For dinitrogen pentoxide the prediction is 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 3. The solid form of this compound consists of NO_2^+ and NO_3^- ions.

We may also predict lattice types for the ionic compounds, using Table 4.4, and compare them with results given in a more detailed text¹⁰ or by Wells⁸: For Li_2O we predict either an antirutile or antifluorite lattice and find the latter; and for BeO we predict either the NaCl or ZnS lattice and find the latter (wurtzite). The calculations for B_2O_3 do not suggest the corundum lattice type; two network polymerization isomers of this compound are known, in which the coordination numbers of boron are 3 and 4, respectively.

When the central *p*-block element is in its group oxidation state -2 , we must allow for this in the calculations, as illustrated in Example 13.4.

Example 13.4

Rationalize the structural trends found among the oxides of the Group 16(VI) elements in the $+4$ oxidation state: Sulfur dioxide (SO_2) is a monomeric covalent molecule; SeO_2 forms a chain polymer; TeO_2 (in one polymerization isomer) forms a layer polymer; and PoO_2 takes the fluorite (CaF_2) ionic lattice structure.

SOLUTION:

The radius ratios for these four dioxides are (unknown), 0.508, 0.881, and 0.857, respectively (the contraction for Po^{4+} is suspect, since few crystal structures have been done of salts of this very radioactive element). From these, we predict *total* coordination numbers of less than 6 for S^{4+} , 6 for Se^{4+} , and 8 for Te^{4+} and Po^{4+} . But at least one position is likely to be occupied by the unshared pair of electrons on each of these ions—since we know from valence shell electron-pair repulsion (VSEPR) theory that unshared electron pairs occupy *more* space than shared electron pairs, it may be that more than one position is needed for each. Given this uncertainty, our predictions of *actual* coordination numbers are necessarily vague: Probably much less than 4 for S^{4+} , less than 4 for Se^{4+} , and less than 6 for Te^{4+} and Po^{4+} . These translate into numbers of vacant coordination sites of much less than 2 for S in SO_2 , less than 2 for Se in SeO_2 , and less than 4 for Te in TeO_2 and Po in PoO_2 .

Such numbers will not predict actual structures, but do illustrate trends: The degree of polymerization should increase on going down this group, as is observed. Actual coordination numbers are 2 for S in SO_2 (which contains a double bond that contributes to

the low coordination number), 3 for Se in SeO_2 , 4 for Te in TeO_2 , and 8 for Po in PoO_2 . Sulfur dioxide is a gas of boiling point -10°C , while SeO_2 and TeO_2 are solids that sublime at 315 and 450°C , respectively.

Table 13.2 summarizes similar calculations for the third-period and the early sixth-period elements in their group oxidation states. Figure 13.2 semiquantitatively graphs the trend in melting points as a period is crossed. This trend shows some striking changes of slope.

1. At the right of a period, high oxidation state monomeric oxides of low melting points prevail: Thus the calculations in Table 13.2 successfully predict sharply lower melting points for the compounds P_2O_5 , SO_3 , Cl_2O_7 , Re_2O_7 , and OsO_4 . As we go to the left, the oxidation number of the central atom decreases and its size increases, both of which result in an increase in the number of vacant coordination sites per central atom. Approximately at the point at which this number rises above 1, the melting points begin to rise sharply as oligomers and chain polymers form. Further left still, very high melting points are exhibited by layer and network polymers and ionic lattice compounds.

2. At the far left, among metal oxides forming ionic lattices, melting and boiling points tend to rise to the right as the charge on the metal ion rises, up to a point. This increase in melting point is a consequence of the increase in Coulombic forces as the ionic charge increases (Chapter 4). Thus melting points increase substantially from KF to CaF_2 , from Na_2O to MgO , and from Cs_2O to HfO_2 . The peak melting points are reached with ionic lattices of high ionic charge and with network polymeric structures, with no obvious distinction between them.

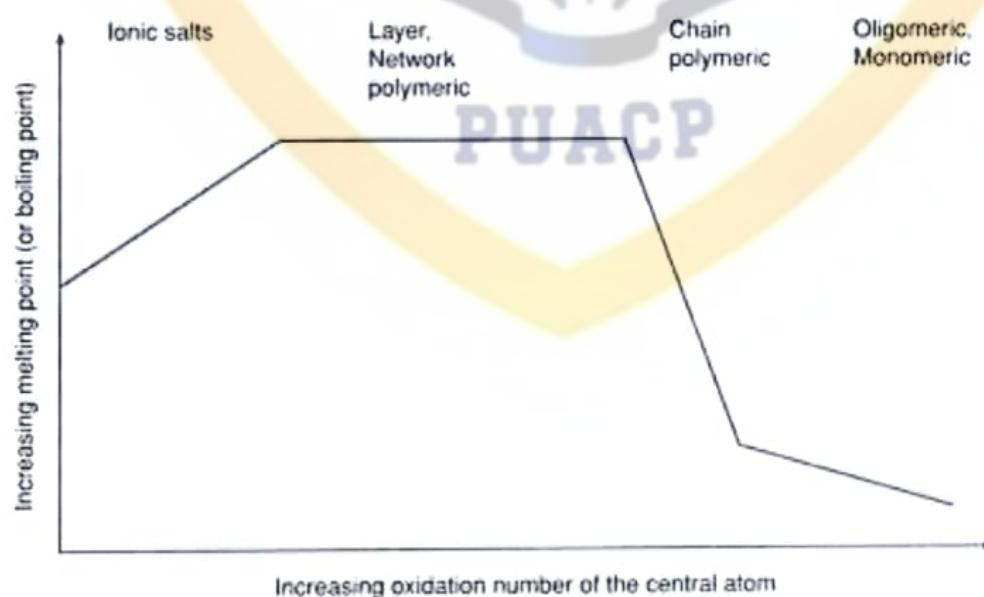


Figure 13.2

Typical trends in melting (or boiling) points of oxides of the elements in their group oxidation states, as the oxidation and group numbers increase.

Table 13.2
Predictions of Physical Properties and Structures of Some Halides and Oxides

Period 3 ^a	NaF	MgF ₂	AlF ₃	SiF ₄	PF ₅	SF ₆	(ClF ₇)	
Radius ratio	0.975	0.723	0.563	0.454	0.437	0.361	0.345	
<i>Predicted</i>								
CN of metal	8	8 or 6	6	6 or 4	6 or 4	6 or 4	6 or 4	
Links per unit	7	6 or 4	3	2 or 0	1 or -1	0 or -2	-1 or -3	
<i>Observed</i>								
CN of metal	6	6	6	4	5	6	6	
Links per unit	5	4	3	0	0	0	-1	
Lattice type	NaCl	CaF ₂	*	molecular	molecular	molecular	(ClF ₆ ⁺)	
Melting point	1012	1263	1272	-86	-75	-64		
Period 3	NaI	MgI ₂	AlI ₃	SiI ₄	PI ₃			
Radius ratio	0.563	0.417	0.325	0.262	0.252			
<i>Predicted</i>								
CN of metal	6	4 or 6	4	4	4			
Links per unit	5	4 or 2	1	0	-1			
<i>Observed</i>								
CN of metal	6	6	4	4	4			
Links per unit	5	4	1	0	-1			
Lattice type	NaCl	*	dimer	molecular	PI ₄ ⁺ I ⁻			
Melting point	651	>700	191	120				
Period 3	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇	
Radius ratio	0.921	0.683	0.532	0.429	0.413	0.341	0.325	
<i>Predicted</i>								
CN of metal	4	6	6	6 or 4	4	4	4	
Links per unit	3	5	4.5	4 or 2	1.5	1	0.5	
<i>Observed</i>								
CN of metal	4	6	6	4	4	4	4	
Links per unit	3	5	4.5	4 or 2	1.5	1	0.5	
Lattice type	anti-fluorite	NaCl	corundum	beta-silica	oligomer	oligomer	Molecular	
Melting point	(1275)	2800	2050	1723	(300)	17	-91	
Period 6	Cs ₂ O	BaO	Lu ₂ O ₃	HfO ₂	Ta ₂ O ₅	WO ₃	Re ₂ O ₇	OsO ₄
Radius ratio	1.437	1.183	0.793	0.675	0.619	0.587	0.537	0.476
(Inverse "")	(0.696)	(0.846)						
<i>Predicted</i>								
CN of metal	3	8	8	6	6	6	6	6
Links per unit	2	7	6.5	4	3.5	3	2.5	2
<i>Observed</i>								
CN of metal	3	6	7	8	6	6	5	4
Links per unit	2	5	5.5	6	3.5	3	1.5	0
Lattice type	^b	NaCl	^b	Rutile	^b	^b	Layer polymer	Molecular
Melting point	490	1920	2487	2900	1870	1473	296	40

^a Melting points in degrees Celsius; if in parentheses these are sublimation temperatures. CN = coordination number.

^b Lattice type is one not described in this text.



13.2 Covalent Oxides: Periodic Trends in Structure and Physical State

As suggested by Figure 13.2, the most important single variable in determining the structure, physical state, and (as we shall see) the acidic or basic properties of an oxide is the oxidation number of the central atom, since this determines the stoichiometry of the structural unit and plays a major role in determining the number of vacant coordination sites in the structural units. Hence, we will organize this discussion by oxidation state/stoichiometry. Next, we follow with the roles of radius ratio, unshared electron pairs in the *p* block, and tendencies to element–oxygen π bonding, all of which play a role in the chemistry of an oxide. Table 13.3 and Figure 13.3 summarize the structures, physical states at room temperature, melting and boiling points, and so on, of most of the important covalent oxides. Note that these oxides are often named using the system of nomenclature for binary covalent substances. Thus although Cl_2O_7 may be perfectly acceptably named chlorine(VII) oxide, it is more commonly named dichlorine heptoxide. Although this system of nomenclature is most commonly used among compounds of the nonmetals, it is also often used with the more covalent oxides of the *d*-block elements [Mn_2O_7 may also be named either manganese(VII) oxide, or dimanganese heptoxide].

Element Tetroxides. In these compounds, the central atoms exhibit the highest known oxidation state, +8; as indicated in Table 13.3, only four of these are known. The central +8 “ions” are rather small, so we calculate fairly low expected coordination numbers (these are not shown in Table 13.3, but can readily be filled in by the student as an exercise). The observed coordination numbers are tabulated and are 4 in all four tetroxides in these tetrahedral monomeric molecules. This low coordination number is undoubtedly due to the presence of π bonding involving oxygen unshared *p* electron pairs and central-atom *d* orbitals, which are contracted enough in such high oxidation states for significant π bonding even in *p*-block atoms such as Xe. Since the central atoms in these molecules are of relatively high atomic weights, these tetroxides are mainly volatile low-melting solids.

Since the +8 oxidation state exceeds the most stable oxidation state of any element, the tetroxides are strongly oxidizing materials. The compound FeO_4 has only been reported by one research group¹¹; the compound XeO_4 is very explosive; RuO_4 and OsO_4 are not explosive but are still strong oxidizing agents. The compound OsO_4 is widely used in biology to stain tissues—it oxidizes the organic material in them and is reduced to brown OsO_2 —but it is quite hazardous because of its high volatility. It readily oxidizes the organic material in the eye, too.

Dielement Heptoxides (central atom oxidation state of +7). Again, only four of these are known for chlorine and the elements of Group 7. Two EO_3 structural units must at least link through the bridging oxygen atom to give an E_2O_7 molecule; only Re_2O_7 links beyond this minimum (using one-half of its Re atoms, which become six-coordinate and link units into a layer polymer while the other one-half of the rhenium atoms remain four coordinate). This high +7 oxidation state is most stable at the bottom of the *d* block in the colorless Re_2O_7 and the yellow volatile Tc_2O_7 ; red Mn_2O_7 and Cl_2O_7 are treacherously explosive. The colors in these compounds are not due to the *d*-block ions per se, since their electron configurations are d^0 ; these are charge-transfer transitions (Section 6.3).

Table 13.3
Higher Oxides of the Elements

A. Tetroxides					
Period	4	5	5	6	6
Oxide	FeO ₄	XeO ₄	RuO ₄	XeO ₄	OsO ₄
Radius ratio	0.492	4	4	4	4
Observed CN(M)	4	0	0	0	0
Vacant coordination sites	0	0	0	0	0
Structure type	FeO ₄	XeO ₄	RuO ₄	XeO ₄	OsO ₄
Physical Properties	exploses	exploses	mp 25 °C bp 100 °C	mp 40 °C bp 130 °C	mp 40 °C bp 130 °C
B. Dielement Heptoxides					
Period	3	4	5	6	6
Oxide	Cl ₂ O ₇	Mn ₂ O ₇	Tc ₂ O ₇	Re ₂ O ₇	UO ₃
Radius ratio	0.325	0.476	0.555	0.532	0.731
Observed CN(M)	4	4	4	4 and 6	6 or 7
Vacant coordination sites	0.5	0.5	0.5	0.5, 1.5	3 or 4
Structure type ^a	Cl ₂ O ₇	Mn ₂ O ₇	Tc ₂ O ₇	Layer	Network
Physical Properties ^d	mp -92 °C bp 82 °C	mp 19 °C exp. 70 °C	mp 220 °C bp 212 °C	mp 450 °C	mp 40 °C bp 130 °C
C. Trioxides					
Period	5	5	5	6	6
Oxide ^a	XeO ₃	SeO ₃	TeO ₃	MoO ₃	ReO ₃
Radius ratio	0.361	0.471	0.487	0.613	0.622
Observed CN(M) ^c	3+;	4	4	6	6
Vacant coordination sites	0	1	1	3	3
Structure type ^a	XeO ₃	(SeO ₃) ₃ ; Chain	Chain	Network Layer	Network
Physical Properties ^d	exp. solid	dec 120 °C	mp 196 °C	mp 795 °C	mp 1473 °C

D. Dielment Pentoxides		E. p-Block Dioxides		F. p-Block Dielement Trioxides	
Period	Oxide ^b	Period	Oxide ^b	Period	Oxide ^b
4	:Br ₂ O ₅	5	I ₂ O ₅	2	N ₂ O ₅
Radius ratio	0.916	Radius ratio	0.227	Radius ratio	0.437
Observed CN(M) ^c	3+; 0*	Observed CN(M) ^c	2 and 3	Observed CN(M) ^c	4 and 6
Vacant coordination sites	0	Vacant coordination sites	1 and 0	Vacant coordination sites	1.5 and 3.5
Structure type ^d	:Br ₂ O ₅ *	Structure type ^d	(NO ₂) ⁺	Structure type ^d	P ₄ O ₁₀
Properties ^d	dec 300 °C	Properties ^d	(NO ₃) ⁻	Properties ^d	subl 347 °C
	mp 37 °C		mp 37 °C		dec 315 °C
					mp 690 °C
					dec 380 °C
					mp 1780 °C
					dec 1470 °C

Period	Oxide ^b	Period	Oxide ^b	Period	Oxide ^b
5	:ClO ₂	3	:SO ₂	5	:TeO ₂
Radius ratio	2+;	Radius ratio	2+;	Radius ratio	0.933
Observed CN(M) ^c	2+;	Observed CN(M) ^c	3+;	Observed CN(M) ^c	0.538
Vacant coordination sites	0	Vacant coordination sites	1	Vacant coordination sites	4+
Structure type ^d	:ClO ₂	Structure type ^d	:SO ₂	Structure type ^d	2+
Physical Properties ^d	mp -59 °C bp 10 °C	Physical Properties ^d	mp -73 °C bp -10 °C	Physical Properties ^d	subl 450 °C
	subl 315 °C		subl 315 °C		dec 500 °C
					subl -78 °C
					mp 1723 °C
					bp 2230 °C
					mp 1116 °C
					bp 21 °C
					subl -78 °C
					mp 1127 °C

Period	Oxide ^b	Period	Oxide ^b	Period	Oxide ^b
6	:N ₂ O ₃	3	:P ₂ O ₅	6	:As ₂ O ₃
Radius ratio	3 and 2+;	Radius ratio	3+;	Radius ratio	0.605
Observed CN(M) ^c	0*	Observed CN(M) ^c	1.5	Observed CN(M) ^c	3+
Vacant coordination sites	:N ₂ O ₃ *	Vacant coordination sites	:P ₄ O ₆	Vacant coordination sites	:As ₄ O ₆
Structure type ^d		Structure type ^d		Structure type ^d	
Physical Properties ^d	mp -102 °C bp 4 °C	Physical Properties ^d	mp 25 °C bp 176 °C	Physical Properties ^d	mp 309 °C bp 737 °C
	mp 25 °C bp 176 °C		mp 656 °C bp 1425 °C		mp 824 °C bp 1890 °C
					mp 450 °C bp 2300 °C
					mp 2053 °C
					mp 1735 °C
					mp 1910 °C
					dec 100 °C

^a "Network" represents either an ionic or a network covalent structure.^b The : represents an unshared *sp* electron pair.^c An * structure includes additional secondary bonds, which are not counted.^d The abbreviation dec is decomposes, subl is sublimes, and exp is explodes.

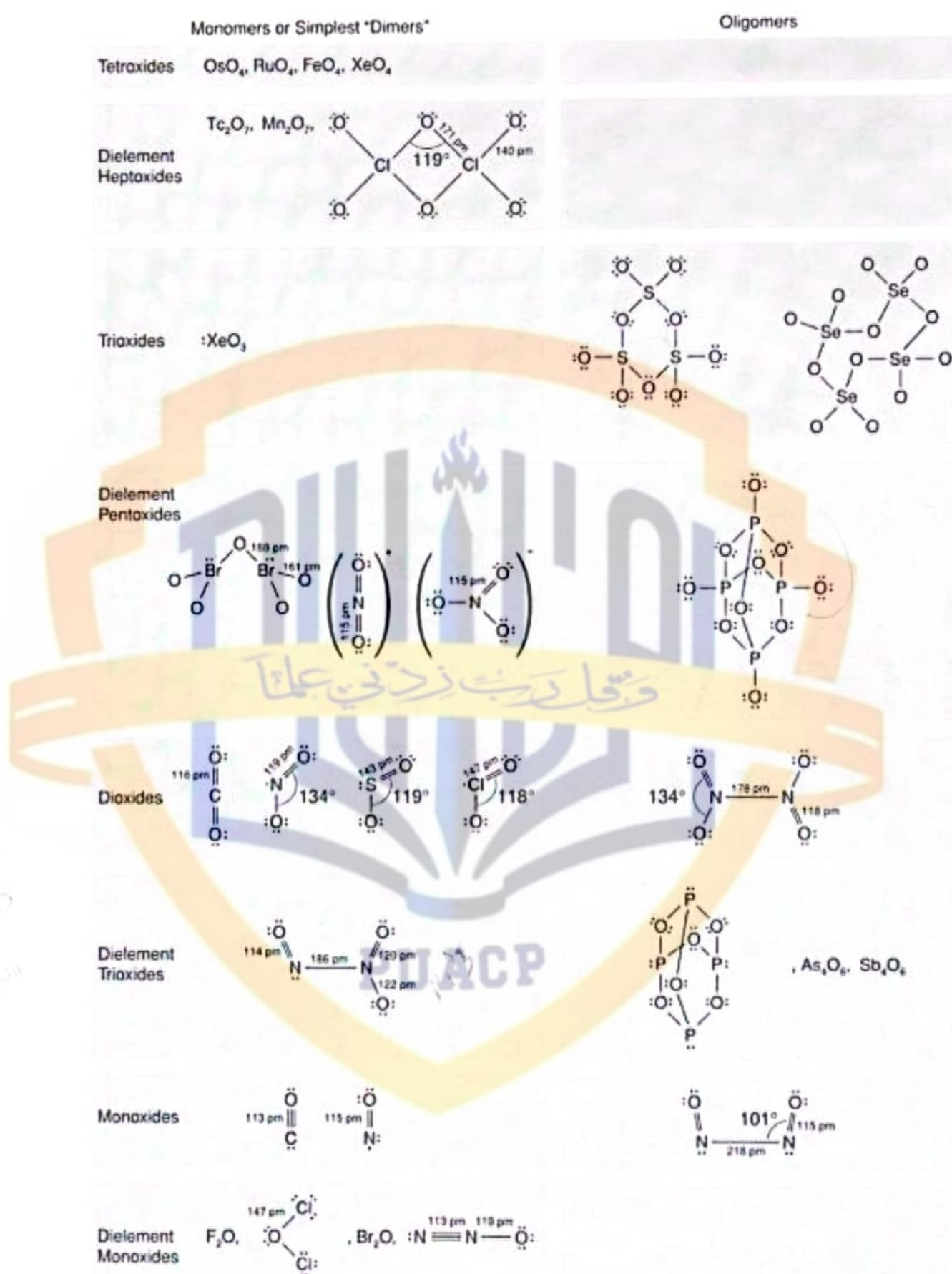


Figure 13.3
Structures of nonpolymeric oxides.

Element Trioxides (central atom oxidation state = +6). This oxidation state is not confined to groups numbered with 6, but can occur in higher groups: The $:XeO_3$ molecule, with a total coordination number of 4, is an explosive, monomeric solid. All other trioxides are found for atoms in Groups 6, 16(VI), and 6F, which are expected to have penultimate coordination numbers of 4 or higher, so these EO_3 structural units have at least one vacant coordination site. Both SO_3 and SeO_3 readily form the oligomers $(SO_3)_3$ and $(SeO_3)_4$; these oxides and CrO_3 form chain polymers such as $\overset{1}{\underset{\infty}{[CrO_3]}}$. The largest atoms in these groups take coordination numbers of 6 (or even 7 for one form of UO_3) in layer or network polymeric structures; the best known of these is the ReO_3 structure (Fig. 13.4). Redox stability and color vary considerably here:

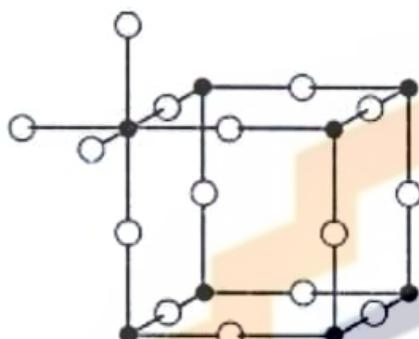


Figure 13.4

Structure of ReO_3 , showing octahedral coordination of Re atoms (filled circles) and linear coordination of oxygen atoms (open circles). [Adapted from F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 5th edition, Wiley-Interscience, New York, 1988, p. 851.]

CrO_3 is red and strongly oxidizing, while MoO_3 and WO_3 are in the most stable oxidation states of these elements and are colorless to yellow; ReO_3 is red, but in this case the central Re^{6+} ion has a d^1 electron configuration.

Dielement Pentoxides. Both $:Br_2O_5$ and $:I_2O_5$ have stereochemically active sp -hybrid electron pairs. The approximate structure¹² of $:Br_2O_5$ has a total coordination number of 4 (Fig. 13.3). For $:I_2O_5$, the radius ratio calculation would predict a total coordination number of 8 for iodine. The structure is similar to that of $:Br_2O_5$, with a total coordination number of 4 for iodine; this appears to be the most serious failure of all our calculations in Table 13.3. However, unlike $:Br_2O_5$, the pentoxide $:I_2O_5$ shows several much longer I-O contacts at distances of 223 pm or higher, which are still within the sum of van der Waals radii. This type of weak secondary bonding (Section 12.2) is not simply predicted or counted, but helps bridge the gap between our predictions and the crystal structure.

Among elements in groups numbered with five, dinitrogen pentoxide is also a surprise: In the solid state, its structure consists of an ionic lattice of $[NO_2]^+$ and $[NO_3]^-$ ions (although in other physical states it readily converts to a molecular form, which accounts for its low melting point). Each of these ions involves π bonding between N and O, which is not predictable by radius ratio calculations.

The somewhat larger (and less prone to π bonding) phosphorus atom adopts a coordination number of 4, leaving 1.5 vacant coordination sites in the structural unit, which suffices to form a cluster tetramer, P_4O_{10} (Fig. 13.3). The other, still larger atoms in this series are predicted to have coordination numbers of 6, and approximately do, with some unpredictable deviations to numbers of 5 and 7. These oxides are either layer or network polymers; P_2O_5 also has a layer-structured polymorph.

Element Dioxides. There are too many of these dioxides among the metals to discuss them in detail now; we may note that most of them adopt either the six-coordinate

rutile (TiO_2) or eight-coordinate fluorite (CaF_2) lattices (Fig. 4.8). Hence, we concentrate on the dioxides of the *p* block. There are more of these than might have been anticipated.

The Group 16(VI) dioxides : EO_2 exhibit a very nice trend showing changes in structure with increasing central-atom radius, as computed in Example 13.4; the simplest of these dioxides, the bent double-bonded SO_2 , is shown in Figure 13.3. Surprisingly, there are two fairly stable dioxides with *odd* numbers of valence electrons: the 17-electron brown gas NO_2 and the 19-electron yellow-red gas ClO_2 (the colors being connected with electronic transitions involving their SOMOs). These are examples of a class of molecules known as **free radicals**. These molecules are usually exceedingly reactive, since they tend to pair up with each other (or with other radicals) to share the odd electrons and form additional covalent bonds, releasing the covalent bond energy. These two free radicals can persist, but they are not highly stable: The radical ClO_2 is explosive unless it is kept highly diluted (e.g., when it is used as a bleach and disinfectant); NO_2 is not explosive but dimerizes at higher pressures and lower temperatures to the colorless gas *dinitrogen tetroxide*, N_2O_4 .

Clearly, it impossible to draw satisfactory Lewis dot structures for these two substances or to use the octet rule to explain why these two free radicals are so much more stable than most free radicals; MO theory is necessary to adequately account for this phenomenon. It should be noted that (a) ClO_2 has not been reported to dimerize; (b) the dimer of NO_2 has an unusually long N–N single bond of 178 pm (Fig. 13.3), but is diamagnetic and definitely bonded; (c) the isoelectronic CO_2^- anion (17 electrons) is not stable but completely dimerizes to the $C_2O_4^{2-}$ (oxalate) anion, which has an approximately normal C–C bond distance. Explaining trends such as these requires the use of quantitative MO calculations, and has not been without controversy.

The Group 14(IV) dioxides are more regular in their chemistry, but also dramatically show the effects of size and π -bonding ability, which is itself a function of size. The π -bonded carbon dioxide is well known as a gas and as a solid (dry ice) that sublimes at $-78^\circ C$; under high pressures it can remain as a liquid at room temperature and is becoming increasingly important as an environmentally friendly solvent.

In SiO_2 , the central-atom coordination number normally doubles to 4, giving two vacant coordination sites in the structural unit, which suffices to produce network polymers [Fig. 13.1(d–f)]. Silica (SiO_2) is a very important compound that has more than 22 phases (some of them necessarily impure, but at least 12 of which can be pure SiO_2). Many of its forms are familiar to collectors: α -quartz (a major component of granite and sandstone), rose quartz, smoky quartz, flint, heliotrope, jasper, onyx, amethyst, citrine, agate, chalcedony, and others. Industrially useful forms include kieselguhr and diatomaceous earth. Less common polymorphs and polymerization isomers include tridymite and cristobalite [Fig. 13.1(e, f)], coesite, and the remarkable stishovite, found in Meteor Crater, Arizona, in which silicon is six coordinate in a rutile lattice. It is not surprising that the high pressure presumably produced by the impact of a meteorite is what is needed to force six oxygen atoms around a small silicon atom. The dioxides of the largest Group 14(IV) elements, SnO_2 and PbO_2 , adopt a structure that we think of as typically ionic, namely, the rutile lattice. The melting points of these compounds show no discontinuity with the melting points of their neighbors—Coulombic attractions and interunit covalent bonds are both strong interunit forces, about equally capable of resisting melting.

Dielement Trioxides of the *p* Block. A complete set of these is available from Group 15(V) with an unshared pair of *sp* electrons, and a set from Group 13(III) is

available without unshared electrons. The Group 15(V) trioxides begin with dinitrogen trioxide, which consists of N_2O_3 molecules not bridged by oxygen but with unusually long N–N bonds of 186 pm length. This structure bears some resemblance to an ionic structure containing a triply bonded NO^+ cation paired with a partially double-bonded NO_2^- ion. The next three dielement trioxides are E_4O_6 cluster oligomers of T_d symmetry (Fig. 13.3); the latter two of these also have polymerization isomers that are layer or double-chain polymers. The Group 13(III) dielement trioxides, with no coordination sites blocked by unshared sp electron pairs, all give network covalent or ionic lattices.

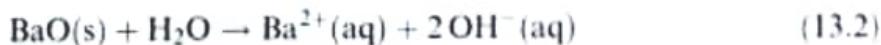
Monomeric *p*-Block Monoxides. Only a few examples of the +2 and +1 oxidation states are found among the oxides of the *p* block. There are only two monomeric monoelement monoxides, carbon monoxide, CO, and *nitric oxide*, NO. Both have low polarities and low molecular weights. Therefore they are gases with low solubilities in water and low boiling points (-190°C and -152°C , respectively). Nitric oxide has one unpaired electron in the gaseous state, but is diamagnetic in the solid state, since it dimerizes as shown in Figure 13.3. Note that the structure has a very long N–N bond of 218 pm. Related to NO are the triple-bonded NO^+ cation, isoelectronic with CO, and the unstable NO^- anion, isoelectronic with O_2 ; the latter dimerizes to give the *hyponitrite* ion, $\text{N}_2\text{O}_2^{2-}$.

In the +1 oxidation state, we may mention four monomeric oxides, the unstable F_2O , Cl_2O , and Br_2O , and the stable *nitrous oxide* or “laughing gas,” N_2O , which has a structure unlike the others (Fig. 13.3). Nitrous oxide has an N–N bond order between 2 and 3. These oxides are polar molecules that are considerably more soluble in water than CO or NO. The compound F_2O is explosively unstable and is best named as oxygen difluoride. Finally, a very unstable oxide of nitrogen in the $+\frac{1}{2}$ oxidation state, N_4O , has been prepared by the reaction of nitrosyl chloride, NOCl , with sodium azide, NaN_3 ; the product is thought of as $\text{N}_3^- \text{NO}^+$, with a chain of four nitrogen atoms.¹³

13.3 Acidity, Solubility, Practical Uses, and Environmental Chemistry of Volatile Oxides and Oxo Acids

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. Recalled from Section 2.7 that 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 two categories.

The **soluble basic oxides** are the oxides of the nonacidic and feebly acidic metal cations in the lower left part of the periodic table. These oxides dissolve in water to give hydroxides of these metal ions, so the solution acquires a high pH.



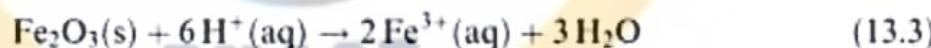
The **insoluble basic oxides** are oxides of the weakly acidic and yet more acidic metal cations; by solubility Rule 1 (Section 4.1) these are insoluble in water, so they do not

Table 13.4
Major Acidic Oxides of the *p*- and *d*-Block Elements^a

$\text{B}_2\text{O}_{3(w)}$	$\text{CO}_{2(m)}$	$\text{N}_2\text{O}_{5(s)}$ $\text{N}_2\text{O}_{3(m)}$		
Al_2O_3	$\text{SiO}_{2(w)}$	$\text{P}_4\text{O}_{10(m)}$	$\text{SO}_{3(s)}$	$\text{Cl}_2\text{O}_{7(vs)}$
Ga_2O_3	GeO_2	$\text{P}_4\text{O}_{6(m)}$ $\text{As}_2\text{O}_{5(m)}$	$\text{SO}_{2(m)}$ $\text{SeO}_{3(s)}$	$\text{Cl}_2\text{O}_{(w)}$
		As_4O_6	$\text{SeO}_{2(m)}$	$\text{Br}_2\text{O}_{(w)}$
	SnO_2	Sb_2O_5	$\text{TeO}_{3(w)}$	$\text{XeO}_{4(s)}$
	SnO PbO_2 PbO	Sb_2O_3	TeO_2	$\text{I}_2\text{O}_{5(s)}$ $\text{XeO}_{3(s)}$
		$\text{V}_2\text{O}_{5(m)}$	$\text{CrO}_{3(s)}$	Mn_2O_7
		Nb_2O_5	$\text{MoO}_{3(w)}$	$\text{Tc}_2\text{O}_{7(vs)}$ $\text{RuO}_{4(?)}$
		Ta_2O_5	WO_3	$\text{Re}_2\text{O}_{7(vs)}$ $\text{OsO}_{4(s)}$

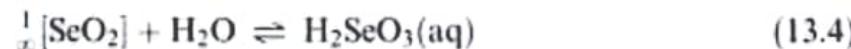
^a Oxides above and to the right of the light and heavy lines are **soluble acidic oxides**: They dissolve in water (at least to some extent) to give oxo acids of the strengths indicated: (vs) = very strong; (s) = strong; (m) = moderate; (w) = weak. Oxides within the light lines are **insoluble acidic oxides**: They are not soluble in water, but do dissolve in (react with) strong bases. Oxides below and to the left of the lines are **amphoteric** (these are not included for the *d*-block elements). The oxides of In and Tl, and Bi_2O_3 , are exclusively basic oxides.

give solutions of elevated pH values. Nonetheless, they do dissolve in, and partially neutralize, strong acids, so they show basic properties.

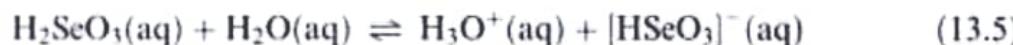


Often, however, the acidity of a very strongly acidic “cation” can prevail over the basicity of the oxide ion, so that many oxides of the nonmetals at the right of the periodic table, or of metals in very high oxidation states, are **acidic oxides**. These oxides can again be subdivided into soluble and insoluble categories (Table 13.4).

Soluble 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 an oxide first reacts reversibly with water to give an oxo acid:



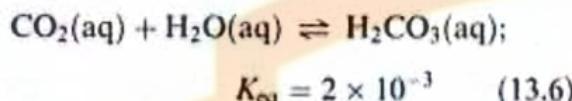
If the resulting oxo acid is very strongly acidic, strongly acidic, or moderately acidic (Section 3.7), a second equilibrium then proceeds appreciably to the right:



For these three categories of oxo-acid acidity, 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: So *oxides that can dissolve to give very strongly acidic, strongly acidic, or moderately acidic oxo acids generally are soluble acidic oxides.*

The Weakness of Carbonic Acid: An Aside

Solutions of H_2CO_3 are less acidic than we would have expected, since it exists in solution mostly as CO_2 rather than as H_2CO_3 molecules:



(In the body, a zinc-containing enzyme, carbonic anhydrase, is necessary to catalyze this reaction.) Similar equilibria have been noted for the other monomeric acidic oxides: XeO_4 , XeO_3 , RuO_4 , OsO_4 , and SO_2 .¹⁴

To explain this, we note that the dissolution of an *oligomeric* or *polymeric* oxide [as in Eq. (13.4)] generally results in an oxo acid in which

the total coordination number of the central atom is unchanged, that is, 4 for Se in ${}_{\infty}^1[\text{SeO}_2]$ and H_2SeO_3 . To add water to a *monomeric* acidic oxide, however, there must be an *increase* in the total coordination number of the central atom (i.e., from 2 for C in CO_2 to 3 in H_2CO_3). There is evidently a significant energy barrier to this increase in coordination number during the process of hydration. In the case of FeO_4 , there is apparently no equilibrium concentration of an oxo acid (no H_2FeO_5 or H_4FeO_6 , in either of which Fe would exceed its allowable penultimate coordination number), since FeO_4 is reported to be extractable by carbon tetrachloride from a strongly basic solution (i.e., to lack acidic properties).

Insoluble Acidic Oxides. Most other nonmetal oxides, and a significant number of metal oxides, do not undergo sufficient ionization analogous to Eq. (13.5) to allow them to dissolve in neutral water, but they will dissolve in strong bases, partially neutralizing them. These compounds may be termed **insoluble acidic oxides**. The oxo acids that correspond to the hydrated forms of these oxides are (at best) weakly acidic; the anions actually formed on the dissolution of these oxides in strong bases are normally not simple oxo anions, but rather hydroxo anions¹⁵:

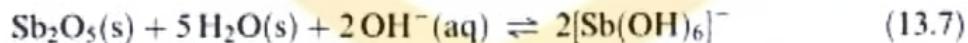


Table 13.5 summarizes, in a general way, the locations of the four principal acid-base classes of oxides. Soluble basic oxides and soluble acidic oxides occupy opposite edges of the periodic table, except that metals in very high oxidation states can also give rise to soluble acidic oxides. In between, we find insoluble basic oxides (more to the left) and insoluble acidic oxides (more to the right).

The realms of insoluble acidic oxides and insoluble basic oxides overlap extensively, however. There are many insoluble oxides such as Al_2O_3 that do not dissolve in water, but dissolve in strong acids *and* (in separate experiments) in strong bases:

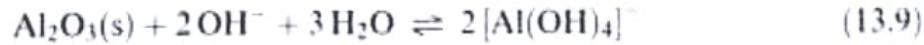
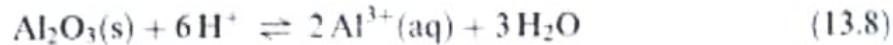
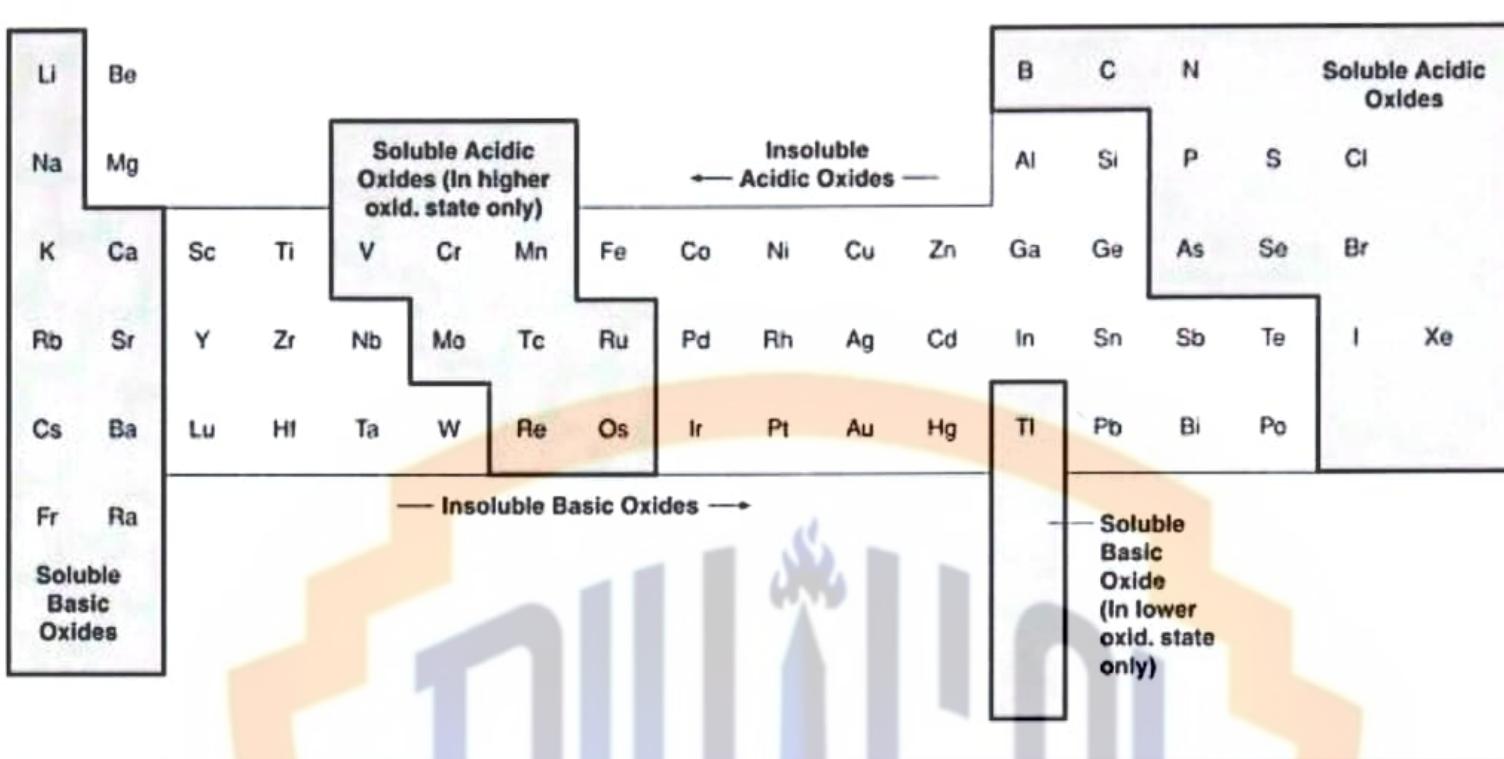


Table 13.5
Soluble and Insoluble Acidic and Basic Oxides



Such oxides are known as **amphoteric oxides**.

Unfortunately, there is no known systematic way of determining which of the many insoluble basic oxides will also show acidic properties (dissolve in strong bases, and hence be classified as amphoteric) and which will not; this problem is a future challenge for some bright student of this textbook! Some insoluble basic oxides derived from even weakly acidic cations (e.g., ZnO) do dissolve in strong bases, and hence are amphoteric; some, derived from moderately or even strongly acidic cations (e.g., Fe_2O_3 and TiO_2), do not. Hence, these compounds are insoluble basic oxides. Judging from the predominance diagrams of Pourbaix, the insoluble basic oxides derived from all weakly, moderately, and strongly acidic cations would probably dissolve in strong bases if the concentrations of base used to dissolve them could be a little higher than is possible in practice.

Finally, 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_2O , and NO . Since these oxides certainly do not have basic properties, they are neutral oxides. In addition, there are a few oxides, such as the free radicals NO_2 and ClO_2 , that do not correspond in oxidation state to a stable or known oxo acid or anion. These oxides can give rise to a mixture of oxo acids or anions by disproportionation (Section 6.9):



Because the acidity of a cation rises rapidly with its charge, there are several *d*-block elements possessing several oxidation states (such as Cr) that have one or more oxides that show only basic properties [chromium(II) oxide, CrO], one or more oxides

that are amphoteric [chromium(III) oxide, Cr_2O_3], and one or more oxides that possess only acidic properties [chromium(VI) oxide, CrO_3]. Clearly, the higher the oxidation number of a given element, the more acidic the corresponding oxide will be.

Lux–Flood Acid–Base Reactions. Since 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), it is not too surprising that basic oxides such as MgO and acidic oxides such as SiO_2 can react directly with each other:



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, since water is not involved in the reaction, can be salts of oxo anions such as SiO_4^{4-} that are too basic to persist in aqueous solution. As we will discuss later in this chapter, direct reactions of acidic and basic oxides are of enormous practical importance in such areas as control of pollution by gaseous acidic oxides and in the production of materials such as concrete, glass, and ceramics.

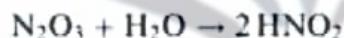
Example 13.5

Complete and balance the following chemical equations for reactions of oxides:

- (a) $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow ?$ (b) $\text{BaO} + \text{OsO}_4 \rightarrow ?$ (c) $\text{SrO} + \text{ZrO}_2 \rightarrow ?$ and (d) $\text{Fe}_3\text{O}_4 + \text{H}^+ \rightarrow ?$

SOLUTION:

(a) The compound N_2O_3 is a nonmetal oxide, so it is most likely an acidic oxide. It corresponds in oxidation state to a moderately acidic oxo acid, HNO_2 , so it is expected to dissolve in water to give HNO_2 :



(b) Barium oxide is the oxide of a feebly acidic cation, Ba^{2+} , so the strong basicity of the oxide ion is virtually undiminished: This is a soluble basic oxide. The hypothetical Os^{8+} cation in OsO_4 is so acidic that the oxide itself might also be expected to be acidic. For the relatively large Os, an oxo anion with six oxygens is expected: OsO_6^{4-} (Table 3.3). The product of the reaction of a basic oxide with an acidic oxide is the salt of an oxo anion. By balancing the -4 charge of this anion with two Ba^{2+} cations, we complete and balance this equation:



(c) The Sr^{2+} ion in SrO is feebly acidic, so the basicity of oxide ion prevails; this is a basic oxide. The Zr^{4+} ion in ZrO_2 is strongly acidic, so its oxide is either basic or amphoteric. Unfortunately, amphotericity is not precisely predictable; if ZrO_2 is also a basic oxide (as it in fact is), there can be no acid–base reaction between these oxides.

(d) The compound Fe_3O_4 is a peculiar oxide (a mixed-metal oxide, to be discussed in Section 13.5), in which the average oxidation state of iron is $+2.67$. This means that two-

thirds of the iron ions are moderately acidic Fe^{3+} and one-third are weakly acidic Fe^{2+} ions. Such oxides are insoluble in water, but do dissolve in acids:



The reactions of acidic and basic oxides to give salts of oxo anions, like other acid-base neutralization reactions, are generally exothermic. Smith¹⁶ noted that the enthalpy change for the reaction in which 1 mol of oxide ion is transferred from the basic oxide to the acidic oxide, ΔH_{A-B} , can be expressed as a function of acidity parameters a of the acidic oxide (a_A) and the basic oxide (a_B):

$$\Delta H_{A-B} (\text{in kJ mol}^{-1}) = -(a_A - a_B)^2 \quad (13.12)$$

Smith notes the parallel between this equation and the Pauling electronegativity equation (7.16); as in Pauling's equation, one parameter must be arbitrarily set, and he selects $a_{\text{H}_2\text{O}} = 1.00$. Bratsch has extended this parallel further, and removed the arbitrariness of the water parameter.¹⁷ Figure 13.5 shows that Smith's a parameters are related to the acidity classifications of the element in the oxide. Hence, Eq. (13.12) shows that the greater the difference in the acidities of the two central elements in the two oxides, the more exothermic is the reaction of their oxides to give a salt of an oxo anion.¹⁸

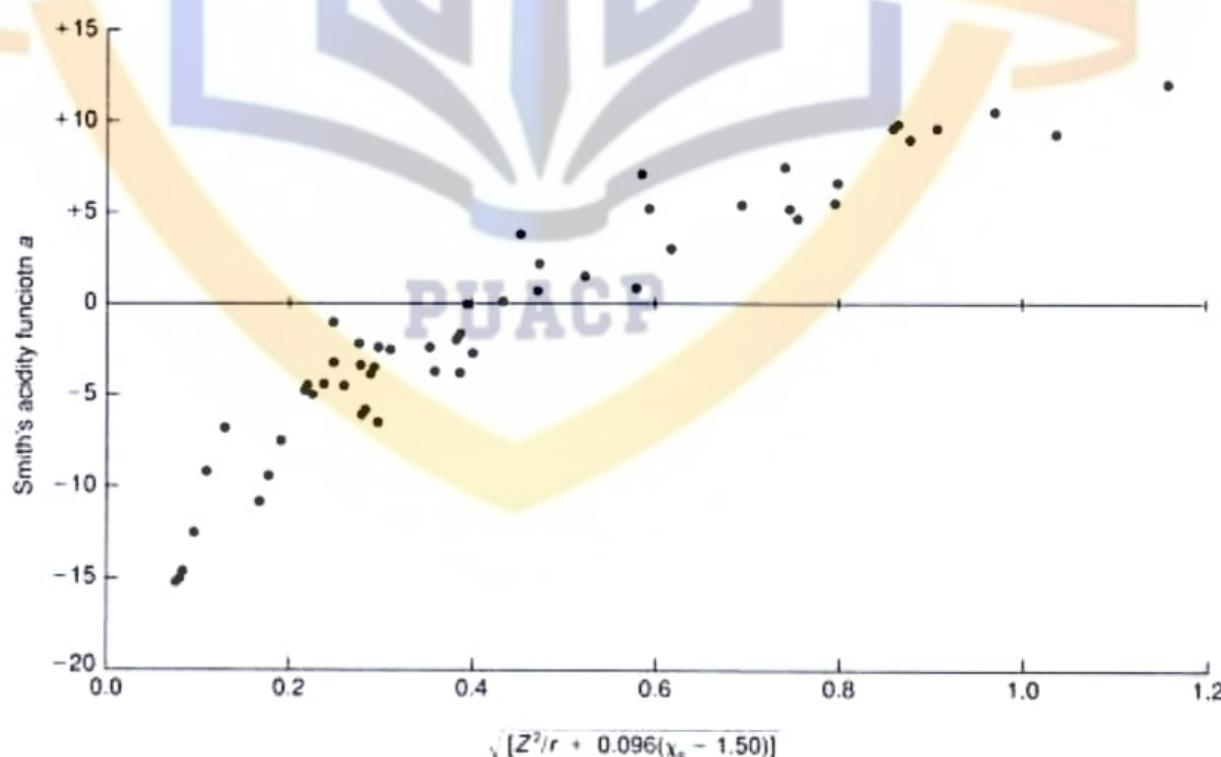


Figure 13.5

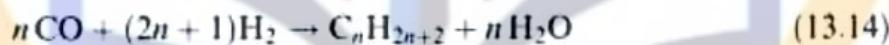
Smith's acidity function a for oxides of elements, plotted as a function of the square root of the modified Z^2/r ratio from Eq. (2.12), $\sqrt{[Z^2/r + 0.096(\chi_p - 1.50)]}$. Acidity functions are adapted from D. W. Smith, *J. Chem. Educ.*, **64**, 481 (1987).

Uses and 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. Any chemicals used in such high tonnage are bound to escape into the environment to some degree. Since these are mainly acidic oxides, we can anticipate that they will not be innocuous components of the environment; since these are volatile oxides we can anticipate that there will be air-pollution problems such as the production of acid rain connected with them. 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.^{19,20} Given the periodic trends we have seen in the previous sections and chapters, we should also be able to predict some uses and environmental chemistry for the other oxides, should they come into widespread use.

Carbon Oxides. Carbon monoxide is produced industrially on a huge scale as a mixture with H₂, by the reaction of steam with hot coal:



(Since this reaction is quite endothermic, air must periodically be blown through the coal to provide energy via oxidation of the coal.) This mixture of carbon monoxide and hydrogen is known as **water gas**; after adjustment of its hydrogen content it is known as **synthesis gas**, since 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, since 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 (Section 12.6):



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 carbon monoxide (of which we have no warning, since it is odorless). In terms of the global atmospheric environment, however, carbon monoxide is not considered a serious pollutant, since (a) natural production of CO (i.e., by the oxidation of CH₄ produced by anaerobic decomposition of organic material in swamps and in the tropics) far outweighs human production, and (b) 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 (·OH) and hydroperoxyl (HO₂·). (Free radicals can persist in the atmosphere, especially the thin upper atmosphere, longer than in solution, since the concentration of any species with which they may react is much lower there than in solution.)

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



Because of its physical properties, water gas 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, of course, 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 CO₂, 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 increase is of concern because of the vital role of CO₂ in the atmosphere: It absorbs IR light (heat) emitted by the earth and returns some of it to the surface of the earth, thereby warming it. This process is popularly known as the **greenhouse effect** (Section 9.5). An increase of only 2 or 3 °C would have profound effects on the climate of the earth; between 1880 and 1940 the mean temperature of the earth rose 0.4 °C. This rise might be due to the evident changes in the atmospheric CO₂ concentration, which is thought to be the result of the combustion of fossil fuels and (more importantly) the cutting and burning of many of the tropical forests of the world. A catastrophe in climate is not assured, however; there is an opposing scattering of incoming solar energy by suspended atmospheric particulates, which may be responsible for the cooling of the earth by 0.1 °C since 1940. Current thinking is that more extremes in weather, rather than just warmer weather, may be the main result of increasing concentrations of greenhouse gases.²¹

Nitrogen Oxides and Nitric Acid. Only three nitrogen oxides are stable enough to be of practical use or of environmental importance. One of these oxides, N₂O (commonly called nitrous oxide) is used as an anaesthetic 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.

There are two common sources of NO (commonly called nitric oxide): catalytic oxidation of ammonia, which comes ultimately from petroleum and air, and 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):

PUACP



After a few days in the atmosphere,²² NO is oxidized by oxygen to NO₂; hence, in air-pollution work these two are often collectively referred to as NO_x. Nitrogen dioxide and its dimer, dinitrogen tetroxide, are readily interconverted in an equilibrium that is visible due to the brown color of nitrogen dioxide:



In the solid state, this system is colorless, as it is completely in the form of N₂O₄. At its boiling point (21 °C), the liquid is deep brown due to an 0.1% content of NO₂. The vapor becomes steadily darker with increasing temperature due to the increasing dissociation of the dimer, which is nearly complete at 140 °C.

Nitrogen dioxide is an acidic oxide that reacts with water to produce nitric acid:



This reaction occurs in the atmosphere and is one of the sources of acid rain and of nitrate as a plant nutrient; it also is 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).

Nitric acid and NO_x are involved in several environmental problems. The acid rain problem, at least as far as damage to lakes is concerned, apparently results more from the solubilization of toxic metal ions at low pH values, as discussed in Section 3.8, than from the toxicity of nitrate ion or even directly of hydrogen ion.

There has been concern about the injection of NO_x into the upper atmosphere (stratosphere) due to high-temperature combustion in the engines of supersonic transport aircraft (SSTs). Ozone (O_3) is an important component of the upper atmosphere, since it absorbs high-energy UV radiation from the sun, preventing it from reaching the surface of the earth, where it would cause extensive skin cancer and genetic mutations. Nitric oxide is known to catalyze the destructive reaction of ozone with atomic oxygen (also present in the upper atmosphere):



The NO produced in Reaction (13.21) is then able to reinitiate Reaction (13.20); thus it is functioning as a catalyst.

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 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.

Physical Properties of Concentrated Oxo Acids. We have not yet had a chance to apply the concepts of this chapter concerning physical properties to the oxo acids discussed in Chapter 3. While we are on the subject of nitric acid, this may be a good time to do so. Unlike oxides, oxo acids have hydrogen atoms directly bonded to oxygen and can thus engage in hydrogen bonding. Hydrogen bonding is substantially stronger than most van der Waals attractions, but is not nearly as strong as Coulombic forces or covalent bonds between units. Hence, pure oxo acids, although smallish molecules, are not gases, but are liquids or solids with rather high boiling points. Pure HNO_3 , for example, has a boiling point of 83°C .

Generally speaking, pure oxo acids are rather difficult to make. Weak oxo acids often decompose to oxides that are polymeric and insoluble in water (Table 13.5) or to gaseous oxides that are readily lost from solution (even in solution, most dissolved CO_2 is not present as carbonic acid, but as hydrated CO_2 molecules). Strong oxo acids such as nitric acid exothermically form hydrated oxo anions and H_3O^+ ions in solution. When one tries to isolate the oxo acids in their anhydrous form, enough stabilization is lost that in many cases the pure oxo acid cannot exist or has greatly reduced stability. The more stable oxo acids are commonly handled as concentrated solutions in water.

In many cases, these are prepared by distilling off water until a mixture of water and acid of constant composition finally distills over (sometimes under reduced pressure to reduce their fairly high boiling points to a temperature low enough that the oxo acid does not decompose). Nitric acid is commonly seen as concentrated HNO_3 (68% HNO_3 , 15 M). It is corrosive to the skin, reacting with skin protein to produce a yellow material called xanthoprotein.

Sulfur Oxides and Sulfuric Acid. Sulfur dioxide is made commercially by the combustion of sulfur, H_2S , or sulfide ores such as FeS_2 . It is a colorless, poisonous gas with a choking odor and a relatively high boiling point (-10°C), and is useful as a solvent, refrigerant, food preservative, and (mainly) in the manufacture of sulfuric acid. In this process, the SO_2 must first be oxidized by air to SO_3 , which is a kinetically slow process, so a catalyst of platinum sponge, V_2O_5 , or NO is required. The SO_3 resulting from this oxidation reacts exothermically with H_2O to give H_2SO_4 . This reaction is impractical in industry, since a mist of H_2SO_4 would be produced in the air that would pass out into the atmosphere. Consequently, the gas stream is bubbled through concentrated sulfuric acid, with which it reacts to generate a polynuclear sulfuric acid (such as will be discussed later in this chapter):



This acid is then *carefully* reacted with the proper amount of water to give concentrated sulfuric acid.

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, is about 18 M, and 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 burns; should a spill occur, the acid should immediately be flushed away with large quantities of water for *at least 15 min*. 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 the elements of water from many organic molecules, converting carbohydrates to carbon, for example.

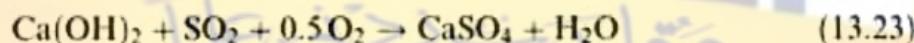
The uses of sulfuric acid are so many and varied that the figures for production of sulfuric acid in a given country has been considered a reliable indicator of that country's industrial development. The largest usage is in the production of fertilizer (see the next subsection, Phosphorus Pentoxide and Phosphoric Acid); other major uses are in refining of petroleum, in metallurgy, and in the manufacture of chemicals. For example, organic nitrations to produce explosives typically use a mixture of HNO_3 and H_2SO_4 , the latter to remove water. This reaction not only generates toxic nitrogen oxides but produces waste dilute sulfuric acids. Clean H_2SO_4 -free nitrating reagents are now being advocated, such as N_2O_5 by itself, or HNO_3 mixed with $\text{Yb}(\text{CF}_3\text{SO}_3)_3$ as an acid catalyst.²³

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 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 . This process is speeded by catalysts such as water droplets and *d*-block metal ions found in atmospheric particles of soot. These conditions, which once prevailed in London fog (as opposed to Los Angeles or photochemical smog), have

been found in many cities of the world in which homes were heated by burning soft coal. It may well be imagined that breathing in droplets of sulfuric acid does not have a desirable effect on the lungs and body. The resulting strain on the lungs and heart has shortened the lives of many people during such episodes of smog.

In the vicinity of smelters in which sulfide ores are 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"), which unfortunately has resulted in the spread of the sulfur oxides and sulfuric acid over whole continents and has helped cause the current problem of acid rain. Acid rain may have pH values as low as 2.1. (The contributions of coal-fired power plants, though never concentrated enough to give rise to local deserts, are collectively larger than those of smelters.) 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_3). Lakes that are in contact with limestone deposits are protected by the same reaction, which neutralizes the acid rain, but those that are not so fortunate become quite acidic, with harmful consequences already discussed. 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, since 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 $\text{Ca}(\text{OH})_2$ can be sprayed down the smokestack of the plant in a scrubber to react with the sulfur oxides according to the reaction:



(Much of the calcium sulfite expected from this reaction is oxidized by the air to calcium sulfate.)

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 $\text{Ca}(\text{OH})_2$. Consequently, for each ton of coal burned, up to 0.2 tons of limestone would be required, and an enormous quantity of wet CaSO_4 would be generated. We have now converted an air-pollution problem to a water-pollution problem or (if we dry out the wet CaSO_4) a solid-waste problem, since there are not enough uses of CaSO_4 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.^{19,20} For example, using $\text{Mg}(\text{OH})_2$ instead of $\text{Ca}(\text{OH})_2$ has advantages despite the fact that $\text{Mg}(\text{OH})_2$, being the hydroxide of a weakly acidic cation, is insoluble in water. After the SO_2 reacts with the slurry of $\text{Mg}(\text{OH})_2$, the resulting MgSO_3 can be heated (in another location) to regenerate the SO_2 :



This reaction is much more feasible than the analogous reaction with CaSO_3 , because there is a greater mismatch of cation and anion radius with MgSO_3 , which favors the formation of MgO at a lower temperature than CaO can be formed. The MgO can be recycled to form $\text{Mg}(\text{OH})_2$; thus there would be no solid waste problem and no great investment in $\text{Mg}(\text{OH})_2$. The SO_2 is formed at a concentration great enough to allow

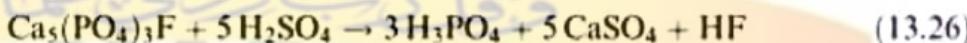
the manufacture of sulfuric acid, which could be sold. However, sulfuric acid is the cheapest acid, and the sale of this acid would not pay for the heat used to decompose the MgSO_3 .

Although many other alternatives exist, each one has a drawback. 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.

Phosphorus Pentoxide and Phosphoric Acid. The acidic P_4O_{10} (commonly named phosphorus pentoxide from its simplest formula unit, without the di-) reacts very completely with water, and hence it is used as a drying agent. But it is dangerous to use P_4O_{10} to dry organic liquids, because it releases so much heat that it can set the organic liquid on fire! It is also involved indirectly in the production of high-purity "syrupy" (85% or 15 M concentrated) phosphoric acid, made by oxidizing elemental phosphorus in the presence of water:



This high-purity acid is used in making detergents, toothpaste, and in foods such as colas ($\sim 0.05\%$ H_3PO_4 , pH 2.3!), but it is too expensive for the main use of phosphoric acid, in making fertilizers. For this purpose, phosphoric acid, being a moderately weak acid, is produced by the reaction of a strong acid with the moderately basic phosphate ion:



This reaction mixture is diluted with water and the insoluble calcium sulfate is filtered off; the solution may then be concentrated. The cost of this process is only one-third as much as the preceding process, but as the phosphate rock used, fluoroapatite, contains many impurities, so does the resulting phosphoric acid. This reaction also produces a serious air pollutant, gaseous HF. For use in fertilizers, it is not necessary to protonate the PO_4^{3-} ion completely. Fluoroapatite is too insoluble to be utilized by plants as a nutrient, but partial protonation of the phosphate ion reduces its basicity, so that the salt $\text{Ca}(\text{H}_2\text{PO}_4)_2$ becomes soluble enough to be used as a nutrient ("super-phosphate" fertilizer).

The three main nutrient elements provided in fertilizers are K, P, and N; the potassium and phosphorus are provided in the form of K^+ and PO_4^{3-} and the nitrogen either as the NH_4^+ ion or the NO_3^- ion. Interestingly, the compositions of fertilizers are often expressed in terms of acidic and basic oxide contents. The potassium ion is expressed as the weight percent of K_2O . The phosphorus ion content is expressed as the percent of P_4O_{10} or P_2O_5 needed to give the actual content of K and P via acidic oxide–basic oxide reactions. (Since the nitrogen may be present as NH_4^+ , which cannot arise from an acidic or basic oxide, its content is given more simply as %N.) A fertilizer labeled 16–48–0 contains 16% N, 48% P_2O_5 , and 0% K_2O .

Perchloric Acid. Perchloric acid (HClO_4) is available commercially as a 72% solution, with a boiling point of 203 °C. Contact of concentrated HClO_4 with organic materials and other easily oxidized materials should be avoided, however, since the products may be treacherous explosives.

13.4 Close Packed Anions, Metal Oxides, and Electrical Conductivity of Solid Ionic Compounds

Close Packed Anions. Before we look at some chemistry of the ionic oxides of metals, we wish 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 one of two close-packing patterns also found among atoms in metals (Section 12.3; Figs. 12.9 and 12.10); the much smaller cations then fill some of the holes or interstices between the anions. Thus if we were packing basketballs and baseballs for shipment in the same large box, we would figure out first how to pack the larger basketballs in the most efficient way possible, with confidence that the baseballs would fit in the spaces between the larger spheres.

There are two types of holes in the hexagonal close-packed (hcp) and cubic close-packed (ccp) lattices: tetrahedral holes and octahedral holes. The locations of these holes may be seen in Figure 12.9(b). Between three anions in the layer drawn in black and the anion in neighboring layer drawn in gray there is a small open space, called a **tetrahedral hole**, since it is surrounded by four large spheres; a small cation put in here would have a coordination number of 4.

Figure 12.9(b) also shows that this arrangement of the lower layer of ions fills in only one-half of the three-sided cavities of the black layer; the other one-half of the three-sided cavities of the black layer match up with three-sided cavities in the gray layer to produce larger **octahedral holes** surrounded by six larger spheres.

It can be shown that 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.

Although these close-packed descriptions are used more frequently with other types of lattices than those found in Table 4.4 (and illustrated in Fig. 4.8), it is useful to show how they may be applied to these simple lattice types. Thus the two ZnS lattice types differ in the type of close packing: The zinc blende structure (Fig. 4.8) has its sulfide ions cubic close-packed, with zinc ions being located in one-half of the tetrahedral holes. The wurzite structure has an obvious hexagonal pattern (hcp sulfide ions), again with zinc ions in one-half of the tetrahedral holes. Sodium chloride has ccp chloride ions, with sodium ions in all of the octahedral holes. The fluorite structure has cubic close-packed *calcium* ions, with the more abundant fluoride ions filling all of the tetrahedral holes. The rutile structure can only indirectly be derived by distorting a hcp structure; the CsCl structure is not close-packed.

Metal Oxides. The physical properties of the ionic metal oxides contrast strikingly with those of the more volatile oxides we have been discussing. Their very high melting points and low volatility make some of them (such as MgO) useful as refractories for providing surfaces capable of withstanding very high temperatures. Magnesium oxide is used not only to line furnaces but to cover the heating elements of electric ranges, since it conducts heat much more readily than it conducts electricity. A related use is that of *thoria* (actually 99% ThO₂ + 1% CeO₂) to provide luminosity to gas flames for lighting purposes: The oxides become white-hot without melting. (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.) The uranium oxide U₃O₈, a waste product of the nuclear power industry, has been found to be an

effective catalyst for the incineration of volatile organics, even chlorocarbons, reducing the temperatures at which the latter can be decomposed from 1000 to 400 °C while preventing the formation of dioxins.²⁴

Titanium dioxide is used extensively for its intense whiteness when cold (e.g., in white paints, where it has replaced very toxic lead compounds). Naturally occurring TiO_2 (the minerals anatase and rutile) is normally darkened with impurities, however, so that TiO_2 must be manufactured chemically. This process is not easy, since the Ti^{4+} ion is strongly acidic, and consequently TiO_2 is quite insoluble. The titanium ore ilmenite, FeTiO_3 , dissolves in hot concentrated sulfuric acid, however; after the solution is diluted and the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is crystallized out, the remaining solution of titanyl sulfate (TiOSO_4) is hydrolyzed to give pure TiO_2 .

Because of their very high melting points, many ionic and macromolecular oxides and related materials find extensive use as **ceramics**: hard, heat- and chemical-resistant materials that keep their strength even when very hot (as most metals and organic polymers do not). Among the best known of these is **silica**; the related polysilicate ceramics and glasses, which have been known and used for thousands of years, will be discussed later. 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.²⁵

The resistance of these materials to heat, chemical attack, and mechanical loads stems from the strong chemical forces linking units, be these covalent bonds or the attractions of oppositely charged ions. Unfortunately, these linking forces are subject to catastrophic failure if they are put under too great a mechanical stress. In ionic oxides, for example, the attraction of the cation for its neighboring anions is very strong. External forces that would result in the anions being pushed away from the cations are resisted mightily—unless the force is strong enough to push the anions far enough from the cations so that their new neighbors are also anions. Suddenly, the attractions are replaced by repulsions, and the material shatters. **Brittleness** is an unfortunate characteristic physical property found in ceramics.

Because ceramics are hard and brittle, they cannot be prepared 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. They can be prepared from molten materials, but these often have impractically high melting points (often as high or higher than the container that would hold them, which might also be a ceramic). Therefore they often must be made 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” the granules together to give a coherent solid, but often voids remain to serve as sources of cracks. Much modern research in ceramics deals with ways to generate fine, homogeneous particles of starting oxides that will sinter together to give dense, strong ceramics with few voids, or will undergo unusual phase transitions when a crack begins that tend to fill the crack (as in zirconia). Or researchers try to overcome some of these problems by creating **composites** of ceramics with either metals or organic or other polymers.

Every solid oxide or solid salt of an oxo anion (in fact, every salt) has a *surface chemistry* that is, in some ways, distinct from the chemistry of the bulk material. Although, for example, the Ca^{2+} and O^{2-} ions in the center of a crystal of CaO do have the expected coordination number of 6, this regular ionic environment must end at the surface: On a clean surface face, the Ca^{2+} must have at least one vacant coordination

site, as must each surface O^{2-} ion. As a consequence of these vacant sites, the Lewis acidity of the surface Ca^{2+} ions and the Lewis basicity of the surface O^{2-} ions are not diminished in the normal way. These surface ionic sites have powerful acidic and basic properties that (we shall see later in the chapter) can catalyze chemical reactions, adsorb molecules or ions with the appropriate charges or partial charges, and so on.

Isomorphous Substitution and Mixed-Metal Oxides. There are a number of technologically important oxides, the simplest formulas of which look like oxo salts (e.g., $BaTiO_3$), but that are not formed from acidic oxides and the structures of 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 compounds, 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. In some of the simplest mixed-metal oxides, a few percent of the metal ions of a second metal (and the corresponding oxide ions) simply enter into the appropriate sites of a metal oxide, leading to **isomorphous substitution** for the first ion and giving a type of solid solution. Dissolving some Cr_2O_3 into the lattice of alumina, Al_2O_3 , gives color to the colorless alumina. The gemstone *ruby* is formed, which is used in lasers (Section 17.5). Similarly, dissolving some Ti_2O_3 in Al_2O_3 results in *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 10–20%.*²⁶

Examination of Table C shows that quite a few sets of ions can be found that have the same charge and very similar ionic radii. Generally speaking, 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 have very similar radii (86 and 92 pm, respectively). Thus 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.

This principle 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 Chapter 4) 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. These problems could be overcome by adding not only sulfate ion but also barium ion. A larger amount of barium sulfate would then precipitate and the radium would substitute isomorphously for the barium. This technique is known as coprecipitation; the

barium ion is said to act as a *carrier* for the Ra^{2+} . (Of course, we would then be confronted with the formidable problem of separating the very similar barium and radium ions, but at least we would be working with a much smaller volume of material.)

Another illustration of this process occurs in a familiar experiment of growing crystals of ionic compounds. For example, large, beautiful octahedral crystals of *alum*, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 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^+ ion can be replaced by other +1 cations of similar radius, such as Rb^+ and NH_4^+ . The Al^{3+} ion can be replaced by numerous other +3 ions of similar radius, such as Cr^{3+} (giving purple crystals of *chrome alum*) or Fe^{3+} (giving pale violet crystals of *ferric alum*). The sulfate ion can even be replaced by the selenate ion. 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^{3+} and Cr^{3+} 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.)

Perhaps the most extensive case of isomorphous substitution occurs in the minerals monazite and xenotime, MPO_4 , and bastnaesite, MFCO_3 . 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.²⁷ [Refer to Tables A–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 (four) than any of the great cities of the world.

The separation of these elements involves quite a complex process of ion exchange. The most troublesome case of isomorphous substitution, however, is that of the elements Zr (Pauling electronegativity 1.33, ionic radius 86 pm) and Hf (Pauling electronegativity 1.3, ionic radius 85 pm). Hafnium occurs isomorphously substituted in all zirconium compounds to the same extent (~2%), so there were no chemical discrepancies in the "pure" samples of zirconium prepared in 1825 and thereafter. Consequently, the presence of Hf went undetected for a whole century!

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 8.10). 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^+ and Zn^{2+} , however, are "silent metals" that lack most or all of these properties. Silent K^+ (radius = 152 pm) can often usefully be substituted with fluorescent and NMR active Tl^+ (radius = 164 pm); colorless Zn^{2+} (88 pm) is usefully replaced

by colored Co^{2+} (88 pm); silent Ca^{2+} (114 pm) can be replaced by Eu^{2+} (131 pm), with seven unpaired electrons.

Nonstoichiometric Oxides. Perhaps the easiest type of mixed-metal-ion oxides to prepare are the **nonstoichiometric oxides** (or compounds, since these phenomena are not restricted to oxides), which are oxides of metals that have cations of more than one oxidation state. Iron(II) oxide as normally prepared gives an actual elemental analysis corresponding to approximately $\text{Fe}_{0.95}\text{O}$; 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. Since most of the *d*-block metals have cations differing by only one unit of charge, there are many nonstoichiometric *d*-block metal oxides, including 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 $\text{VO}_{0.79}$ to $\text{VO}_{1.29}$, while nickel(II) oxide ranges only from $\text{NiO}_{1.000}$ to $\text{Ni}_{1.001}$. These nonstoichiometric oxides are often intensely colored due to charge-transfer transitions, which take an electron from one of the M^{2+} to one of the M^{3+} ions. Such transitions are of especially high probability when the two ions are of the same metal.

Electrical Conductivity. 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. However, some metal oxides have enhanced electrical conductivity due to the easy transfer of *electrons*. In the nonstoichiometric early *d*-block metal oxides of the fourth period, TiO_x and VO_x ($x \approx 1.0$), metal-like conductivity is present due to the overlap of metal t_{2g} orbitals on next-neighboring cations with each other to create extensive MOs through which *d* electrons can travel. This is not possible for the later fourth-period *d*-block metal oxides, in which the *d* orbitals are too contracted to overlap with each other.²⁸

Overlap of *d* orbitals also plays a role, not only in making an early *d*-block oxide, TiO_2 , a semiconductor with a band gap of 3.23 V, but also a *photocatalyst*. (For other examples of photocatalysts, see Section 17.6.) Titanium dioxide has the ability to harness the energy of sunlight to promote the oxidation in air of almost any organic vapor. In TiO_2 light promotes an electron from the highest occupied molecular orbital (HOMO), an oxide ion lone pair, to the delocalized lowest unoccupied molecular orbital (LUMO), based on Ti 3*d* orbitals, producing a transient excited state resembling $(\text{Ti}^{4+})(\text{e}^-)(\text{O}^{2-})(\text{O}^-)$. The excited electrons react with atmospheric O_2 to generate superoxide ions, O_2^- , which are potent oxidizers of organic vapors. The seven valence electron O^- ion reacts with atmospheric H_2O , removing a hydrogen atom from it to give an HO^- ion in the solid lattice and a hydroxide free radical, $\cdot\text{OH}$, in the atmosphere; the hydroxide radical is also a potent oxidizer. Titanium dioxide is of great interest to environmental chemists because of its seeming ability, in sunlight, to oxidize almost anything (nitrogen oxides, cigarette smoke, grease, bacteria, and chlorobenzenes).²⁹

Nonstoichiometry and improved electrical conductivity can be created by incorporating other metal ions into metal-oxide lattices. It is possible to heat NiO with a source of Li_2O in an oxygen atmosphere; under these conditions a semiconducting

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nonstoichiometric mixed-metal oxide, $\text{Li}_x\text{NiO}_{1+x}$, is produced, in which some of the Li^+ ions are doped into positions normally occupied by Ni^{2+} ions. Since the overall charge balance must be maintained, an equal number of other Ni^{2+} ions must simultaneously be oxidized by the oxygen to Ni^{3+} ions. Thus it becomes feasible for electrical semiconduction to occur by the thermally activated process of electrons hopping between nickel ions of different charges.

In certain types of lattices and under certain conditions *ions* can move in solids, and 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, superionic conductors, and fast-ion conductors. These materials are important for their potential uses in high-energy density batteries and fuel cells and in lasers.³⁰

Oxide ions can be the mobile phase in a lattice composed of larger cations, for example, between 500 and 1000 °C in zirconia (ZrO_2) doped with CaO . When a Ca^{2+} ion replaces a Zr^{4+} ion in the zirconia lattice, charge neutrality of the lattice is maintained by deleting an oxide ion as well. The resulting *vacancies* in the lattice act as tetrahedral holes into which other oxide ions can move (and hence carry current) if enough thermal energy is available.

It is more common, of course, for the anions to be larger than the cations. Some solid *iodides* allow superionic conduction of soft-acid cations into tetrahedral holes. For example, the structures of copper(I) and silver(I) tetraiodomercurates, Cu_2HgI_4 and Ag_2HgI_4 , feature four-coordinate soft-acid metal ions but only three-coordinate iodide ions; one-fourth of the tetrahedral holes about the large (approximately ccp) 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^+ and yellow for the Ag^+ salt). At a specific temperature (50 °C for the Ag^+ 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^+ salt and orange in the Ag^+ salt). Similar types of phenomena are found in solid AgI itself, as well as in RbAg_4I_5 .

Sometimes the holes in which cations can move can be quite large indeed. The β - and β'' -aluminas are two classes of mixed-metal oxides built from the oxides of aluminum and sodium; sodium β -alumina has an approximate composition of $\text{Na}_{1.2}\text{Al}_{11}\text{O}_{17.1}$. In these oxides, the Al^{3+} ions are present in dense Al_2O_3 slabs separated from each other by widely spaced oxide-ion “pillars”; there are broad vacancies between these oxide ions. Parked like cars among the pillars of a parking garage are a few of the Na^+ cations, which are quite free to move, and conduct electricity about as well as in aqueous Na^+Cl^- . This property was discovered in 1965 by Yung-Fan Yao and J. T. Kummer of Ford Motor Company, who applied it to devise a revolutionary new battery. This battery operated at 300 °C, using molten sodium as the positive electrode and molten sulfur as the negative electrode; sodium- β -alumina served as a ceramic membrane (analogous to a salt bridge but lighter and less reactive) to separate these reactive liquids while allowing ions (but not electrons) to pass between them. Because of the very open spaces between the alumina slabs, ion exchange is easily carried out on these aluminas: immersion of sodium- β -alumina in a molten salt for a few minutes allows complete exchange of the Na^+ ions for K^+ , Rb^+ , Cs^+ , Cu^+ , Ag^+ , and Tl^+ ; divalent and even trivalent cations can exchange for Na^+ ions, then carry current, in the even more open sodium- β'' -alumina.

13.5 Spinels, Perovskites, High-Temperature Superconductors, and Cooperative Magnetic Properties in Mixed-Metal Oxides

An important class of mixed-metal oxides are known as the spinels, AB_2O_4 . (This class is named after the mineral spinel, MgAl_2O_4 .) In spinels, the oxide ions are ccp. 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. These spinels have stoichiometry $\text{M}^{2+}(\text{M}^{3+})_2(\text{O}^{2-})_4$ or M_3O_4 , and seem to share fractional oxidation numbers because of the presence of two different oxidation states in the same compound. The spinels Mn_3O_4 , Fe_3O_4 , and Co_3O_4 are all intensely black, and much darker than the simple oxides of these metals, due to charge-transfer transitions; Fe_3O_4 has 1 million times the electrical conductivity of Fe_2O_3 .

These spinels exhibit the two most common forms of *cooperative magnetic properties*, ferromagnetism and antiferromagnetism (Section 12.4). Unfortunately, it is not so easy to predict in oxides whether the direct ferromagnetic or the indirect anti-ferromagnetic interaction will prevail. Among the mixed-metal spinels, Mn_3O_4 and Co_3O_4 are antiferromagnetic, while only Fe_3O_4 (the mineral *magnetite* or *lodestone*) shows the much more important property of ferromagnetism. Microscopic crystals of magnetite have been found in a number of different living organisms, including bacteria, pigeons, salmon, and (perhaps) in human brain tissue, which might confer sensitivity to magnetic fields similar to the earth's.³¹ Similarly, among the simple *d*-block dioxides, VO_2 and MnO_2 are antiferromagnetic, while CrO_2 is used in magnetic storage devices for its ferromagnetic properties (both magnetite and chromium dioxide have Curie temperatures above room temperature). Spinels in general are very important in the solid-state electronics industry for their electric and magnetic properties.

Another important class of mixed-metal oxides are the **perovskites**, ABO_3 , of which the prototype is CaTiO_3 (perovskite). It has an unusual ccp lattice of oxide and calcium ions (Fig. 13.6), in the octahedral holes of which the much smaller Ti^{4+} ions can “rattle around”.

There are many other perovskites, which can be generated from the structure of CaTiO_3 through the application of either the first or the second principle of **isomorphous substitution**. This latter 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 replacing ions must equal the total charge of the replaced ions. This means that isomorphous substitution can occur even if the new ion C have a charge one greater than the old ion A, *if there is simultaneous substitution by a new ion D with a charge one less than the old ion B*. This conserves the electroneutrality of the salt, since the sum of charges of the new ions C and D equals the sum of charges of the old ions A and B. Table 13.6 shows sets of common ions that frequently substitute for one another.

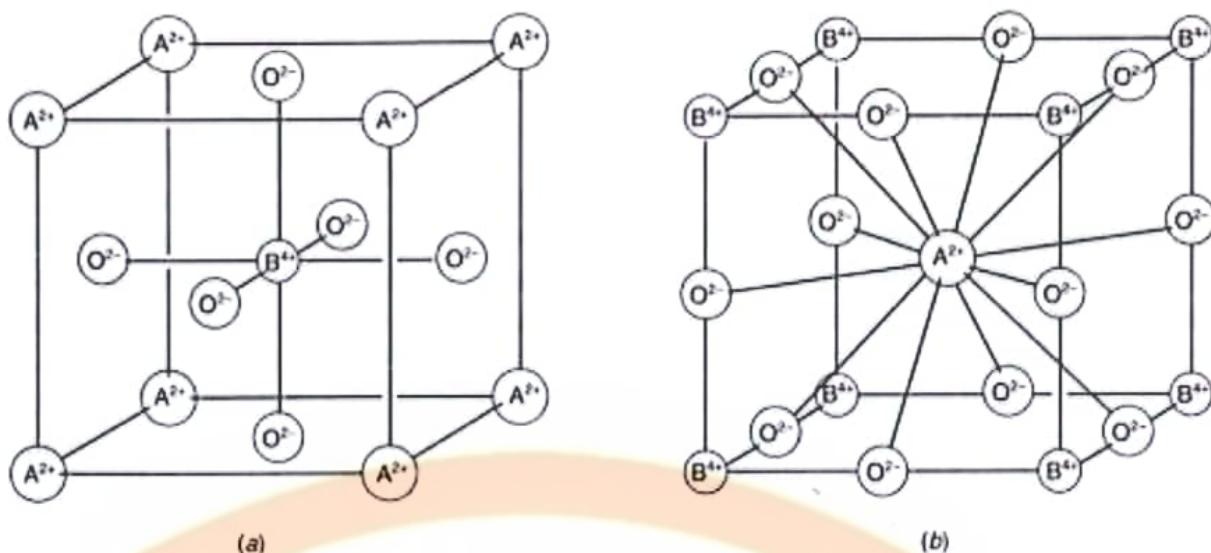


Figure 13.6

The structure of perovskites, ABO_3 (e.g., $\text{A}=\text{Ca}^{2+}$, $\text{B}=\text{Ti}^{4+}$ in CaTiO_3), shown (a) with B^{4+} at the center of the unit cell and emphasizing the octahedral coordination of B^{4+} , (b) with A^{2+} at the center of the unit cell and emphasizing the dodecahedral (12) coordination of A^{2+} .

Table 13.6

Sets of Common Ions Suitable for Isomorphous Substitution

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

^a Radii listed in parentheses are in picometers (pm).

^b Lanthanide ions = Ln^{3+} .

Example 13.6

Which of the following minerals could arise by isomorphous substitution processes in leucite, KAlSi_2O_6 ? (a) KYSi_2O_6 ; (b) $\text{RbAlSi}_2\text{O}_6$; (c) $\text{BaBeSi}_2\text{O}_6$; or (d) $\text{BaAlSi}_2\text{O}_6$.

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 it 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^{3+} replaces Al^{3+} ; in (b), Rb^+ replaces K^+ ; in (c), Ba^{2+} and Be^{2+} replace K^+ and Al^{3+} ; in (d), Ba^{2+} replaces K^+ . Substitution product (d) cannot exist.

Also note 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.) 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^+ (166 pm) is close in size to K^+ (152 pm), and in (c) Ba^{2+} (149 pm) is close to K^+ (152 pm), and Be^{2+} is close to Al^{3+} .

The perovskite structure type requires that the sum of the charges of the A and B metal ions be +6 and that they be quite different in size from each other. Thus, other perovskites such as $\text{Li}^+\text{Nb}^{5+}(\text{O}^{2-})_3$ are also known, as are fluoride perovskites such as $\text{Na}^+\text{Fe}^{2+}(\text{F}^-)_3$. If the temperature is not too high, the Ti^{4+} 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^{4+} 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**,³² makes perovskites and the form of SiO_2 known as quartz 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.

Example 13.7

Verify that the unit cell drawings of perovskite shown in Figure 13.6 show the ions in the proper stoichiometry.

SOLUTION:

In the structure of a crystalline solid, unit cells are repeated in all three dimensions. Consequently, any atom or ion appearing on the *surface* of the unit cell also appears in the neighboring unit cell(s). More specifically: (a) each atom or ion found at the *corner* of a unit cell is also shared with seven adjacent unit cells, so it counts as only *one-eighth* of an atom or ion in the given unit cell; (b) each atom or ion found along the *edge* of a unit cell is shared among four unit cells, so it is *one-fourth* in the given unit cell; (c) each atom or ion found inside the *face* of a unit cell is *one-half* in that cell; and (d) each atom or ion found in the *interior* of a unit cell is *completely* in that unit cell.

Hence, in the perovskite unit cell as drawn in Figure 13.6(a) we find eight A^{2+} ions on corners of the unit cell, which gives *one* A^{2+} per unit cell (the same result occurs with the unit cell of Figure 13.6(b), since there is one A^{2+} in the interior). In Fig. 13.6(a), we find one B^{4+} in the interior of the unit cell, which counts as one B^{4+} . The six O^{2-} ions in Fig. 13.6(a) are in faces, so they count as three O^{2-} ions, which add up correctly for the stoichiometry ABO_3 . (In Fig. 13.6(b) there are 12 O^{2-} ions along edges, shared among four touching unit cells, so that this also totals three O^{2-} ions per unit cell.)

Tungsten bronzes, Na_xWO_3 , ($0.32 < x < 0.93$), made by reduction of sodium tungstate, are perovskite-like materials (when $x \geq 0.44$) that are deficient in sodium ions. Their conductivity is based on movement of electrons in delocalized MOs, and ranges from metallic to semiconducting, depending on the value of x —as does their metallic luster and color, which ranges from blue ($x \approx 0.4$) to violet ($x \approx 0.57$) to red, orange, and yellow ($x \approx 0.8$).

High-Temperature Superconductors. In 1987,³³ the scientific world was very much surprised to learn that mixed-metal oxides can show the property of superconductivity (Section 12.4), previously considered characteristic only of metals and alloys; with critical temperatures, T_C , at or below 23 K, these require the use of a very expensive coolant, liquid helium. So it was significant to expand the search to another class of materials, the mixed-metal oxides, and even more significant that the very first of these oxides, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, showed a higher T_C , 30 K, than any of the metals or alloys. Very soon a mixed-metal oxide system with a T_C of about 90 K was discovered, $\text{YBa}_2\text{Cu}_3\text{O}_7$, familiarly known as “123” for the ratios of the metal ions in the formula. With a T_C exceeding 77 K, the much cheaper and more abundant coolant, liquid nitrogen, could be used. This oxide is prepared by sintering the oxides Y_2O_3 , CuO , and the oxide precursor BaCO_3 at 950 °C for an extended time, followed by a slow cooling and exposure to O_2 at 500–600 °C, whereupon one-third of the Cu^{2+} ions are evidently oxidized to Cu^{3+} ions. Above T_C these superconductors show the antiferromagnetic properties that are common in metal oxides.

The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is related to that of perovskite; this relationship can be seen if one takes three adjacent A-centered unit cells (Fig. 13.7), and allows Y^{3+} to occupy the A position in the central cell and Ba^{2+} 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 actual $\text{YBa}_2\text{Cu}_3\text{O}_7$ 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. This, of course, changes the polyhedra of the copper ions. The d^8 Cu^{3+} ions found on the top and bottom surfaces of the new, larger unit cell of Figure 13.7 (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 the figure. In contrast, the d^9 Cu^{2+} ions found in the center of the new unit cell (sandwiched between Ba and Y) lose only one oxide neighbor, so 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^{2+} polyhedra. Experimentally, it is found that (a) 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!); (b) slight replacement (doping) of the Cu^{3+} ions from the chains of CuO_4 square planes with other +3 charged ions such as Ga^{3+} lowers T_C , but not as severely as does (c), slight replacement of the Cu^{2+} ions from the planes of CuO_5 square pyramids with divalent ions such as Zn^{2+} . Reduction of the oxygen content of the superconductor can occur until the composition $\text{YBa}_2\text{Cu}_3\text{O}_6$ is reached. This reduction does not alter the planes of CuO_5 square pyramids, but does reduce the chains of Cu^{3+} containing CuO_4 squares to sticks of linear two-coordinate Cu^+ containing CuO_2 units, and does destroy the superconductivity property.

A variety of related “cuprate” high-temperature superconductors has since been discovered and discussed.³⁴ Both $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ add additional

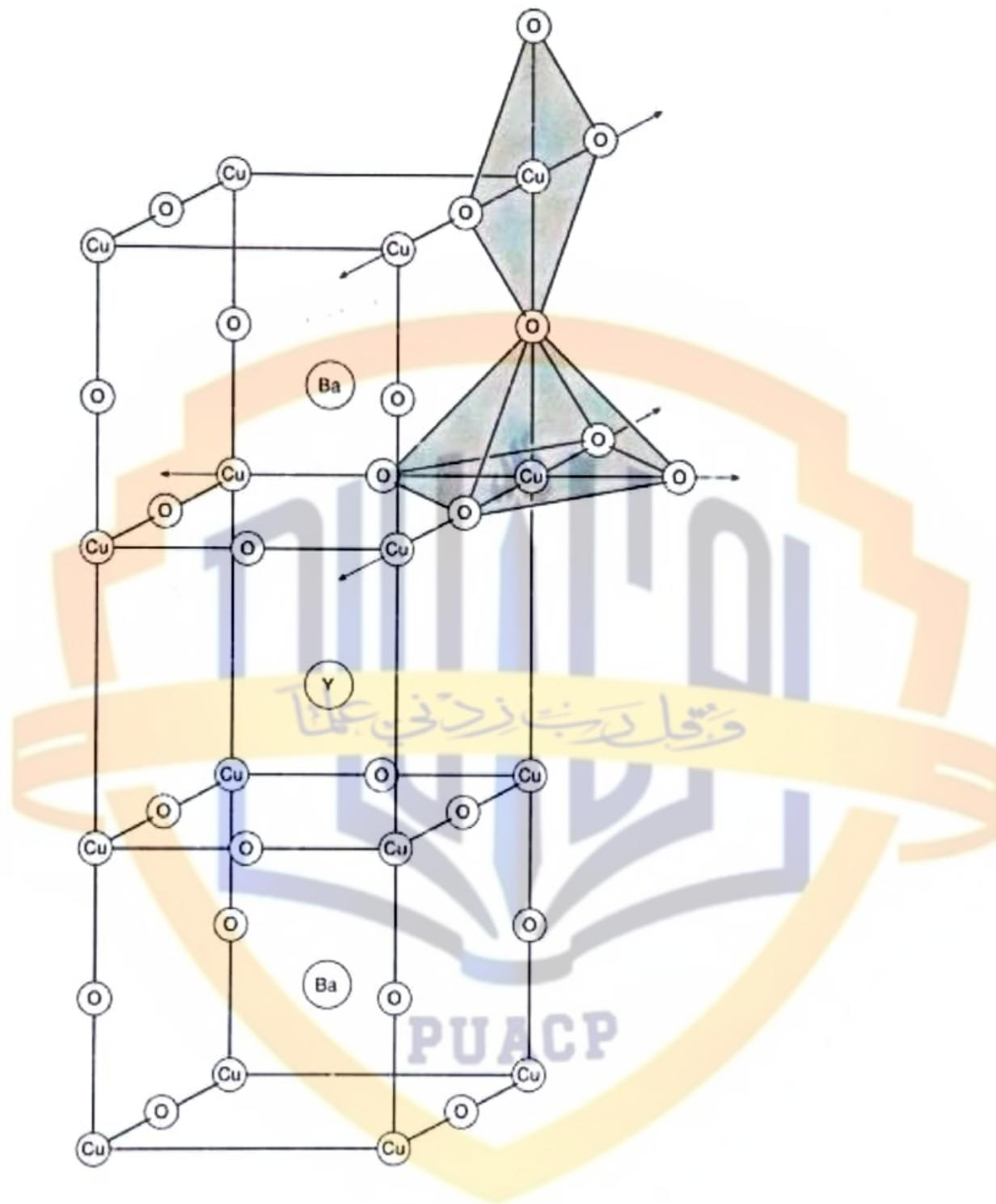


Figure 13.7

The structure of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ as related 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.

chains of CuO_4 squares; but the most dramatic improvements in T_C result from incorporating heavy *p*-block metal ions of mercury, thallium, and bismuth, resulting in idealized formulas including $\text{HgBa}_2\text{CuO}_4$, $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, $\text{Tl}_2\text{Ba}_2\text{CuO}_6$, and $\text{TlBa}_2\text{Cu}_2\text{O}_5$; the highest T_C values yet found, 125 K and 133 K, belong to superconductors having three layers of Cu ions, $\text{Tl}_2\text{Ba}_2\text{CaCu}_3\text{O}_{10}$ and $\text{HgBa}_2\text{CaCu}_3\text{O}_8$, respectively. These structures lack chains of CuO_4 squares but still have the planes of cuprate units, confirming their importance in superconductivity. (The first oxide superconductor, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, also has planes of ordinary Jahn-Teller-distorted CuO_6 octahedra, although the average oxidation state of the Cu^{2+} here is unambiguously greater than +2.)

It is fascinating, of course (and potentially profitable), to speculate about the possible applications of high-temperature superconductors.³⁵ Some applications involving low magnetic fields and electric current density and using liquid nitrogen cooling are near to realization: microwave devices such as microwave cavities and wave guides and frictionless bearings; superconducting quantum interference devices (SQUIDs) already use high-temperature superconductors.³⁶

High magnetic fields cause a breakdown of the superconductivity of these materials at 77 K, so the idea of a magnetically levitated train running at 400 miles per hour using cheap liquid-nitrogen cooling is not just around the corner. But materials scientists continue to be challenged by the characteristics of such oxides: the high temperatures required to get their components to react, and the long times required for so many different metal ions to diffuse over long distances between grains before they can be thoroughly mixed to give homogeneous products; the difficulties of insuring 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, which are very difficult to draw into wires or to deposit as films (although substantial progress in producing flexible cuprate tapes has occurred).³⁷ In addition, with the presence of the high Cu^{3+} oxidation state, $\text{YBa}_2\text{Cu}_3\text{O}_7$ is air- and moisture-sensitive, and the production of the thallium- and mercury-containing cuprates is limited by the toxicity and high-temperature volatility of Tl_2O and HgO , which have low lattice energies, and hence relatively high vapor pressures at temperatures at which the other oxides react to give superconductors.

These difficulties have increased the importance of finding alternate routes to high-temperature sintering of oxides for the production of these solids.³⁸ Some methods will be discussed in Section 14.6. For now, we mention the possibility of obtaining better mixing of the component metal ions by the process of *homogeneously coprecipitating* them at low temperatures in one isomorphously substituted product, or if that is not feasible, of simultaneously precipitating separate but very finely divided, hence well-mixed, metal-ion-containing products. These products need not be oxides if they can be converted to oxides at temperatures below normal sintering temperatures.

Thus, simultaneous precipitation of mixed gelatinous metal *hydroxides* would be good, because these can generally be dehydrated to oxides at comparatively moderate temperatures. Unfortunately, the feeble acidity of Ba^{2+} does not match the weak acidity of Y^{3+} and Cu^{2+} ; $\text{Ba}(\text{OH})_2$ is a soluble metal hydroxide. Better success may be achieved using the larger carbonate ion, CO_3^{2-} ; its size match with Ba^{2+} allows precipitation of carbonates of all three metals. These metals can be heated to give oxides plus $\text{CO}_2(\text{g})$. Success has also been achieved by coprecipitating the *oxalates* of these three metal ions; oxalates (salts of the $\text{C}_2\text{O}_4^{2-}$ ion) are easily oxidized to $\text{CO}_2(\text{g})$ and oxides. Because of the charge and size differences among the three metal ions, we may

not be expected to be so lucky as to find isomorphous substitution of the three ions in the same salt, however. Other workers have attempted (fruitlessly so far) to find some exotic complex ions that would precipitate containing the three metal ions in the proper ratios, and from which the organic ligands could simultaneously be oxidized. Some success has been achieved by heating a mixture of the three acidic cations, oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, and urea, NH_2CONH_2 . The latter compound slowly hydrolyzes to CO_2 and ammonia, which increases the pH and precipitates the three cations as an intimate mixture of hydroxides, oxalates, and carbonates, all of which are converted to oxides on heating in air at 900°C .³⁹

13.6 Polysilicates: Basic Structural Types, Uses, and Chemistry

Of overwhelming importance in the geochemistry of the earth's crust are the compounds formed by the reaction of the acidic oxide silica, SiO_2 , with various basic metal oxides. These are not really mixed-metal oxides such as were discussed in Section 13.5, since definite silicon oxo anions, with covalent Si–O bonds, are present. But most of them do not have the simple silicate ion SiO_4^{4-} that we discussed in Chapter 2, but rather have many two-coordinate oxygen atoms covalently linking different silicon atoms into oligomeric or one-, two-, or three-dimensional polysilicate ions. Regardless of the degree of polymerization of the polysilicate ions, these are finally linked into three-dimensional ionic lattices by counterions. Nonetheless, we will see some differences in physical properties caused by the different degrees of polymerization of the covalent bonding in the polysilicate ions themselves. These more complex silicates are the most common of the polyoxometallates or polynuclear oxo anions (the structural units are often called the “nuclei” of the oxo anions). After examining the polysilicates in some detail, at the end of this chapter we will look briefly at the polyoxometallate anions of other elements.

The simple silicate ion SiO_4^{4-} (also called *orthosilicate* ion, to distinguish it from the polysilicate ions) 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 ; the garnets, $(\text{M}^{2+})_3(\text{M}^{3+})_2(\text{SiO}_4)_3$ ($\text{M}^{2+} = \text{Ca, Mg, and Fe}$; $\text{M}^{3+} = \text{Al, Cr, and Fe}$); and olivine, $(\text{M}^{2+})_2\text{SiO}_4$ ($\text{M}^{2+} = \text{Mg and Fe}$). 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, for example, olivine is often written $(\text{Fe,Mg})_2\text{SiO}_4$, with commas separating ions that can and do substitute for each other in any proportion.

Chain Oligosilicates. We can suppose that the process of linking simple silicate units is one of acid–base neutralization. In order to make room for a bridging oxygen from one SiO_4^{4-} , an oxide ion must be removed from another:



In the resulting disilicate ion, the basic structural unit is now $\text{SiO}_{3.5}^{3-}$, with one-half vacant coordination site per structural unit and a lower charge density than pres-

Study Objectives

- Predict trends in melting points among fluorides or oxides (a) across a period of elements, (b) up or down a group of elements, and (c) of a given element in different oxidation states. Exercises 1–5.
- Know the common nonmetal oxides and tell whether each has a structure based on (a) small molecules, (b) oligomeric molecules, or (c) macromolecules or an ionic lattice. Tell whether each is (a) a solid with high melting and boiling points, or (b) a gas, liquid, or solid with relatively low melting and boiling points. Exercises 6–13.
- Rank a series of oxides or hydroxides from the same group, period, or element (with different oxidation numbers for the element) in order of increasing basicity. Decide whether a given oxide is likely to be (a) soluble in water, (b) insoluble in water but soluble in strong acids, (c) insoluble in water but soluble in strong bases, or (d) insoluble in water but soluble both in strong acids and in strong bases. Exercises 14–21.
- Write balanced chemical equations including the products when (a) basic oxides react with water or with strong acids; (b) acidic oxides react with water or with strong bases; (c) amphoteric oxides react with strong acids or with strong bases; (d) acidic and basic oxides react with each other in the absence of water. Rank the degree of exothermicity in different acid–base reactions of oxides. Exercises 22–26.
- Know the names of, main uses of, and environmental problems (if any) associated with the main oxides of the nonmetals. Exercises 27–30.
- Know how many tetrahedral and how many octahedral holes occur per anion in close-packed structures, and how these relate to the stoichiometry of the salt. Exercise 31.
- Identify mixed-metal oxides that could adopt the spinel structure, the perovskite structure, and nonstoichiometric (defect) structures. Exercises 32–38.
- Given the drawing of a unit cell, determine the simplest formula of the corresponding solid. Determine from the simplest formula whether a given metal ion is present in two oxidation states, and if not describe what kind of substitution would be necessary to achieve this. Exercises 39–42.
- Given the formula of a silicate mineral, tell whether it contains simple silicate ions, linear oligomeric silicate ions, cyclic or chain polysilicate ions, double chains, layer polysilicate ions, or network structures, and describe the relative basicity of its anion. Exercises 43–50.
- Given a table of ionic radii, select ions that are likely to be found in the same silicate (or other) minerals by the process of isomorphous substitution; identify some ions that are unlikely to substitute for any other common ions and explain why. Exercises 51–58.
- Given formulas of several silicate minerals, tell which will be weathered most rapidly. Exercises 59–61.
- Know which elements are prone to forming polymeric oxo anions; describe the structures and uses of some of these. Exercises 62–67.

Exercises

- *The “cations” Be^{2+} , Si^{4+} , P^{5+} , Se^{6+} , and Br^{7+} each have a radius of about 50 pm. Assuming this radius: (a) Calculate the radius ratio of these cations to that of the fluoride ion. What two coordination numbers are most likely for each cation? Use the larger of these two numbers in the remainder of the problem. (b) Predict the number of vacant coordination sites in the structural unit of the neutral fluoride of each element. (c) Assuming that these calculations give accurate predictions, classify the fluoride of each of these elements as monomeric, oligomeric, polymeric, or nonexistent. (d) With the same assumption, select one of the following melting points as the most likely one for each of the fluorides that does exist: -50°C ; 75°C ; and 1000°C .
- The “cations” Al^{3+} , Ge^{4+} , Sb^{5+} , Te^{6+} , and I^{7+} each have a radius of about 70 pm. Assuming this value: (a) Calculate the radius ratio in their fluorides. Each cation would be expected to have what total coordination number? How many vacant coordination sites would be present in each structural unit? (Consider the structural unit to be the neutral fluoride.) (b) Assuming that these calculations give accurate predictions, predict whether the fluoride of each of these cations would be monomeric, oligomeric, polymeric, or nonexistent. (c) With the same assumption, select one of the following melting points as the most likely one for each of the fluorides that does exist: -50°C ; 75°C ; and 1000°C .
- Use radius ratio calculations to justify and interpret (in terms of plausible degrees of polymerization of structural units) the melting-point data given in Table 13.1 for the highest fluorides of (a) the fifth-period elements in the *d* block; (b) the seventh-period elements in the *f* block; and (c) the Group 15(V) elements.
- *Put the following series of oxides in order of increasing melting points, and decide which are gases at room temperature: (a) Na_2O , Cr_2O_3 , CO_2 , SiO_2 , P_4O_{10} and (b) ZrO_2 , CO_2 , SrO , Rb_2O , Y_2O_3 .
- Assuming that all of the following compounds are stable, predict where melting points will increase and where they will decrease in 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 and (b) MnO , Mn_2O_3 , MnO_2 , Mn_2O_7 .
- The following nonmetals show polymerization isomerism of their oxides of the type such that a given oxide can exist as at least two of the three structural types: monomer; oligomer; and polymer. Answer the following questions about one of the following nonmetals: (a) S; (b) Se; (c) N; (d) P; (e) As; and (f) Sb. (1) Read through the Section 13.3 on the nonmetal oxides and identify the oxide or oxides that show polymerization isomerism. (2) If possible, carry out the radius ratio type calculations to predict the expected coordination numbers of the nonmetal and oxygen. Which structural forms correspond to your prediction? Is the radius ratio close to a boundary value, so that you might have predicted isomerism? (3) The melting points, and so on, of these polymerization isomers are complicated by the fact that their bonds can rearrange at some temperature to give rise to another isomer. Assuming that this was not possible, predict whether each polymerization isomer would then be a gas, liquid, low-melting solid, or high-melting solid.

7. *Which of the following oxides are monomeric, which are oligomeric, and which are ionic or macromolecular substances? (a) Na_2O ; (b) Cr_2O_3 ; (c) CO_2 ; (d) SiO_2 ; (e) P_4O_{10} ; (f) BaO ; (g) Tl_2O ; (h) SO_2 ; and (i) Al_2O_3 .
8. Selenium trioxide occurs in three forms: (a) as monomeric covalent molecules, (b) as tetrameric covalent molecules, and (c) as chain polymeric molecules. Draw the structure of selenium trioxide in each of these three forms.
9. There is expected to be π bonding from O to the central atom in the tetroxides MO_4 .
 (a) In such π bonding, electrons would be donated from what types of orbitals on oxygen to what types of orbitals on the central atom? (b) Based on periodic trends discussed in Chapters 1 and 3, which two of the following four tetroxides should show the greatest degree of π bonding? Why? Tetroxides: FeO_4 ; RuO_4 ; OsO_4 ; XeO_4 .
10. (a) Name the six most important oxides of nitrogen. (b) Draw the Lewis dot structures of any three of these oxides. (c) Which (if any) of these are gases at room temperature?
11. Contrast the structures found in the following solids: (a) CO_2 and SiO_2 ; (b) BF_3 and AlF_3 ; (c) BF_3 and BeF_2 ; and (d) HNO_3 and "HPO₃."
12. *The compound SiO_2 exists in different phases: quartz, cristobalite, coesite, and stishovite. The latter two forms are found only in meteor craters. Carbon dioxide has only one form, which is completely different from any form of SiO_2 . The quite different physical properties and conditions of formation of these oxides result from their differing structures, which in turn can be rationalized on the basis of the differing size of C and Si. (a) Do radius ratio calculations for C^{4+} , Si^{4+} and O^{2-} . What are the actual coordination numbers found for C in CO_2 and Si in the common forms of SiO_2 (e.g., quartz)? (b) What are the actual coordination numbers of oxygen in CO_2 and in quartz? Use these numbers to explain why CO_2 is a gas while quartz is a solid with a very high melting point. (c) Stishovite has the less common coordination number for silicon in SiO_2 . Identify this number, and predict the lattice type that stishovite is likely to take. (d) Calculate the lattice energies of quartz and of stishovite. (e) Does this calculation necessarily predict the most stable form of SiO_2 ? Explain why stishovite is only found in meteor craters.
13. (a) If you were to list *all* compounds and ions in which the central atom shows oxidation number +7, which would you list more of and why: fluorides or iodides; oxides or sulfides; and oxo anions or fluoro anions. (b) Would all oxo anions of these elements have equivalent formulas (i.e., would all be EO_4^-)? If not, would the oxo anions of formula EO_4^- have the same, greater, or lesser basicity than the oxo anions of the other formulas? In general, would the salts of oxo anions EO_4^- give precipitates with the same cations as the oxo anions of the other formula? (c) All of the oxides of these elements in the +7 oxidation state would necessarily have the same simplest formula, E_2O_7 , but they could have different molecular structures. Discuss how the structure of E_2O_7 might change as one went down a group of elements E, and describe the effects this would have on its physical state and melting point.
14. *Consider the following oxo acids: (a) H_2SeO_5 ; (b) H_6TeO_6 ; (c) HMnO_4 ; (d) H_2PtO_6 (an imaginary acid); (e) H_3PO_4 ; (f) H_4XeO_6 ; (g) H_4SnO_3 ; (h) H_3VO_4 ; (i) H_2XeO_4 ; and (j) HTeO_4 . 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); and (4) whether it will be soluble or insoluble in water.
15. *Classify each of the following oxides 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 ; (e) P_4O_{10} ; (f) BaO ; (g) Ti_2O ; (h) SO_2 ; and (i) Al_2O_3 .
16. Arrange the following oxides in order of decreasing acidity/increasing basicity:
(a) Na_2O , Cr_2O_3 , CO_2 , SiO_2 , P_4O_{10} ; (b) ZrO_2 , CO_2 , SrO , Rb_2O , Y_2O_3 ; (c) MnO , MnO_2 , Mn_2O_3 , Mn_2O_7 ; and (d) TiO_2 , TeO_2 , SO_2 , ThO_2 .
17. Suppose that the following five oxides of new elements have been discovered: hoffmon tetroxide, HmO_4 (Hm = fourth period element); dimongium heptoxide, Mi_2O_7 (Mi = sixth period element); yangium dioxide, YaO_2 (Ya = second period element with no unshared sp electron pairs); vermillium dioxide, VeO_2 (Ve = fifth period element with one unshared sp electron pair); and linium dioxide, LmO_2 (Lm = fifth period element with no unshared sp 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 two oxides are most likely to be strong oxidizing agents? (e) Which oxide is most likely to be useful for making ceramic plates to shield space shuttles from the heat of reentry into the atmosphere?
18. 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^{2+} 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.
19. The research group of Academician V. I. Spitsyn and co-workers¹¹ reported the first synthesis of the compound iron(VIII) oxide (iron tetroxide): (a) What are the solubility properties and boiling-point-related data given for this compound? Why are these not expected for any other possible oxide of iron (especially Fe_2O_7 or FeO_3)? (b) If these oxides, and the known oxide OsO_4 , were to act as acidic oxides upon dissolution in base, predict the formulas of the oxo anions that would be formed; compare with the known oxo anions (Chapter 2). Would FeO_4 be classified as an acidic oxide, a basic oxide, an amphoteric oxide, or a neutral oxide? Contrast this with the classifications of the hypothetical iron oxides Fe_2O_7 and FeO_3 , as well as the classification of OsO_4 .
20. Consider the following set of oxides: SrO , ZrO_2 , TeO_3 , XeO_4 . (a) Which one of these oxides is a solid, insoluble in water, that reacts with the acidic oxide SiO_2 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. (d) Which oxide would you be most likely to use in a scrubber for removing sulfur oxides from smokestack gases?

21. Consider the following set of oxides: MnO_2 , OsO_2 , SnO_2 , CO_2 , OsO_4 , XeO_4 , FeO_4 .
 (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.
22. *Complete and balance the following chemical equations (or tell if no reaction will occur):
- (a) $\text{Tl}_2\text{O} + \text{H}_2\text{O} \rightarrow$ (e) $\text{B}_2\text{O}_3 + \text{OH}^- + \text{H}_2\text{O} \rightarrow$
 (b) $\text{I}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow$ (f) $\text{FeO} + \text{P}_4\text{O}_{10} \rightarrow$
 (c) $\text{ClO}_2 + \text{OH}^- \rightarrow$ (g) $\text{MnO} + \text{H}^+(\text{aq}) \rightarrow$
 (d) $\text{La}_2\text{O}_3 + \text{H}^+ \rightarrow$
23. Complete and balance the following chemical equations (or tell if no reaction will occur):
- (a) $\text{SrO}(\text{s}) + \text{MoO}_3(\text{s}) \rightarrow$ (d) $\text{CaO}(\text{s}) + \text{MnO}(\text{s}) \rightarrow$
 (b) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow$ (e) $\text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow$
 (c) $\text{CaO}(\text{s}) + \text{TeO}_3(\text{s}) \rightarrow$
24. *Consider the following set of oxides: SrO , ZrO_2 , MoO_3 , 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) would be monomeric molecular substances? (d) Which of these oxides (if any) would most easily become a gas? (e) Which one of these oxides would most likely be a basic oxide that would be *insoluble* in water? Write an example of an equation for a chemical reaction that would justify classifying it as a basic oxide. (f) Which two of the above oxides will react *most exothermically* with each other? Write an equation for this reaction.
25. Classify each oxide below as acidic, basic, and so on. Then complete and balance the following equations, or note if no reaction is to be expected.
- (a) $\text{BaO}(\text{s}) + \text{P}_4\text{O}_{10}(\text{s}) \rightarrow$ (g) $\text{Y}_2\text{O}_3(\text{s}) + \text{P}_4\text{O}_{10}(\text{s}) \rightarrow$
 (b) $\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O} \rightarrow$ (h) $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O} \rightarrow$
 (c) $\text{Cr}_2\text{O}_3(\text{s}) + \text{H}^+(\text{aq}) \rightarrow$ (i) $\text{Na}_2\text{O}(\text{s}) + \text{V}_2\text{O}_5(\text{s}) \rightarrow$
 (d) $\text{Cr}_2\text{O}_3(\text{s}) + \text{H}_2\text{O} \rightarrow$ (j) $\text{Na}_2\text{O}(\text{s}) + \text{BaO}(\text{s}) \rightarrow$
 (e) $\text{SiO}_2(\text{s}) + \text{OH}^- \rightarrow$ (k) $\text{Na}_2\text{O}(\text{s}) + \text{P}_4\text{O}_{10}(\text{s}) \rightarrow$
 (f) $\text{TeO}_3(\text{s}) + \text{I}_2\text{O}_5(\text{s}) \rightarrow$ (l) $\text{Fe}_2\text{O}_3(\text{s}) + \text{BaO}(\text{s}) \rightarrow$
26. Which of the oxide acid–base reactions that you balanced in (a) Exercise 22; (b) Exercise 23; (c) Exercise 25 would be the most exothermic per mole of oxide ion transferred?
27. Describe the air-pollution problems associated with nonmetal oxides specified by your instructor, and devise some possible abatement procedures that might be tried.
28. *(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 (“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.

29. Write three balanced chemical equations showing the three steps by which ammonia is converted industrially to nitric acid.
30. Write an equation showing the low-cost process for making fertilizer-grade phosphoric acid from a common mineral source. Briefly describe one pollution problem that can arise from the manufacture of fertilizer-grade phosphoric acid in this manner.
31. Which of the following structural descriptions is/are inconsistent with the stoichiometry of the salt being described? (a) The compound CdCl_2 adapts an hep lattice of chloride ions in which all of the octahedral holes are occupied by cadmium ions. (b) The compound CdCl_2 adapts a ccp lattice of chloride ions in which one-half of the octahedral holes are occupied by cadmium ions. (c) The compound Li_2SO_4 adapts an hep lattice of sulfate ions in which all of the tetrahedral holes are occupied by lithium ions. (d) The compound $(\text{CH}_3)_4\text{NF}$ adapts a ccp lattice of tetramethyl-lammonium ions in which all of the octahedral holes are occupied by fluoride ions. (e) The compound $\text{Rb}_2\text{CsC}_{60}$ adopts a close-packed lattice in which the Rb^+ ions occupy all octahedral holes and the Cs^+ ions occupy all tetrahedral holes.
32. With reference to Tables B and C, describe some low oxidation number metal oxides that might be nonstoichiometric in a manner analogous to $\text{Fe}_{0.95}\text{O}$. Why would you not expect very high oxidation number oxides such as Mn_2O_7 and OsO_4 to be nonstoichiometric (i.e., $\text{Mn}_{2.2}\text{O}_7$ or $\text{Os}_{1.13}\text{O}_4$)?
33. *Which of the following formulas correspond to possible nonstoichiometric oxides? $\text{Ca}_{0.95}\text{O}$; $\text{Fe}_{0.95}\text{O}$; $\text{Co}_{0.95}\text{O}$; $\text{C}_{0.95}\text{O}$; $\text{Cr}_{0.95}\text{O}_3$; and $\text{Eu}_{0.95}\text{O}$.
34. *In the following list, (a) Which oxides are likely to be spinels? (b) Which oxides could be perovskites? NiFe_2O_4 , BaFe_2O_4 , BaTiO_3 , BeTiO_3 , BaSO_3 , TiZn_2O_4 , Ni_3O_4 , Pb_3O_4 , NaTaO_3 .
35. In the following list, (a) Which oxides are likely to be spinels? (b) Which oxides could be perovskites? TiCo_2O_4 , NaTaO_3 , SrTiO_3 , Zn_2SiO_4 , ZnSeO_3 , CoFe_2O_4 , FeCo_2O_4 .
36. Consider the following series of oxides: MnO , MnO_2 , Mn_2O_3 , Mn_2O_7 , Mn_3O_4 .
 - (a) Which of these will be most acidic? (b) Which of these will be most basic?
 - (c) Which is most likely to be soluble in water? (d) Which of these is least likely to show a nonstoichiometric (defect) structure? (e) Which (if any) of these would show a perovskite structure? (f) Which (if any) of these would show a spinel structure?
 - (g) Which (if any) of these would consist of (nonpolymerized) covalent molecules?
 - (h) Which would have the lowest melting point? (i) Which one is a liquid at room temperature? (j) Which would the rest be: gases, or solids? (k) Which is most likely to be amphoteric?
37. Choose the appropriate classification(s)—perovskite, spinel, nonstoichiometric, defect perovskite, superconductor—for each of the following mixed-metal oxides:
 - (a) BaTiO_3 ; (b) $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$; (c) $\text{Fe}_{0.95}\text{O}$; (d) Fe_3O_4 ; and (e) $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$.
38. Which of the following formulas correspond to possible nonstoichiometric oxides? $\text{Sr}_{0.95}\text{O}$, $\text{Fe}_{0.95}\text{O}$, $\text{Ni}_{0.95}\text{O}$, $\text{C}_{0.95}\text{O}$, $\text{Cr}_{0.95}\text{O}$, and $\text{N}_{0.95}\text{O}$.

39. *(a) Verify that the large unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ shown in Figure 13.7 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?
40. Determine the coordination number and list the nearest neighbors of the oxide ions in (a) perovskite; (b) $\text{YBa}_2\text{Cu}_3\text{O}_7$. (c) Confirm that Eq. (4.15) applies to these mixed-metal oxides if it is modified to read: Σ (Coordination No. of M) (No. of M in formula) = (Coordination No. of anion) (No. of anions in formula).
41. Do crystal field stabilization energies (Chapter 8) favor placing the Cu^{3+} ions in the square planar CuO_4 sites in the chains and the Cu^{2+} ions in the square pyramidal CuO_5 sheets, or do they favor the opposite placement?
42. Assign likely oxidation numbers to each element in the superconductors other than $\text{YBa}_2\text{Cu}_3\text{O}_7$ discussed in Section 13.5. In which of these would it be necessary to substitute other metal ions in order for the superconductor to contain both Cu^{2+} and Cu^{3+} ions? Describe the types of ions you would introduce in order to achieve this.
43. *Select one of the following minerals—(1) wollastonite = CaSiO_3 ; (2) talc = $\text{Mg}_3(\text{OH})_2(\text{Si}_4\text{O}_{10})$; (3) grunerite = $\text{Fe}_7(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; (4) monticellite = CaMgSiO_4 ; (5) stishovite = SiO_2 —as an 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 sheet polysilicate ion; (e) the mineral that would weather the most rapidly; (f) the mineral that would weather the most slowly.
44. Classify each of the following silicates as (1) a sheet polysilicate, (2) a chain or cyclic polysilicate, (3) a simple silicate, or (4) a double-chain polysilicate: (a) bustamite = $\text{CaMn}(\text{SiO}_3)_2$; (b) spudomene = $\text{LiAl}(\text{SiO}_3)_2$; (c) tremolite = $\text{Ca}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; (d) coffinite = $\text{U}(\text{SiO}_4)$; and (e) kaolinite = $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$.
45. Show that you understand the condensed drawings of the fragments of polysilicate structures shown in Figure 13.10 by redrawing them, using closed circles for Si atoms and open circles for O atoms, as in Figure 13.8. Redraw the following: (a) $\frac{1}{x}[\text{SiO}_3^{2-}]$; (b) $\frac{1}{x}[\text{Si}_4\text{O}_{11}^{6-}]$; and (c) $\frac{2}{x}[\text{Si}_4\text{O}_{10}^{4-}]$.
46. Select the proper structural type—framework aluminosilicate, sheet polysilicate; chain or cyclic polysilicate, simple silicate, double-chain polysilicate, sheet aluminosilicate—for each of the following silicates: (a) ureyite = $\text{NaCr}(\text{SiO}_3)_2$; (b) natrolite = $\text{Na}_2[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 2\text{H}_2\text{O}$; (c) biotite = $\text{K}(\text{Mg},\text{Fe})_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$; (d) cummingtonite = $\text{Mg}_7(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; (e) willemite = $\text{Zn}_2(\text{SiO}_4)$; (f) celsian = $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$; (g) chabazite = $\text{Ca}_6[\text{Al}_{12}\text{Si}_{24}\text{O}_{72}]$; (h) tremolite = $\text{Ca}_2(\text{Mg},\text{Fe})_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; and (i) phenacite = $\text{Be}_2(\text{SiO}_4)$.
47. *Consider the following silicates and aluminosilicates: tremolite = $\text{Ca}_2(\text{Mg},\text{Fe})_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; ureyite = $\text{NaCr}(\text{SiO}_3)_2$; chabazite = $\text{Ca}_6[\text{Al}_{12}\text{Si}_{24}\text{O}_{72}]$; kaolinite = $\text{Al}_4(\text{OH})_8(\text{Si}_4\text{O}_{10})$; and phenacite = $\text{Be}_2(\text{SiO}_4)$. (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 (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, $\text{Al}_4(\text{OH})_8[\text{Si}_4\text{O}_{10}]$.

48. The mineral used in construction as an asbestos replacement, xonotlite, $\text{Ca}_6(\text{OH})_{2-}(\text{Si}_6\text{O}_{17})$, is also a double-chain polysilicate, but it differs slightly in structure: propose a structure for xonotlite.
49. Predict the basicity classification of the anion in each of the following polysilicates or 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) $\text{Si}_2\text{O}_7^{6-}$; (b) $\text{Si}_3\text{O}_9^{6-}$; (c) $\text{Si}_4\text{O}_{11}^{6-}$; (d) $\text{Si}_4\text{O}_{10}^{4-}$; (e) anion of orthoclase; (f) anion of celsian; (g) anion of sodalite; (h) anion of ZSM-5; (i) anion of montmorillonite if only one-fourth of the aluminum ions are isomorphously substituted by magnesium ions.
50. Estimate the pK_a values of the corresponding conjugate acids of the silicate and aluminosilicate anions in the previous exercise, assuming that the hypothesis in it has some validity. If so, which of the above polysilicates, when ion exchanged into the H^+ forms, would be very strongly acidic?
51. *You are studying the mineral hornblende, $\text{Ca}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$, and find samples in which isomorphous substitution of the magnesium and the calcium has occurred. Which of the following are possible minerals which could result from isomorphous substitution processes in hornblende? (a) $\text{Y}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; (b) $\text{Na}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; (c) $\text{Na}_2\text{Mg}_3(\text{Fe}^{III})_2(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; (d) $\text{Y}_2\text{Mg}_3\text{Li}_2(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; and (e) $\text{Sr}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$.
52. Devise a possible asbestos substitute that would be the aluminosilicate obtained from asbestos by isomorphous substitution of the second kind.
53. The formula of the common form of the mineral garnet, andradite, can be written as $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$; there is a family of garnets including those listed later. For each member of the family, tell which principle (or principles) of isomorphous substitution is/are used to generate that member from common garnet (and confirm that it applies), and identify the oxidation state of any *d*-block metal ions: (a) almandite, $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; (b) grossularite, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; (c) spessartite, $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; (d) uvarovite, $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$; (e) the synthetic "YAG," used in lasers: $\text{Y}_3\text{Al}_5\text{O}_{12}$; and (f) the synthetic $\text{Y}_3\text{Fe}_5\text{O}_{12}$, of importance for its magnetic properties.
54. *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) $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; (b) $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KCr}(\text{SO}_4)_2$; (c) $\text{Pb}_5\text{Cl}(\text{PO}_4)_3$ and $\text{Pb}_5\text{Cl}(\text{VO}_4)_3$; (d) $\text{Rb}[\text{AlSi}_3\text{O}_8]$ and $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$; and (e) $\frac{3}{x}\{\text{SiO}_2\}_{24}$ and $\frac{3}{x}\{\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\}$.
55. Explain why Cu^{2+} should be less likely to be found isomorphously substituted in minerals than most other +2 charged *d*-block metal ions of similar size.
56. You are studying the feldspar $\text{K}[\text{AlSi}_3\text{O}_8]$, 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) $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$; (b) $\text{Rb}[\text{AlSi}_3\text{O}_8]$; (c) $\text{Na}[\text{AlSi}_3\text{O}_8]$; and (d) $\text{Ba}[\text{AlSi}_3\text{O}_8]$.

57. The formula of the mineral tremolite is $\text{Ca}_2(\text{Mg},\text{Fe})_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$. Interpret the part of the formula which is written $(\text{Fe},\text{Mg})_5$. What is the term for this phenomenon in geochemistry?
58. *You are in charge of disposing of asbestos being removed from schools, where it was used as insulation. Devise a reasonable scheme for chemically destroying the asbestos.
59. The relative availability of nutrient elements in soil as a function of soil pH is shown in Figure 13.13. Using the principles in the book to date, insofar as you can explain why each element is available and unavailable at the pH value given.
60. *Consider the following types of silicates or related soil minerals: sheet aluminosilicates; sheet polysilicates; chain or cyclic polysilicates; simple silicates; three-dimensional polymeric metal oxides (e.g., TiO_2); 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?
61. Consider the following minerals and oxides: lime = CaO ; ureyite = $\text{NaCr}(\text{SiO}_3)_2$; chabazite = $\text{Ca}_6[\text{Al}_{12}\text{Si}_{24}\text{O}_{72}]$; zirconia = ZrO_2 ; tremolite = $\text{Ca}_2(\text{Mg},\text{Fe})_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$; olivine = $(\text{Fe},\text{Mg})_2(\text{SiO}_4)$; kaolinite = $\text{Al}_4(\text{OH})_8(\text{Si}_4\text{O}_{10})$. (a) Which one would weather most quickly? (b) Which one would most characteristically be found on the 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?
62. To which type of oligomeric silicate anion is the anion found in Portland cement most closely related?
63. *Give the symbols for six elements that readily form polymeric oxo anions.
64. With reference to Table C, find other "cations," each of a different charge, that could substitute for P^{5+} in the phosphomolybdate ion. Give the resulting formula and charge of each heteromolybdate ion that results; rank these heteromolybdates in order of increasing basicity.
65. Molybdenum forms many heteropolymolybdate ions such as $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. (a) Are these chain, linked-chain, sheet, and so on polymers like the polysilicates? If so, tell which type of structure they have; if not, tell how their structures differ from the polysilicates. (b) Give two uses for such heteropolymolybdates.
66. Classify the basicity (weakly basic, etc.) of each of the following simple oxo anions. (Also provide the name if that is not given; provide the formula if that is not given.) Then tell whether the polyoxometallic anion listed is a weaker or stronger base than the simple oxo anion. (a) Chromate and dichromate and (b) molybdate and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.
67. Complete and balance: $\text{H}^+(\text{aq}) + [\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow$.
68. You are studying the feldspar mineral orthoclase, $\text{K}[\text{AlSi}_3\text{O}_8]$, and find samples in which isomorphous substitution of some of the ions has occurred. (a) State the principles that govern the possible choices of foreign ions that can substitute for given ions in minerals without altering the crystal lattice type (i.e., which can substitute isomorphously). Which of the following formulas represent minerals that could be

found in solid solution in orthoclase, as a result of isomorphous substitution (replacement) of ions in orthoclase? (1) $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$, (2) $\text{Rb}[\text{AlSi}_3\text{O}_8]$, (3) $\text{Na}[\text{AlSi}_3\text{O}_8]$, (4) $\text{Ba}[\text{AlSi}_3\text{O}_8]$, (5) $\text{K}[\text{YSi}_3\text{O}_8]$, (6) $\text{K}[\text{AlSi}_3\text{S}_8]$, and (7) $\text{Na}[\text{Al}_2\text{Si}_2\text{O}_8]$. (b) You are hoping to find a good mineral source of the element yttrium, Y, for use in high-temperature superconductors. Which of the following minerals would (at least in theory) be likely places in which to find an appreciable concentration of yttrium as the compound indicated? (1) in Bi_2S_3 as Y_2S_3 , (2) in orthoclase as $\text{K}[\text{YSi}_3\text{O}_8]$, (3) in CePO_4 as YPO_4 , (4) in sea water as $\text{Y}(\text{H}_2\text{O})_n^{3+}$, (5) in the core of the earth (largely metallic iron and nickel) as metallic Y, and (6) in deposits of $\text{Ca}_2\text{Mg}_5(\text{OH})_2(\text{Si}_4\text{O}_{11})_2$ as $\text{Y}_2\text{Mg}_5(\text{OH})_2[\text{Al}_2\text{Si}_2\text{O}_{11}]_2$. (c) If you are indeed able to find samples of the minerals $\text{K}[\text{YSi}_3\text{O}_8]$ and $\text{Y}_2\text{Mg}_5(\text{OH})_2[\text{Al}_2\text{Si}_2\text{O}_{11}]_2$, you would expect them to be examples of which classes of silicate minerals? (1) Framework (three-dimensional) aluminosilicates. (2) Chain or cyclic polysilicates. (3) Simple silicates. (4) Double-chain polysilicates. (5) Sheet aluminosilicates. How many oxygen atoms would you expect to find around each silicon atom in these minerals? Would you anticipate finding a larger or smaller number of oxygen atoms around the yttrium?

Notes

1. Note to the Instructor: If Chapter 12 has not yet been covered, it will be desirable to cover Section 12.1 before beginning this chapter.
2. If we need to avoid fractional numbers of atoms, as in nomenclature, we may write, for example, Re_2O_7 as the *simplest formula unit*.
3. Although isomers of organic compounds have the same molecular formula, which these do not. Among elements, the term *allotropes* covers this distinction; some have advocated using this term among compounds as well.
4. More elaborate but more precise methods for predicting structure are given by I. D. Brown: *Acta Crystallogr., Sect. B*, **44**, 545 (1988); **48**, 533 (1992).
5. Recall that some of the heavier **and d-block** elements show relativistic or crystal-field effects that routinely produce unusually low coordination numbers.
6. In principle, the number of unshared electron pairs should be multiplied by a factor greater than 1, since unshared electron pairs take extra space. However, it is difficult to know in practice exactly what value that factor would have.
7. For radius ratios over 1.0, the inverse radius ratio $r_{\text{anion}}/r_{\text{cation}}$ should be used in the prediction, as mentioned in Section 4.7.
8. A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, UK, 1984.
9. Melting and boiling points are taken from M. C. Ball and A. H. Norbury, *Physical Data for Inorganic Chemists*, Longmans, London, 1974, or from the *Handbook of Chemistry and Physics*, 50th ed., Chemical Rubber Publishing Company, Cleveland, OH, 1969. Values were also checked for consistency with data given in the *Alfa Catalog 1983-1984*, Danvers, Morton-Thiokol Inc., MA, 1983.
10. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 5th ed., Wiley-Interscience, New York, 1988; N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984.
11. Yu. M. Kiselev, N. S. Kopelev, V. I. Spitsyn, and L. I. Martynenko, *Dokl. Chem.*, **292**, 29 (1987).
12. D. Leopold and K. Seppelt, *Angew. Chem. Int'l. Ed. Engl.*, **33**, 975 (1994); K. Seppelt, *Acc. Chem. Res.*, **30**, 111 (1997).
13. A. Schulz, I. C. Tornieporth-Oetting, and T. M. Klapötke, *Angew. Chem. Int'l. Ed. Engl.*, **32**, 1610 (1993).
14. Several of these monomeric oxides, being nonpolar covalent molecules, are actually more soluble in carbon tetrachloride than they are in water.