

# Periodicity

The most fascinating aspect of inorganic chemistry as well as its most difficult problem is the diversity of reactions and structures encountered in the chemistry of somewhat over one hundred elements. The challenge is to be able to treat adequately the chemistry of boranes and noble gas fluorides and ferrocene and lanthanum compounds without developing a separate set of rules and theory for each element. The tool that has kept the inorganic chemist from throwing up his hands in despair is the periodic table, now slightly over one hundred years old.<sup>1</sup> It is of such overwhelming importance in the correlation of the properties of the elements that entire books have been written on this theme.<sup>2</sup> It is considered so essential that no general chemistry textbook would be complete without a discussion of the trends summed up in Chapter 2 (pp. 38–50). Unfortunately the impression is often given that all of the periodic properties vary smoothly.

## Fundamental trends

The fundamental trends of the periodic chart have been discussed in Chapter 2. They may be summarized as follows. Within a family there are increases in size and decreases in ionization energy, electron affinity, electronegativity, etc. Increasing the atomic number across a given period results in concomitant increases in ionization energy, electron affinity, and electronegativity but a decrease in size. The change in effective atomic number within a period is reasonably smooth, but the various periods differ in length (8, 18, and 32 elements). The properties of an element will depend upon whether it follows an 8, 18, or 32 sequence. One of the best known examples is the similarity in properties of

<sup>1</sup> Periodic classifications of the elements by Dmitri Mendeleev and by Lothar Meyer appeared in 1869. For a centennial-celebrating discussion of the periodic table, see J. W. van Spronsen, "The Periodic System of Chemical Elements," Elsevier, Amsterdam, 1969.

<sup>2</sup> R. Rich, "Periodic Correlations," Benjamin, New York, 1965; R. T. Sanderson, "Chemical Periodicity," Van Nostrand-Reinhold, New York, 1960. The latter book was rewritten but kept the periodicity theme and appeared under the title "Inorganic Chemistry" in 1967.

hafnium, tantalum, tungsten, and rhenium to those of zirconium, niobium, molybdenum, and technetium, respectively, as a result of the lanthanide contraction (see Chapter 12). Similar effects follow the filling of the *d* levels (very rarely referred to as the "scandide" contraction). A second factor tending to affect the regularity of properties is the absence of *d* orbitals in the elements lighter than sodium. This results in a discontinuity of properties from the second-row elements, Li–F, to the heavier congeners.

## FIRST- AND SECOND-ROW ANOMALIES

In many ways the first ten elements differ considerably from the remaining 90%. Hydrogen is a classic example—it belongs neither with the alkali metals nor with the halogens although it has some properties in common with both. Thus it has a +1 oxidation state in common with the alkali metals, but the bare  $H^+$  has no chemical existence<sup>3</sup> and hydrogen tends to form covalent bonds that have properties more closely resembling those of carbon than those of the alkali metals. With the halogens it shares the tendency to form a –1 oxidation state, even to the extent of forming the hydride ion,  $H^-$ ; however, the latter is a curious chemical species. In contrast to the proton which was anomalous because of its vanishingly small size, the hydride ion is unusually large. It is larger than any of the halide ions except iodide!<sup>4</sup> The source of this apparent paradox lies in the lack of control of a single nuclear proton over two mutually repelling electrons. Since the hydride ion is large and very polarizable it certainly does not extend the trend of  $I^-$  through  $F^-$  of decreasing size and increasing basicity and hardness.

The elements of the second row also differ from their heavier congeners. Lithium is anomalous among the alkali metals and resembles magnesium more than its congeners. In turn, in Group IIA beryllium is more closely akin to aluminum than to the other alkaline earths. The source of this effect is discussed below. We have already seen that fluorine has been termed a superhalogen on the basis of its differences from the remainder of Group VIIA.

One simple difference that the elements Li to F have with respect to their heavier congeners is in electron-attracting power. Thus fluorine is much more reactive than chlorine, bromine, or iodine; lithium is less reactive than its congeners.<sup>5</sup> The most electronegative and smallest element of each family will be those of the second row.

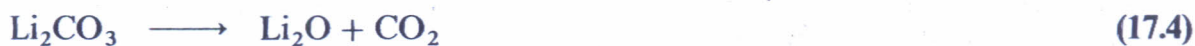
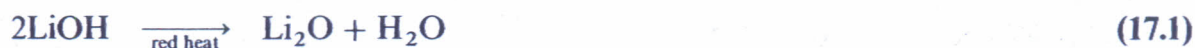
The great polarizing power of the  $Li^+$  cation was commented upon in Chapter 3. As a result of its small size and higher electronegativity this ion destabilizes salts that

<sup>3</sup> Those who disapprove of writing  $H_3O^+$  often point out that the hydration number of the  $H^+$  is uncertain and "all cations are hydrated in solution." To treat  $H^+$  (rather than  $H_3O^+$ ) as a cation similar to  $Na^+$ , for example, is to equate nuclear particles with atoms, a discrepancy by a factor of about  $10^5$ .

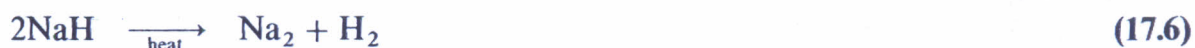
<sup>4</sup> Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, 1960, p. 514, has provided an estimate of 208 pm for the hydride ion compared to 216 pm for  $I^-$ . To be sure, the existence of an unpolarized hydride ion is even less likely than an unpolarized anion of some other kind, but insofar as ionic radii have meaning this would be the best estimate of the size of a free hydride ion.

<sup>5</sup> The inherent unreactivity of lithium is offset in aqueous solution by the exothermic hydration of the very small  $Li^+$  ion. Nevertheless, in general, lithium is a less reactive metal than Na, K, Rb, or Cs.

are stable for the remaining alkali metals:



In contrast, for the large polarizable hydride ion which can bond more strongly by a covalent bond the lithium compound is the *most* stable:



### The diagonal relationship

It was mentioned previously that a strong resemblance obtained between Li and Mg, Be and Al, C and P, and other "diagonal elements," and it was pointed out that this could be related to a size-charge phenomenon (see p. 130). Some examples of these resemblances are as follows:

*Lithium-magnesium.* There is a large series of lithium alkyls and lithium aryls which are useful in organic chemistry in much the same way as the magnesium Grignard reagents. Unlike Na, K, Rb, or Cs, but like Mg, lithium reacts directly with nitrogen to form a nitride:



Finally, the solubility of several lithium compounds more nearly resembles those of the corresponding magnesium salts than of other alkali metal salts.

*Beryllium-aluminum.* These two elements resemble each other in several ways. The oxidation *emfs* of the elements are similar ( $\mathcal{E}_{\text{Be}}^0 = 1.85$ ;  $\mathcal{E}_{\text{Al}}^0 = 1.66$ ), and although reaction with acid is thermodynamically favored, it is rather slow, especially if the surface is protected by the oxide. The similarity of the ionic potential (see p. 130) for the ions is remarkable ( $\text{Be}^{+2} = 6.45$ ,  $\text{Al}^{+3} = 6.00$ ) and results in similar polarizing power and of the cations. For example, the carbonates are unstable, the hydroxides dissolve readily in excess base, and the Lewis acidities of the halides are comparable.

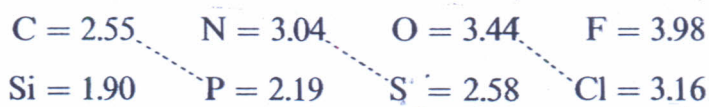
*Boron-silicon.* Boron differs from aluminum in showing almost no metallic properties and its resemblance to silicon is greater. Both boron and silicon form volatile, very reactive hydrides; the hydride of aluminum is a polymeric solid. The halides (except  $\text{BF}_3$ ) hydrolyze to form boric acid and silicic acid. The oxygen chemistry of the borates and silicates also has certain resemblances.

**Table 17.1** Maximum coordination numbers of the nonmetals as shown by the fluorides

CF <sub>4</sub>	NF <sub>3</sub> <sup>a</sup>	OF <sub>2</sub> <sup>a</sup>	FF(F <sub>3</sub> <sup>-</sup> )
SiF <sub>6</sub> <sup>-2</sup>	PF <sub>6</sub> <sup>-</sup>	SF <sub>6</sub>	ClF <sub>5</sub> <sup>a</sup>
			⋮
			IF <sub>7</sub> (IF <sub>8</sub> <sup>-</sup> )

<sup>a</sup> N, O, and other elements can achieve higher coordination in onium salts, e.g., NH<sub>4</sub><sup>+</sup>.

*Carbon–phosphorus, nitrogen–sulfur, and oxygen–chlorine.* All metallic properties have been lost in these elements, and so charge-to-size ratios have little meaning. However, the same effects appear in the electronegativities of these elements, which show a strong diagonal effect.<sup>6</sup>



The similarities in electronegativities are not so close as those of the ionic potential for Be<sup>+2</sup> and Al<sup>+3</sup>. The heavier element in the diagonal pair always has a lower electronegativity, but the effect is still noticeable. Thus, when considering elements that resemble carbon, phosphorus is as good a choice as silicon, and the resemblance is sufficient to establish a base from which notable *differences* can be formulated.

## THE USE OF *d* ORBITALS BY NONMETALS

It is an obvious fact that the elements Li to F are restricted to the set of *s* and *p* orbitals, but their heavier congeners such as Na to Cl can use 3*s*, 3*p*, and 3*d* orbitals. This provides extra opportunities for bonding in the heavier elements that their light congeners do not enjoy. The extent to which these elements use valence shell *d* orbitals is a matter of some controversy. Some of the experimental evidence will be discussed first, followed by theoretical interpretations.

### Experimental evidence for $\sigma$ bonds involving *d* orbitals

It is a fact that the second-row elements, Li to F, show a maximum covalence of 4,<sup>7</sup> corresponding to a maximum hybridization of *sp*<sup>3</sup>. In contrast, third-row and heavier elements show 5, 6, and 7 coordination (Table 17.1) consistent with use of *d* orbitals.

<sup>6</sup> These values are Pauling thermochemical electronegativities rather than those based on ionization energy–electron affinity. This choice of empirical values was made to obviate the necessity to choose (arbitrarily) the proper hybridization.

<sup>7</sup> In the metallic state lithium and beryllium have coordination numbers greater than 4, as does elemental boron in icosahedral structures. In each of these examples multicenter bonding occurs and the concept of fixed bonds is not applicable.

A second factor which may affect the coordination number and which does not require the assumption that *d* orbitals participate is size. One would expect that the coordination number would increase upon progressing down the chart, and indeed it does. Thus the number of  $\sigma$  bonds a nonmetal forms may be determined as much by the number of substituents that can fit as by the number of orbitals available.

Experimental evidence for  $\pi$  bonding;  
the phosphorus–oxygen bond in phosphoryl compounds

In the case of  $\pi$  bonding we again find the old problem of detecting the existence of a bond. We can infer the presence of a  $\sigma$  bond when we find two elements at distances considerably shorter than the sum of their van der Waals radii. The detection of a  $\pi$  bond depends on more subtle criteria: shortening or strengthening of a bond, stabilization of a charge distribution, etc., experimental data which may be equivocal.

One example of the apparent existence of  $\pi$  bonding is in phosphine oxides. Most tertiary phosphines are unstable relative to oxidation to the phosphine oxide:



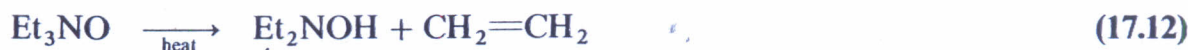
This reaction takes place so readily that aliphatic phosphines must be protected from atmospheric oxygen. The triarylphosphines are more stable in this regard but still can be oxidized readily:



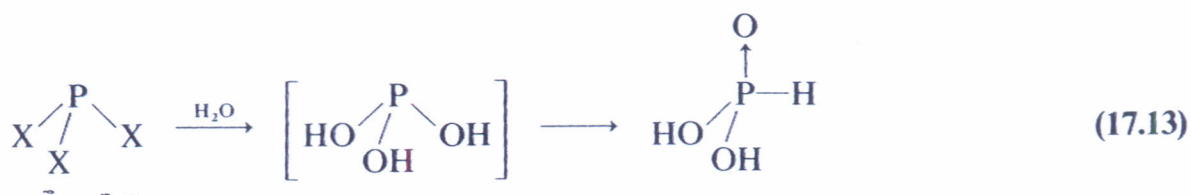
In contrast, aliphatic amines do not have to be protected from the atmosphere although they can be oxidized:



However, the amine oxides decompose upon heating:



a reaction completely unknown for the phosphine oxides, which are thermally stable. In fact, it has been said that "tertiary phosphine oxides have the reputation of being the most stable chemical structures in the family of organophosphorus compounds."<sup>8</sup> They are not reduced even by heating with metallic sodium. The tendency of phosphorus to form such P → O or P=O linkages is one of the driving forces of phosphorus chemistry and may be used to rationalize and predict reactions and structures. For example, the lower phosphorus acids exist in the 4-coordinate structures even though they are prepared by the hydrolysis of 3-coordinate halides:



<sup>8</sup> J. R. Van Wazer, "Phosphorus and Its Compounds," Wiley (Interscience), New York, 1958, Vol. I, p. 287.



**Table 17.2** Infrared stretching frequencies of some phosphoryl compounds

Compound	$\bar{\nu}_{\text{PO}}$ (cm <sup>-1</sup> )	$\Sigma \chi_{\text{MJ}}$
F <sub>3</sub> PO	1404	11.70
F <sub>2</sub> ClPO	1358	10.75
Cl <sub>3</sub> PO	1295	8.85
Cl <sub>2</sub> BrPO	1285	8.52
ClBr <sub>2</sub> PO	1275	8.19
Br <sub>3</sub> PO	1261	7.86
$\phi_3\text{PO}$	1190	(7.2)
Me <sub>3</sub> PO	1176	(6.0)

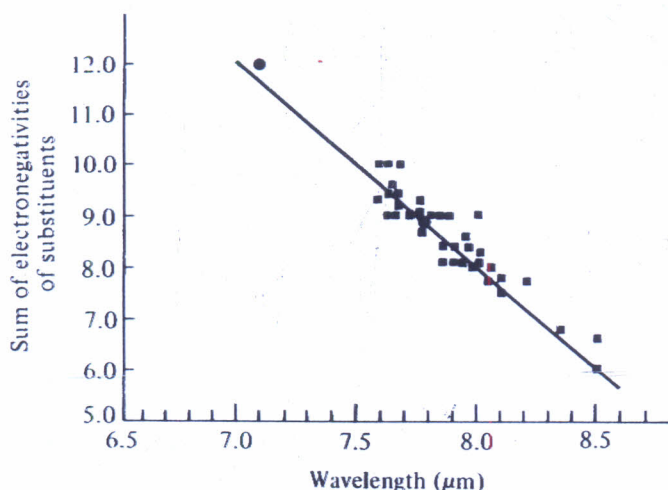
The double bond character introduced by the latter strengthens the bond and accounts for the extraordinary stability of the phosphorus oxygen linkage. Note that this extra stability cannot be attributed to ionic resonance energy (*a priori* a reasonable suggestion since the difference in electronegativity is greater in P—O than N—O) because the dipole moment of the *nitrogen* compound is greater than that of the phosphorus compound, a result completely unexpected on the basis of electronegativities, unless consideration is taken of canonical form 17.19 (II), which would be expected to lead to a reduced moment.

✓ A comparison of the bond energies also supports the above interpretation. The dissociation energies of P=O bonds in a variety of compounds lie in the range of 500–600 kJ mol<sup>-1</sup> compared with values for N→O of about 200–300 kJ mol<sup>-1</sup>.<sup>10</sup> The value for the latter is typical of what we might expect for a single bond, but 600 kJ mol<sup>-1</sup> is stronger than any known single bond (see Chapter 6, p. 263). A closer examination of the strengths of various P=O bonds in terms of infrared stretching frequencies shows some interesting trends. For a series of similar molecules, such as the phosphine oxides, the stretching frequency provides an indication of the strength of the bond (Table 17.2).<sup>11</sup> The highest stretching frequency among the phosphoryl compounds is that of F<sub>3</sub>PO, and the lowest of the halides is that of Br<sub>3</sub>PO (the iodo compound is unknown). When the stretching frequencies (in the form of wavelength,  $\lambda = 1/\bar{\nu}$ ) are plotted as a function of the sum of the electronegativities of the substituents, a straight line is obtained (Fig. 17.1). This relationship has been used to obtain group electronegativities from the stretching frequencies of phosphine oxides, for example, which are internally self-consistent and which agree with those obtained by other means (see Table 3.13) except in the case of groups such as —NH<sub>2</sub> which can compete in the  $\pi$  bonding.<sup>12</sup>

<sup>10</sup> R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, 1965, pp. 67–70.

<sup>11</sup> Note that the dissociation energy, R<sub>3</sub>PO → R<sub>3</sub>P + O, is not a sensitive measure of the P=O bond energy since the remaining three bonds may be strengthened or weakened in the dissociation process. The IR stretching frequency is a function of the force constant, *k*, and the reduced mass,  $\mu$ , of the molecule. If the molecule is assumed to be a light oxygen atom vibrating on a "fixed" larger mass of the R<sub>3</sub>P group, the reduced mass is constant, and so changes in frequency will reflect corresponding changes in the force constant. For similar molecules the force constant will be related to the total bond energy.

<sup>12</sup> J. V. Bell et al., *J. Am. Chem. Soc.*, 1954, 76, 5185. See also M. A. Davis, *J. Org. Chem.*, 1967, 32, 1161, and papers cited therein.



**Fig. 17.1** The relation between the stretching frequency (expressed as wavelength) and the electronegativity of the substituents. Circles represent halides, squares other substituted P = O compounds. [From J. V. Bell et al., *J. Am. Chem. Soc.*, 1954, 76, 5185. Reproduced with permission.]

The correlation between the electronegativity of substituent groups and the strength of the P=O bond provides support for a  $\pi$ -bonding model but not for the alternative dative  $\sigma$ -only model. The latter might be expected to be destabilized as electron density is removed from the phosphorus, requiring it to withdraw electrons from the P → O bond, weakening it. In contrast, if the oxygen can back bond to the phosphorus through a  $d-p$   $\pi$  bond, the induced charge on the phosphorus can be diminished and the P=O bond strengthened.

The bond lengths in phosphoryl compounds are in accord with the concept of double bond character.<sup>13</sup> In the simplest case, that of P<sub>4</sub>O<sub>10</sub>, there are two P—O bond lengths. There are 12 relatively long ones (163 pm) within the cage framework proper and 4 shorter ones (139 pm) between the phosphorus atoms and the oxygen atoms external to the cage. It is interesting to note that the ratio of these two bond lengths (~0.85) is about the same as C=C to C—C or C=O to C—O.

Isoelectronic with the phosphine oxides are the phosphonium ylids, R<sub>3</sub>PCH<sub>2</sub>.<sup>14</sup> Like the oxides, two resonance forms

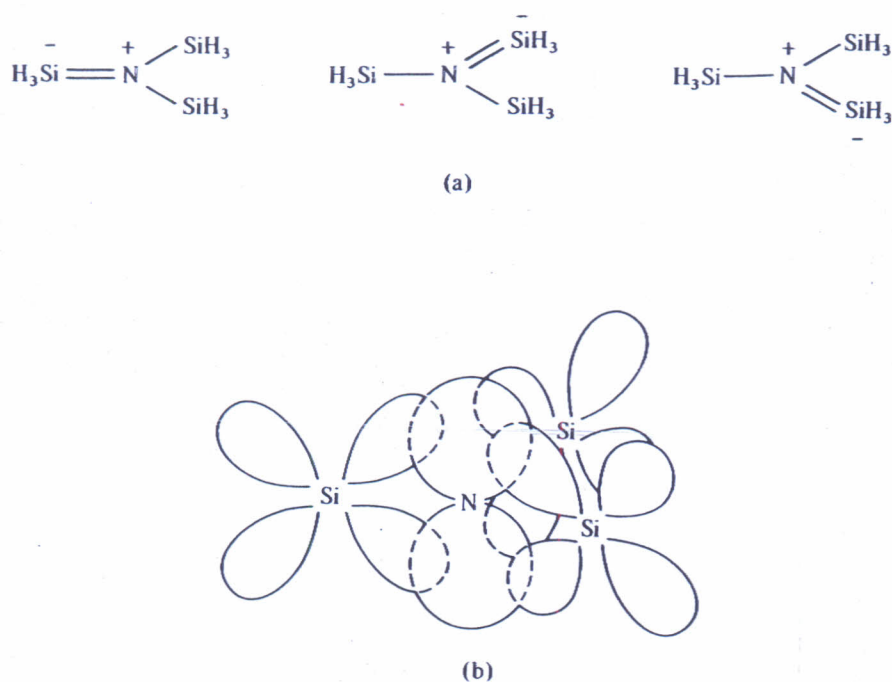


contribute to the stability of the phosphonium ylids but not the corresponding ammonium ylids, R<sub>3</sub>N<sup>+</sup>—C<sup>-</sup>H<sub>2</sub>. This difference is reflected in the reactivity. The ammonium ylids are generally quite basic and quite reactive; the phosphonium ylids are much less so,

<sup>13</sup> The complete discussion, including partial ionic character, is too long to present here. See R. F. Hudson, *Adv. Inorg. Chem. Radiochem.*, 1963, 5, 347, and K. A. R. Mitchell, *Chem. Rev.*, 1969, 69, 157.

<sup>14</sup> The nomenclature is unfortunate since the “-onium” name used with the ylids focuses attention on the polar nature (resonance structure (I)) whereas the “-ine oxide” name seems to focus more on the covalent nature (resonance structure (II)). Electronically, both types of molecules are resonance hybrids of (I) and (II).





**Fig. 17.2** Delocalization of the lone pair in trisilylamine. (a) Resonance structures. (b) Overlap of  $d_{\text{Si}}$  and  $p_{\text{N}}$  orbitals.

many not being sufficiently basic to abstract a proton from water and, in fact, not dissolving in water unless strong acids are present.<sup>15</sup>

#### Evidence from bond angles

The trimethylamine molecule has a pyramidal structure much like that of ammonia with a  $\text{CH}_3\text{—N—CH}_3$  bond angle of  $107.8^\circ \pm 1^\circ$ . In contrast, the trisilylamine molecule is planar. Although steric effects of the larger silyl groups might be expected to open up the bond angles, it seems hardly possible that they could force the lone pair out of a fourth "tetrahedral" orbital and make the molecule perfectly planar (even  $\phi_3\text{N}$  has bond angles of  $116^\circ$ ). It seems more likely that the lone pair adopts a pure  $p$  orbital on the nitrogen atom because orbitals on the three silicon atoms can overlap with it and delocalize the lone pair over the entire system (Fig. 17.2).

Rather similar results are obtained by comparing the bond angles in the silyl and methyl ethers (Fig. 17.3) and isothiocyanates (Fig. 17.4). In the former the oxygen is hybridized approximately  $sp^3$  with two lone pairs on the oxygen atom in dimethyl ether as compared to an approximate  $sp^2$  hybrid in disiloxane with  $\pi$  bonding. In the same way the methyl isothiocyanate molecule,  $\text{CH}_3\text{N=C=S}$ , has a lone pair localized on the nitrogen atom, hence is bent ( $\text{N} \sim sp^2$ ), but the delocalization of this lone pair into a back-bonding  $\pi$  orbital to the silicon atom of  $\text{H}_3\text{SiN=C=S}$  leads to a linear structure for this molecule.

The hypothesized delocalization of lone pair electrons in the above silicon compounds is supported by the lowered basicity of the silyl compounds as compared to the

<sup>15</sup> A. W. Johnson, "Ylid Chemistry," Academic Press, New York, 1966.

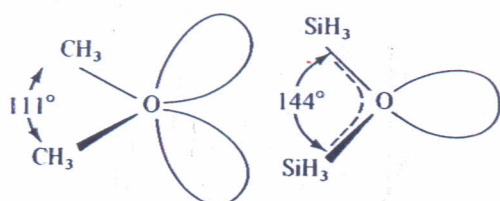


Fig. 17.3 Comparison of the molecular structure of dimethyl ether and disiloxane.

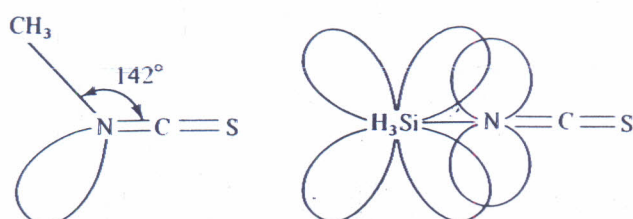


Fig. 17.4 Comparison of the molecular structure of methyl isothiocyanate and silyl isothiocyanate.

corresponding carbon compounds. This reduced basicity is contrary to that expected on the basis of electronegativity effects operating through the  $\sigma$  system since silicon is less electronegative than carbon. It is consistent with an "internal Lewis acid-base" interaction between the nitrogen and oxygen lone pairs and empty acceptor  $d$  orbitals on the silicon. Experimentally this reduced basicity is shown by the absence of disiloxane adducts with  $\text{BF}_3$  and  $\text{BCl}_3$ :



and by the absence of trisilylammonium salts. Instead of onium salt formation trisilylamine is cleaved by hydrogen chloride:



#### Theoretical arguments against $d$ orbital participation in nonmetals

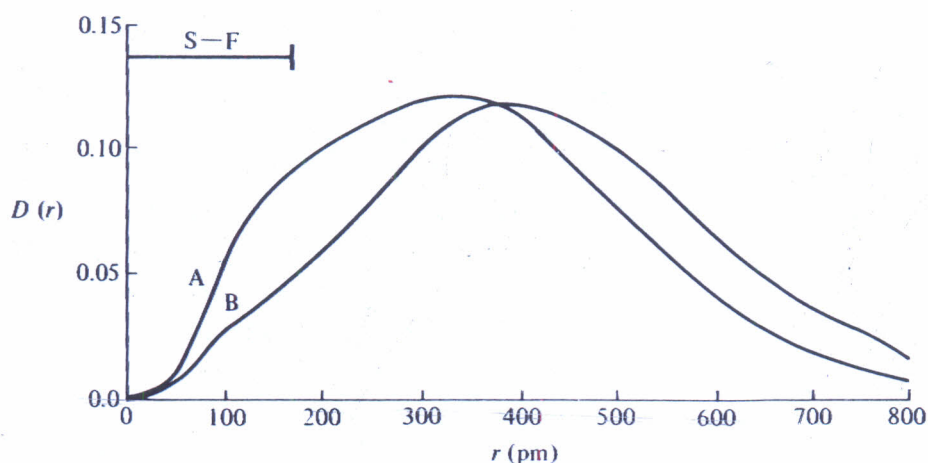
Several workers have objected to the inclusion of  $d$  orbitals in bonding in nonmetals. The principal objection is to the large promotion energy required to effect:



where  $m = 0$  (P), 1 (S), or 2 (Cl), to achieve a maximum multiplicity and availability of electrons for bonding. A second factor which does not favor the utilization of  $d$  orbitals is the poor overlap that they make with the orbitals of neighboring atoms. The  $3d$  orbitals of the free sulfur atoms, for example,<sup>16</sup> are shielded completely<sup>17</sup> by the lower-lying

<sup>16</sup> These same general arguments apply to the other nonmetals as well.

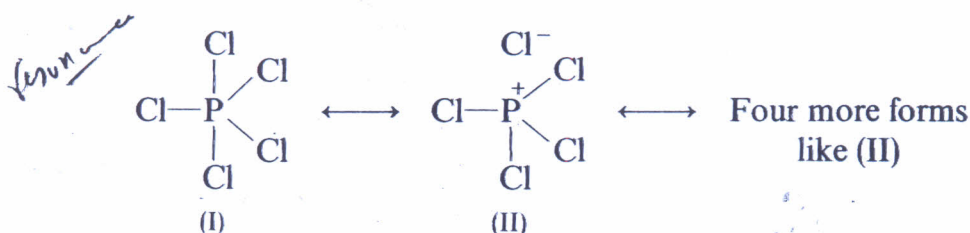
<sup>17</sup> In the simplified Slater scheme (p. 36) the  $d$  orbitals are assumed to be shielded to the extent of 1.0 electronic unit for each electron lying "below" them.



**Fig. 17.5** The  $3d$  orbital distribution functions in  $d^1$  configurations: (A) in the  ${}^6D$  term of  $P(sp^3d)$ ; (B) in the  ${}^5D$  term of  $S(s^2p^3d)$ . Line represents a typical S—F bond length. [Modified from K. A. R. Mitchell, *Chem. Rev.*, **1969**, 69, 157. Reproduced with permission.]

electrons and hence do not feel the nuclear charge as much as the  $3s$  and  $3p$  electrons. As a result they are extremely diffuse, having radial distribution maxima at a distance which is approximately *twice* a typical bond distance (Fig. 17.5). This results in extremely poor overlap and weak bonding.<sup>18</sup>

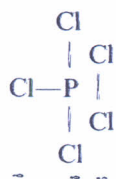
Two alternatives have been provided to account for the higher oxidation states of the nonmetals without invoking the use of the high energy  $d$  orbitals. Pauling has suggested that resonance of the following type could take place.<sup>19</sup>



Only structure I involves  $d$  orbitals, and so the  $d$  character of the total hybrid is small. Each P—Cl bond has 20% ionic character and 80% covalent character from resonance structures such as II. Pauling has termed the “extra” bonds formed (over and above the

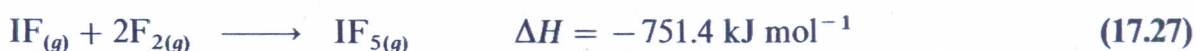
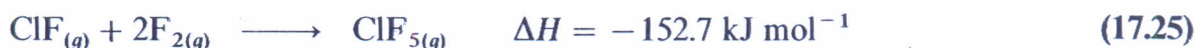
<sup>18</sup> A point that may easily be overlooked in this regard is that the poor overlap results not only from the poor spatial arrangement of a diffuse orbital but also from the concomitant low value of the wave function,  $\Psi_s$ , at any particular point in space, and so a low buildup of electron density from  $\Psi_s \cdot \Psi_s$ .

<sup>19</sup> Pauling listed a third type of canonical structure,



but pointed out that the Cl—Cl interaction is a very “long bond” and does little to stabilize the molecule. [L. Pauling, “The Nature of the Chemical Bond,” 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp. 177–179.]

four in a noble gas octet or "argononic" structure) as "transargononic" bonds and pointed out that they tend to be weaker than "normal" or "argononic" bonds and form only with the most electronegative ligands. Thus the average bond energy in  $\text{PCl}_3$  is  $317 \text{ kJ mol}^{-1}$  but in  $\text{PCl}_5$  it is only  $165 \text{ kJ mol}^{-1}$ .<sup>20</sup> The same effect is found in  $\text{PF}_3$  and  $\text{PF}_5$ , but in this case the difference in bond energy is only  $61.1 \text{ kJ mol}^{-1}$ , corresponding to the stabilization of the structure by increased importance of the ionic structures in the fluorides. The stabilization of these structures by differences in electronegativity is exemplified by the tendency to form the higher halogen fluorides.<sup>21</sup> The enthalpies of fluorination of the halogen monofluorides are:



The second alternative is the three-center, four-electron bond developed by simple molecular orbital theory for the noble gas fluorides (see pp. 767–769). Since this predicts that each bonding pair of electrons (each "bond") is spread over three nuclei, the bond between two of the nuclei is less than that of a normal two-center, two-electron bond. Furthermore, since the nonbonding pair of electrons is localized on the fluorine atoms, there is a separation of charge ("ionic character"). In both respects, then, this interpretation agrees with Pauling's approach and with the experimental facts.

#### Theoretical arguments in favor of *d* orbital participation

In contrast to the arguments presented against participation by *d* orbitals in the bonding of nonmetals, several workers have pointed out that the large promotion energies and diffuse character described above are *properties of an isolated sulfur atom*. What we need to know are the *properties of a sulfur atom in a molecule*, such as  $\text{SF}_6$ . This is an exceedingly difficult problem and cannot be dealt with in detail here.<sup>22</sup> However, we have seen how it is possible to calculate such properties as electronegativity on isolated atoms as charge is added or withdrawn (see pp. 153–155) and how this might *approximate* such properties in a molecular environment.

It is apparent from the preceding discussions that participation of *d* orbitals, if it occurs at all, is found only in the nonmetals when in high oxidation states with electronegative substituents. The partial charge induced on the central P or S atom will be large merely from the electronegativity of the fluorine (as in  $\text{PF}_5$ ,  $\text{SF}_6$ ) or oxygen (as in  $\text{OPX}_3$ ,  $\text{O}_2\text{SX}_2$ ) irrespective of any bonding model (such as Pauling's or the three-center bond) invoked.

<sup>20</sup> For a more complete discussion of this point, see L. Pauling, "General Chemistry," 3rd ed., Freeman, San Francisco, 1970, pp. 244–247.

<sup>21</sup> See Table 15.2 and attendant discussion. The values in Eqs. 17.25–17.27 differ slightly from those given by Pauling (footnote 20) in order to be self-consistent with the values in Table 15.2.

<sup>22</sup> For a detailed discussion of this complex problem, see K. A. R. Mitchell, *Chem. Rev.*, 1969, 69, 157, and references therein.

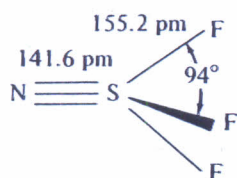


Fig. 17.6 Molecular structure of thiazyl trifluoride,  $\text{NSF}_3$ .

We have seen in Chapter 2 that the  $3d$  orbital lies above the  $4s$  orbital at atomic number 20 but falls below as the atomic number increases. Furthermore, in the  $\text{M}^{+2}$  ions the  $3d$  orbital lies below the  $4s$  orbital at least as soon as atomic number 22 ( $\text{Ti}^{+2}$  is  $d^2$ , not  $s^2$ ). This is a general phenomenon: Increasing effective nuclear charge makes the energy levels of an atom approach more closely the degenerate levels of the hydrogen atom. We might expect, in general, that increasing the effective nuclear charge on the central atom as a result of inductive effects would result in the lowering of the  $d$  orbitals more than the corresponding  $s$  and  $p$  orbitals since the former are initially shielded more and hence will be more sensitive to changes in electron density. The promotion energy would thus be lowered. A second effect of large partial charges on the central atom will be a shrinking of the large, diffuse  $d$  orbitals into smaller, more compact orbitals that will be more effective in overlapping neighboring atomic orbitals. For example, sample calculations indicate that in  $\text{SF}_6$  the  $d$  orbitals have been contracted to an extent that the radius of maximum probability is only 130 pm compared with the large values in the free sulfur atom.

#### Experimental evidence for $d$ orbital contraction and participation

One of the most remarkable molecules is thiazyl trifluoride,  $\text{NSF}_3$  (Fig. 17.6). This compound is very stable. It does not react with ammonia at room temperature, with hydrogen chloride even when heated, or with metallic sodium at temperatures below  $400^\circ\text{C}$ . The S—N bond, 141.6 pm, is the shortest known between these two elements. The FSF bond angles of  $94^\circ$  are compatible with approximate  $sp^3$  bonding<sup>23</sup> and the presence of an  $sp^3$  hybrid  $\sigma$  bond and two  $p$ — $d$   $\pi$  bonds between the sulfur and the nitrogen. The contraction of the  $d$  orbitals by the inductive effect of the fluorine atoms presumably permits effective overlap and  $\pi$ -bond formation. The alternative explanation would require a double dative bond from the sulfur atom, extremely unlikely in view of the positive character of the sulfur atom.

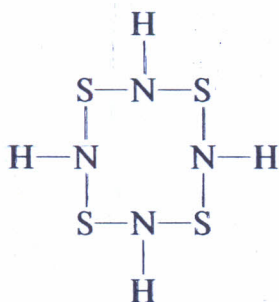
The bond length is consistent with a triple bond. Bond lengths of 174 pm for single S—N bonds (in  $\text{NH}_2\text{SO}_3\text{H}$ ) and 154 pm for double S=N bonds (in  $\text{N}_4\text{S}_4\text{F}_4$ ) are consistent with a bond order of 2.7 in thiazyl trifluoride. This value is also in agreement with an estimate based upon the force constant.<sup>24</sup> The relative bond lengths of S—N, S=N,

<sup>23</sup> Some  $d$  orbital hybridization may enter into the  $\sigma$  system, reducing the bond angles.

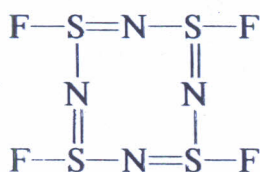
<sup>24</sup> Of course, this involves certain assumptions about the relation between the force constant and bond order. For a more complete discussion of bond length and bond order in these compounds, see O. Glemser and M. Fild, *Halogen Chem.*, 1967, 2, 1. See also O. Glemser and R. Mews, *Adv. Inorg. Radiochem.*, 1970, 14, 33.

and  $S\equiv N$  bonds are thus 1.00:0.88:0.81 compared with similar shortenings of 1.00:0.87:0.78 for corresponding  $C-N$ ,  $C=N$ , and  $C\equiv N$  bonds.

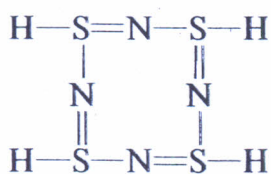
Two other molecules indicating the influence of fluorine substitution on  $d$  orbital participation are  $S_4N_4H_4$  and  $N_4S_4F_4$  (see pp. 716–718). Tetrasulfur tetraimide is isoelectronic with the  $S_8$  molecule and so the structure:



and corresponding crown conformation appear quite reasonable. The fluoride, however, has an isomeric structure with substitution on the sulfur atoms:



Double bonding in this molecule is clearly shown by the alternation in  $S-N$  bond lengths in the ring (see Fig. 14.21b). Now both the above electronic structure for  $S_4N_4F_4$  and that for  $S_4N_4H_4$  are reasonable but raise the question: Why doesn't tetrasulfur tetraimide isomerize from the N-substituted form to the S-substituted form isoelectronic with the fluoride:

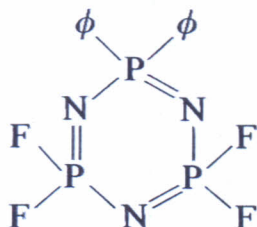


retaining the same number of  $\sigma$  bonds and gaining four  $\pi$  bonds? Apparently the reason the isomerism does not take place is that although  $\pi$  bonding is feasible in the presence of the electronegative fluorine atoms, it is so weak with electropositive hydrogen substituents that it cannot compensate for the weakening of the  $\sigma$  bonding as the hydrogen atom shifts from the more electronegative nitrogen atom to the less electronegative sulfur atom.<sup>25</sup>

Presumably substitution by halogens in the phosphonitrilic series results in contracted  $d$  orbitals and more efficient  $\pi$  bonding in the ring. It was noted previously (see

<sup>25</sup> This argument is based on the stabilization of the  $H-X$   $\sigma$  bonds by ionic resonance energy and is supported by the bond energies in  $NH_3$  ( $391 \text{ kJ mol}^{-1}$ ) and  $H_2S$  ( $347 \text{ kJ mol}^{-1}$ ).

p. 708) that unsymmetrical substitution may allow the normally planar trimeric ring to bend. A good example of this is found in 1,1-diphenylphosphonitrilic fluoride trimer:<sup>26</sup>



3,3,5,5 Tetrafluoro  
triphosphazene

The three nitrogen atoms and the fluoro-substituted phosphorus atoms are coplanar (within 2.5 pm), but the phenyl-substituted phosphorus atom lies 20.5 pm above this plane. The explanation offered is that the more electropositive phenyl groups cause an expansion of the phosphorus *d* orbitals, less efficient overlap with the *p* orbitals of the nitrogen atom, and a weakening of the  $\pi$  system at that point. This allows<sup>27</sup> the ring to deform and the  $\phi_2\text{P}$  moiety to bend out of the plane.

A further example of the jeopardy involved in casually dismissing *d* orbital participation is the findings of Haddon and co-workers<sup>28</sup> that *d*-orbital participation is especially important in  $\text{S}_4\text{F}_4$ , which is nonplanar, and also that it accounts for about one-half of the delocalization energy in the one-dimensional conductor  $(\text{SN})_x$ . In the latter case, the low electronegativity of the *d* orbitals (see p. 181) increases the ionicity of the S—N bond and stabilizes the structure.

Finally, it will be recalled that the existence of strong  $\text{P}=\text{O}$  bonds in  $\text{OPF}_3$  (see p. 828) is consistent with enhanced back donation of electron density from the oxygen atom to the phosphorus atom bearing a positive partial charge from the four  $\sigma$  bonds to electronegative atoms. In light of the above discussion of the contraction of phosphorus and sulfur *d* orbitals when bearing a positive charge, better overlap may be added to the previous discussion as a second factor stabilizing this molecule.

The question of *d* orbital participation in nonmetals is still an open controversy. In the case of  $\sigma$ -bonded species such as  $\text{SF}_6$  the question is not of too much importance since all of the models predict an octahedral molecule with very polar bonds. Participation in  $\pi$  bonding is of considerably more interest, however. Inorganic chemists of a more theoretical bent tend to be somewhat skeptical, feeling that the arguments regarding promotion energies and poor overlap have not been adequately solved. On the other hand, chemists interested in synthesis and characterization tend to favor the use of *d* orbitals in describing these compounds, pointing to the great heuristic value that has been provided by such descriptions in the past and feeling that until rigorous *ab initio* calculations<sup>29</sup> on these molecules show the absence of significant *d* orbital participation it is too soon to abandon a useful model.

<sup>26</sup> C. W. Allen et al., *J. Am. Chem. Soc.*, 1967, 89, 6361.

<sup>27</sup> Note that this explanation provides a rationale which allows the bending but does not provide a driving force to make the ring bend; however, if the ring is sufficiently weakened, small perturbing forces such as those of crystal packing might be sufficient to deform the ring even though the same forces would have little effect in an unweakened ring system.

<sup>28</sup> R. C. Haddon et al., *J. Am. Chem. Soc.*, 1980, 102, 6687.

<sup>29</sup> Not likely in the near future.

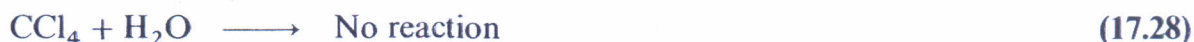
## π bonding in the heavier congeners

In view of the uncertainty with which  $\pi$  bonding is known in the very well studied phosphorus and sulfur systems, it is not surprising that little can be said concerning the possibility of similar effects in arsenic, antimony, selenium, tellurium, etc. In general it is thought that the problems faced in phosphorus and sulfur chemistry concerning promotion energies and diffuse character may be even larger in the heavier congeners. In the latter regard it is interesting to note the apparent effectiveness of  $\pi$  bonding in metal complexes. To the extent that softness in a ligand can be equated with the ability to accept electrons from soft metal ions in  $d_{\pi}-d_{\pi}$  "back bonds," information can be obtained from the tendency to complex with "b" metal ions (see p. 313):  $P > As > Sb$ . This order would indicate that the smaller phosphorus atom can more effectively  $\pi$  bond with the metal atom. With the halide ions the order is reversed:  $I^{-} > Br^{-} > Cl^{-}$ . Whether this is a result of the importance of polarizability in this series or more effective use of  $d$  orbitals by iodine is unknown.

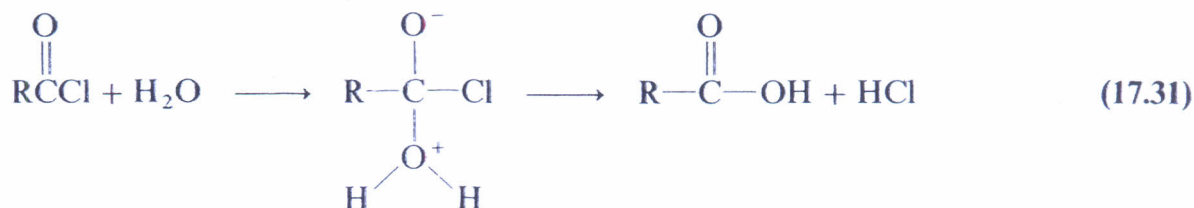
## REACTIVITY AND $d$ ORBITAL PARTICIPATION

It has been pointed out above that the elements of the second row (Li to F) not only resemble their heavier congeners to a certain extent (as far as formal oxidation state, at least) but also the lower right diagonal element (as far as charge, size, and electronegativity are concerned). For example, both silicon and phosphorus form hydrides that have some properties in common with alkanes, although they are much less stable. As a result of the electronegativity relationships the P—H bond more closely approaches the polarity of the C—H bond than does the Si—H bond. The resemblance of phosphorus to carbon has even been extended to the suggestion that a discipline be built around it in the same manner as organic chemistry is built on carbon.<sup>30</sup>

There is one important aspect of the chemistry of both silicon and phosphorus which differs markedly from that of carbon. Consider the following reactions:



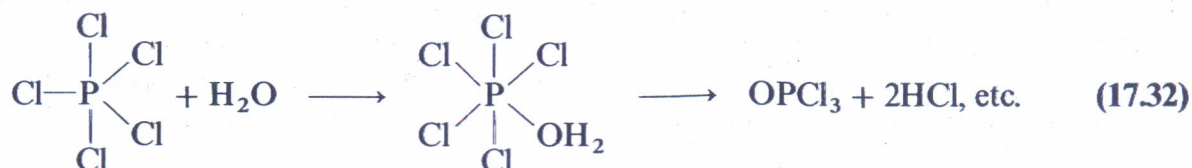
In contrast to the inertness of carbon halides, the halides of silicon and phosphorus are extremely reactive with water, to the extent that they must be protected from atmospheric moisture. A clue to the reactivity of these halides is provided by the somewhat similar reactivity of acid halides in which the carbon-halogen bond is readily attacked:



<sup>30</sup> J. R. Van Wazer, "Phosphorus and Its Compounds," Wiley (Interscience), New York, 1958, Vol. I, pp. vii-ix.



The unsaturation of the carbonyl group provides the possibility of the carbon expanding its coordination shell from 3 to 4, thereby lowering the activation energy. Carbon tetrahalide cannot follow a similar path, but the halides of silicon and phosphorus can employ  $3d$  orbitals to expand their octets:

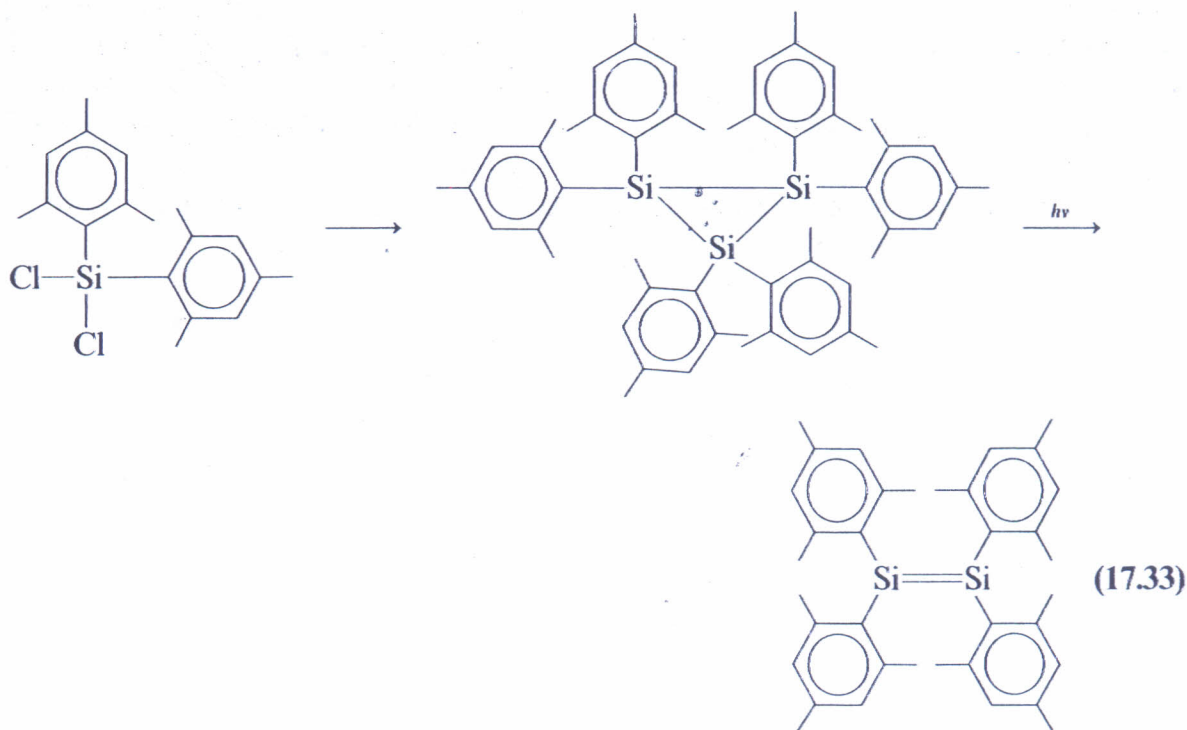


This enhanced reactivity of compounds of silicon and phosphorus is typical of all of the heavier nonmetals in contrast to the elements of the second row.

### THE USE OF $p$ ORBITALS IN $\pi$ BONDING

#### Carbon-silicon similarities and contrasts

In view of the extensive chemistry of alkenes it was only natural for organic and inorganic chemists to search for analogous  $\text{Si}=\text{Si}$  doubly bonded structures. For a long time such attempts proved to be fruitless. Recently the first stable  $\text{C}=\text{Si}$ <sup>31</sup> and  $\text{Si}=\text{Si}$ <sup>32</sup> compounds were synthesized. One synthesis involves the rearrangement of cyclotrisilane:

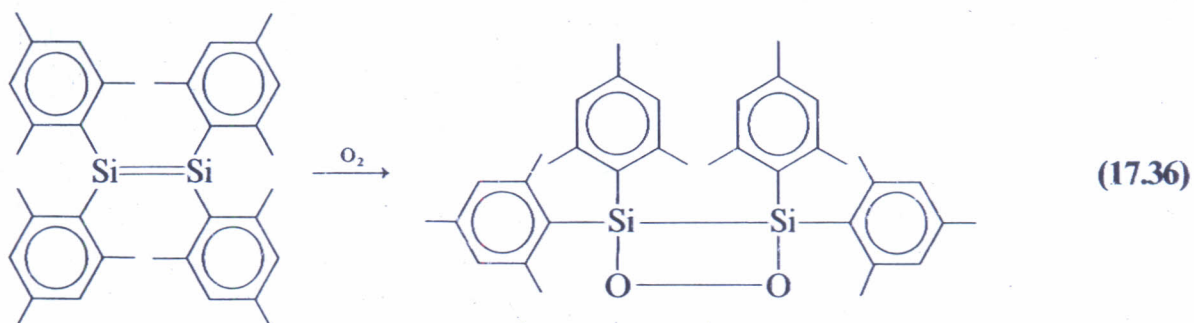
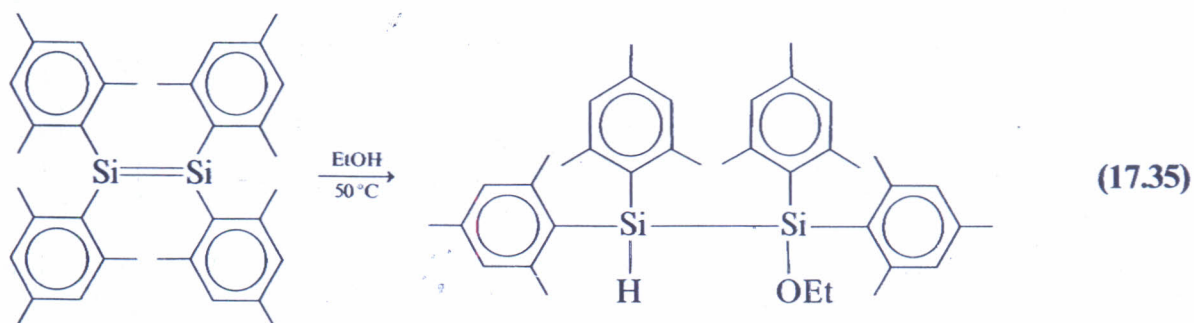
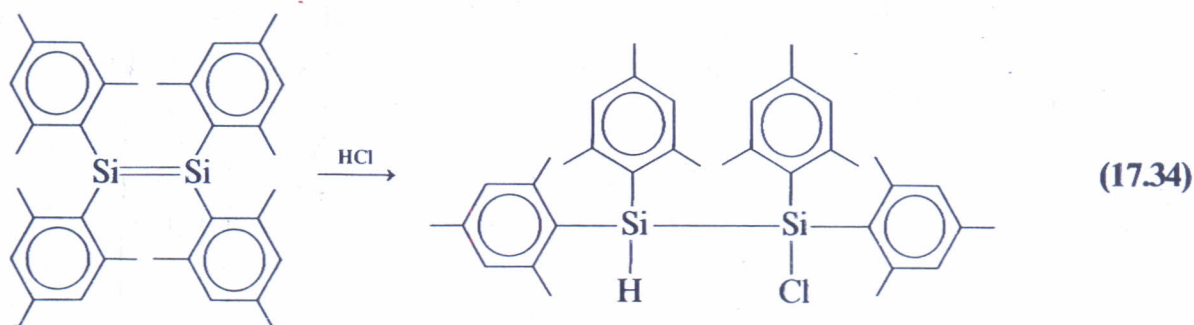


It is possible to add reagents across the  $\text{Si}=\text{Si}$  double bond in some ways analogous to

<sup>31</sup> A. G. Brook et al., *Chem. Commun.*, 1981, 191.

<sup>32</sup> R. West et al., *Science*, 1981, 214, 1343; S. Matsumune et al., *J. Am. Chem. Soc.*, 1982, 104, 1153.

the C=C bond in alkenes:

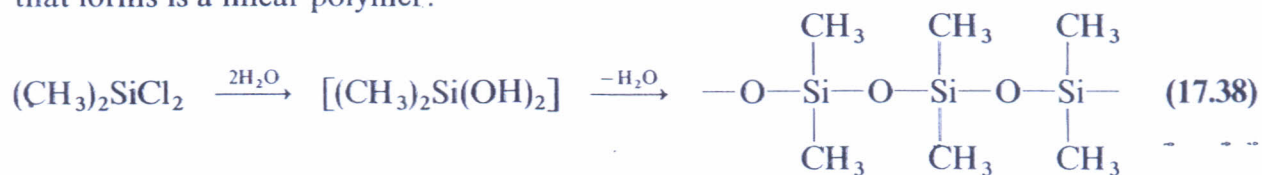


The successful isolation of these compounds is more a tribute to the persistence with which they were pursued than to any inherent stability of the Si=Si double bond. To invert George Leigh Mallory's remark about Mt. Everest, the extraordinary efforts expended on this class of compounds stemmed from the fact that they *weren't* there.

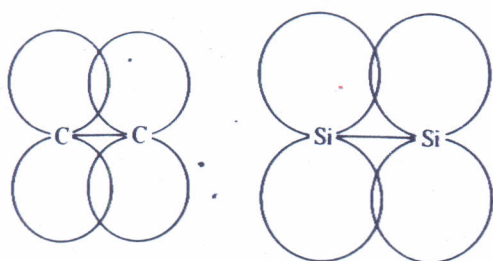
Compounds that are formally analogous to carbon compounds are found to have quite different structures. Thus carbon dioxide is a gaseous monomer but silicon dioxide is an infinite single-bonded polymer. In a similar manner, *gem*-diols are unstable relative to ketone



and the analogous silicon compounds are also unstable, but the "dimethylsilicone"<sup>33</sup> that forms is a linear polymer:



<sup>33</sup> The term "silicone" was coined by analogy to *ketone* under the mistaken belief that monomeric  $\text{R}_2\text{Si}=\text{O}$  compounds could be isolated.



**Fig. 17.7** Diagrammatic representation of the possibly poorer overlap of the  $p$  orbitals in C—C and Si—Si to form  $\pi$  bonds.

There are two possible sources of instability of doubly bonded silicon structures involving  $p_{\pi}-p_{\pi}$  bonds. It may be that the longer  $\sigma$  bond in the silicon system reduces the sideways overlap of the  $p$  orbitals (Fig. 17.7). Mulliken has objected that the overlap is *not* reduced and has advanced the idea that  $d$  orbital participation may favor two “single” bonds over the one double bond. This viewpoint would emphasize that all Si—X bonds (where X = N, O, halogens) will have some double bond character (even though much less than that of a full bond) from back bonding using the  $d$  orbitals. Hence formal “single bonds” actually would be stronger than a simple  $\sigma$  bond and more than half as strong as the hypothetical  $p_{\pi}-p_{\pi}$  double bonds.<sup>34</sup>

#### Nitrogen-phosphorus analogies and contrasts

The stable form of nitrogen at room temperature is  $N_2$ , which has an extraordinarily strong ( $946 \text{ kJ mol}^{-1}$ ) triple bond. In contrast, white phosphorus consists of  $P_4$  molecules (see p. 723), and the thermodynamically stable form is black phosphorus, a polymer. At temperatures above  $800^\circ\text{C}$  dissociation to  $P_2$  molecules does take place, but these are considerably less stable than  $N_2$  with a bond energy of  $488 \text{ kJ mol}^{-1}$ . In this case, too, in the heavier element several single bonds are more effective than one multiple bond.

In 1961 the phosphorus analogue of hydrogen cyanide was prepared:<sup>35</sup>



In contrast to the stability of hydrogen cyanide, HCP is a highly pyrophoric gas which polymerizes above  $-130^\circ\text{C}$ .

During the past five years the number of molecules containing  $\text{C}\equiv\text{P}$  bonds has increased to about a dozen. One method of obtaining them is dehydrohalogenation:<sup>36</sup>

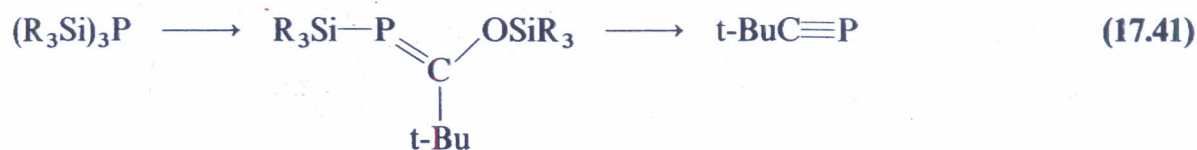


<sup>34</sup> For further discussion, see W. E. Dasent, “Nonexistent Compounds,” Dekker, New York, 1965, Chap. 4; B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, **1968**, *11*, 249. For a discussion of bond energies in silicon compounds, see R. Walsh, *Acc. Chem. Res.*, **1981**, *14*, 246.

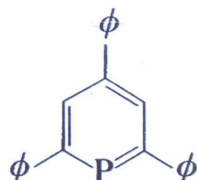
<sup>35</sup> T. E. Gier, *J. Am. Chem. Soc.*, **1961**, *83*, 1769.

<sup>36</sup> H. W. Kroto et al., *J. Am. Chem. Soc.*, **1978**, *100*, 446.

A stable, liquid phosphalkyne has recently been synthesized:<sup>37</sup>



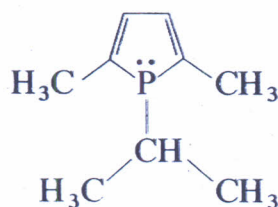
For a considerable period of time it seemed impossible to prepare doubly bonded phosphorus analogues of nitrogen. Finally, phosphorus analogues of pyridine of the type:



were synthesized,<sup>38</sup> and now all of the group VA analogues of pyridine have been prepared:<sup>39</sup>



However, these compounds must be considered the exception rather than the rule as far as the heavier elements are concerned. In fact, when the barrier to inversion of the pyramidal phosphole:



was found to be only half as large as the usual value for pyramidal phosphines,  $R_3P$ , it was immediately reported as evidence that aromaticity (analogous to that of pyrrole) was responsible for lowering the activation energy. Note, however, that the aromatic stabilization is insufficient to keep the phosphole molecule planar—the ground state pyramidal with the lone pair localized on the phosphorus atom rather than delocalized in the  $\pi_p$  system.<sup>40</sup>

<sup>37</sup> See H. W. Kroto and J. F. Nixon, "Phosphorus Chemistry," L. D. Quin and J. G. Verkade, eds., *ACS Symp. Ser. 171*, 1981, Paper 79.

<sup>38</sup> G. Märkl, *Angew. Chem. Int. Ed. Engl.*, 1966, 5, 846; A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, 93, 3293.

<sup>39</sup> A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, 93, 6690; A. J. Ashe, III, and M. D. Gordon, *J. Am. Chem. Soc.*, 1972, 94, 7596; A. J. Ashe, III et al., *J. Am. Chem. Soc.*, 1976, 98, 5451.

<sup>40</sup> W. Egan et al., *J. Am. Chem. Soc.*, 1970, 92, 1442. The evidence from the barrier to inversion is somewhat ambiguous—other factors may also be important (see R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, 1971, 93, 773).

The isolation of compounds containing simple C=P double bonds parallels the triple-bond work. The first stable phosphalkene was synthesized but five years ago. Again, base-induced dehydrohalogenation and stabilization by bulky groups is important.<sup>41</sup>



The steric hindrance is critical: If R = phenyl or 2-methylphenyl, the bulkiness is insufficient to stabilize the molecules, but the 2,6-dimethylphenyl and 2,4,6-trimethyl derivatives are stable.

## PERIODIC ANOMALIES OF THE NONMETALS AND POSTTRANSITION METALS

It is generally assumed that the properties of the various families of the periodic chart change smoothly from less metallic (or more electronegative) at the top of the family to more metallic (or less electronegative) at the bottom of the family. Certainly for the extremes of the chart—the alkali metals on the left and the halogens and noble gases on the right—this is true; the ionization potentials, for example, vary in a rather monotonous way. This is not true for certain central parts of the chart, however.

### Reluctance of fourth-row nonmetals to exhibit maximum valence

There is a definite tendency for the nonmetals of the fourth row—As, Se, and Br—to be unstable in their maximum oxidation state. For example, the synthesis of arsenic pentachloride eluded chemists until recently<sup>42</sup> (AsBr<sub>5</sub> and AsI<sub>5</sub> are still unknown) although both PCl<sub>5</sub> and SbCl<sub>5</sub> are stable. The only stable arsenic pentahalide is AsF<sub>5</sub>.

In Group VIA the same phenomenon is encountered. Selenium trioxide is thermodynamically unstable relative to sulfur trioxide and tellurium trioxide. The enthalpies of formation of SF<sub>6</sub>, SeF<sub>6</sub>, and TeF<sub>6</sub> are -1210, -1030, and -315 kJ mol<sup>-1</sup>, respectively. This indicates comparable bond energies for S—F and Te—F bonds (326 kJ mol<sup>-1</sup>), which are 42 kJ mol<sup>-1</sup> more stable than Se—F bonds.

The best known exceptions to the general reluctance of bromine to accept a +7 oxidation state are perbromic acid and the perbromate ion, which were unknown prior to 1968 (see p. 782). Their subsequent synthesis has made their "nonexistence" somewhat less crucial as a topic of immediate concern to inorganic chemists, but bromine certainly continues the trend started by arsenic and selenium. Thus the perbromate ion is a stronger oxidizing agent than either perchlorate or periodate.

<sup>41</sup> See T. A. van der Knaap et al., "Phosphorus Chemistry," L. D. Quin and J. G. Verkade, eds., *ACS Symp. Ser. 171*, 1981, Paper 82.

<sup>42</sup> K. Seppelt, *Z. anorg. Chem.*, 1977, 434, 5.

## Anomalies of Groups IIIA and IVA

Before seeking an explanation of the reluctance of As, Se, and Br to exhibit maximum oxidation states, a related phenomenon will be explored. This involves a tendency for germanium to resemble carbon more than silicon. Some examples are:<sup>43</sup>

1. *Reduction of halides (X) with zinc and hydrochloric acid.* Germanium resembles carbon and tin resembles silicon:



2. *Hydrolysis of the tetrahydrides.* Silane hydrolyzes in the presence of catalytic amounts of hydroxide. In contrast, methane, germane, and stannane do not hydrolyze even in the presence of large amounts of hydroxide ion.

3. *Reaction of organolithium compounds with (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>MH.* Triphenylmethane and triphenylgermane differ in their reaction with organolithium compounds from triphenylsilane and triphenylstannane:



4. *Alteration in enthalpies of formation.* There is a tendency for the enthalpies of formation of compounds of the Group IVA elements to alternate from C—Si—Ge—Sn—Pb. Although closely related to the previous phenomena, this variation is also related to the “inert pair effect” and will be discussed further below.

The elements of Group IIIA show similar properties, although, in general, the differences are not so striking as for Group IVA.<sup>44</sup> It may be noted that the covalent radius of gallium appears to be slightly smaller than that of aluminum in contrast to what might have been expected. The first ionization energies of the two elements are surprisingly close (578 and 579 kJ mol<sup>-1</sup>), and if the sum of the first three ionization energies is taken, there is an alternation in the series: B = 6887, Al = 5044, Ga = 5521, In = 5084, Tl = 5439 kJ mol<sup>-1</sup>.

<sup>43</sup> A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **1958**, *5*, 269.

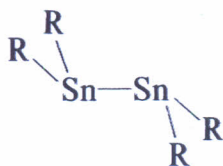
<sup>44</sup> R. T. Sanderson, *J. Am. Chem. Soc.*, **1952**, *74*, 4792. This was the first paper to call attention to the anomalies discussed in this chapter and may be consulted for further details on several of the topics.

**Table 17.3** Ionization energies of *s* electrons in  $\text{kJ mol}^{-1}$  (eV)

Element	$\text{IE}_2 + \text{IE}_3$	Element	$\text{IE}_3 + \text{IE}_4$
B	6 090 (63.1)	C	10 820 (112.1)
Al	4 550 (47.2)	Si	7 580 (78.6)
Ga	4 940 (51.2)	Ge	7 710 (79.9)
In	4 520 (46.9)	Sn	6 870 (71.2)
Tl	4 840 (50.2)	Pb	7 160 (74.2)

### The "inert *s*-pair effect"

Among the heavy posttransition metals there is a definite reluctance to exhibit the highest possible oxidation state or the greatest covalence. Thus, although carbon is universally tetravalent except as transient carbene or methylene intermediates, it is possible to prepare divalent germanium, tin, and lead compounds. For example, if bulky substituents [ $\text{R} = \text{CH}(\text{SiMe}_2)_2$ ] are present, the compounds  $\text{R}_2\text{Ge}$ ,  $\text{R}_2\text{Sn}$ , and  $\text{R}_2\text{Pb}$  exist as diamagnetic monomers in solution, although there is a tendency to dimerize in the solid.<sup>45</sup> The molecular structure of the tin dimer has been determined and found to be in the *trans* conformation:



Further examples of the stability of divalent compounds of the heavier congeners may be found in the oxidation state in principally ionic compounds. Thus in Group IVA, tin has a stable +2 oxidation state in addition to +4 and for lead the +2 oxidation state is far more important. Other examples are stable  $\text{Tl}^+$  (Group IIIA) and  $\text{Bi}^{+3}$  (Group VA). These oxidation states, two less than the group number, have led to the suggestion that the pair of *s* electrons is "inert" and only the *p* electrons are employed in the bonding. It has even been suggested that the unreactivity of metallic mercury is a result of the fact that the only bonding electrons it has are the "inert 6*s* electrons." Although the term "inert pair" provides a convenient label for the phenomenon, it does little to promote understanding. Indeed, it has been pointed out that the pair of *s* electrons is certainly not stereochemically inert in the tin(II) halides—they are bent as expected for a divalent molecule with a lone pair. On the other hand, the *s* pair *does* seem to be stereochemically inert in  $\text{SbBr}_6^-$ ,  $\text{TeCl}_6^-$ , and  $\text{TeBr}_6^-$  (see p. 217).

It can readily be shown that there is no exceptional stability of the *s* electrons in the heavier elements. Table 17.3 lists the ionization energies of the *s* electrons of the valence

<sup>45</sup> M. F. Lappert, in "Inorganic Compounds with Unusual Properties," R. B. King, ed., *Advances in Chemistry Series*, No. 150, American Chemical Society, Washington, D.C., 1976, pp. 256–265. Also see P. J. Davidson et al., *J. Chem. Soc., Dalton*, 1976, 2268.

Table 17.4 Enthalpies of dissociation,  $\text{MX}_n \rightarrow \text{MX}_{n-2} + \text{X}_2$  in  $\text{kJ mol}^{-1}$ 

Element	Fluorides	Chlorides	Bromides	Iodides
B		+301		
Al		+335		
Ga		+343		
In		+305		
Tl		+209		
Ge	+694	+381	+259	+167
Sn	+544	+276	+243	+142
Pb	+385	+121	+88	+17

shell of the elements of Groups IIIA and IVA. Although the 6s electrons are “stabilized” to the extent of  $\sim 300 \text{ kJ mol}^{-1}$  (3 eV) over the 5s electrons, this cannot be the source of the “inert pair effect” since the 4s electrons of Ga and Ge have even greater ionization energies and these elements do not show the effect—the lower valence  $\text{Ga}^{\text{I}}$  and  $\text{Ge}^{\text{II}}$  compounds are obtained only with difficulty.

The pragmatic criterion of the presence or absence of an “inert pair effect” can be given as the tendency (or lack thereof) for the following reaction to proceed to the right:<sup>46</sup>



We might then inquire into the possibility of systematic variations in the lattice energies of either the higher or lower halides. Although such lattice effects could be responsible for differential stability of the solids, in those cases for which accurate data for the gas phase are available the same trends exist. In Table 17.4 are listed some enthalpies for the following reaction:



There is a tendency for the reaction to proceed more readily (although endothermic for all the compounds listed) with the heavier elements, especially thallium and lead.

The relative instability of the higher oxidation state for the heavier elements stems from a general weakening of the bonds (1) in the higher oxidation state and (2) with higher atomic number (Table 17.5). As a result of these two trends the difference between  $n$  weaker bonds and  $n - 2$  slightly stronger bonds becomes less and less. Tending to promote dissociation is the driving force of the bond energy of the halogen molecule  $\text{X}_2$ .

Drago has provided an analysis of the factors important in the bonding which are responsible for observations (1) and (2) above.<sup>47</sup> He assumed the Pauling values for the electronegativity of the heavy elements: Ga = 1.6, In = 1.7, Tl = 1.8; Ge = 1.8, Sn = 1.8, Pb = 1.8. If the electronegativities of these elements are essentially constant, the ionic character of the bonds should be nearly constant, and hence any changes in bond energy are a result of changes in the covalent portion of the bonding.

<sup>46</sup> Although the tendency for lower oxidation states to be stable is found in many series of compounds in addition to the halides, the latter will be used in the following discussion since we have better thermodynamic data for them.

<sup>47</sup> R. S. Drago, *J. Phys. Chem.*, 1958, 62, 353.



**Table 17.5** Bond energies of some group IVA halides in  $\text{kJ mol}^{-1}$ 

Element	$\text{MF}_2$	$\text{MF}_4$	$\text{MCl}_2$	$\text{MCl}_4$	$\text{MBr}_2$	$\text{MBr}_4$	$\text{MI}_2$	$\text{MI}_4$
Si	—	565	—	380	—	310	—	230
Ge	481	452	385	354	326	275	264	218
Sn	481	414	386	323	329	273	262	205
Pb	394	330	304	240	260	200	205	140

The relatively small decrease in average bond energy upon going from the lower oxidation state to the higher oxidation state can be attributed to the promotion energy ( $s^2p^n \rightarrow s^1p^{n+1}$ ), which is almost compensated by the improved bonding of hybrid orbitals. Data on promotion energies for the heavier elements are rather uncertain, but it does not appear that they are an important factor in the problem at hand other than causing all elements to have weaker bonds in the higher oxidation state compound. More important appears to be the inherent weakness of the bonding of the heavier elements. Drago ascribed this to two factors: (1) poorer overlap of the orbitals of the larger atoms; and (2) repulsion of inner electrons, most pronounced in Ga and Ge (the first posttransition metals) and Tl and Pb (the first postlanthanide posttransition metals).

#### The electronegativities of the elements of Group IVA

Before discussing the bonding in Groups IIIA and IVA further, it is necessary to digress momentarily to examine work on the electronegativity of the Group IVA elements that turns out to be intimately involved in the "inert pair effect." From various physical measurements<sup>48</sup> Allred and Rochow<sup>49</sup> began to suspect that the "conventional" order of electronegativities for the Group IVA elements was not correct. They suggested that a constant value<sup>50</sup> of 1.8 for the elements Si, Ge, Sn, and Pb did not adequately account for the properties of these elements. Consider the "anomalous" reactions of the Group IIIA and IVA elements discussed previously. The general tendency for germanium to parallel carbon indicates that the electronegativity of germanium is higher than that of silicon, making it more nearly approach that of carbon. Consider the hydrolysis of silane. Since only catalytic amounts of hydroxide ion are required, it is suggested that it forms a complex ion to effect the reaction and is then regenerated:



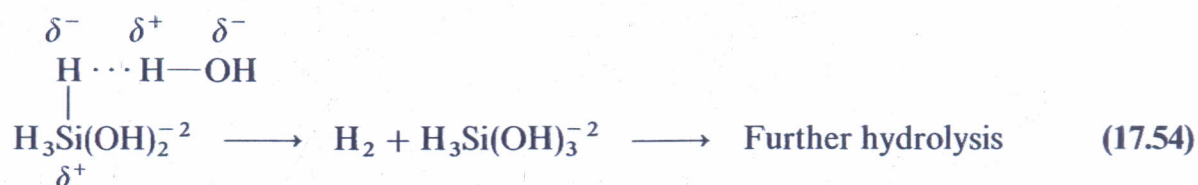
Hydrogen is more electronegative than silicon and so will carry a negative charge in silane (which will be increased in the negative dihydroxo anion) and behave as a hydridic hydrogen

<sup>48</sup> One important source of data was the measurement of NMR chemical shifts which give an indication of the shielding of the nucleus of an atom by electrons. Electronegativity effects obviously are important in determining electron density about a nucleus, but unfortunately other factors are also involved in chemical shifts and it is impossible to assign unequivocally the role of electronegativity.

<sup>49</sup> A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **1958**, 5, 269.

<sup>50</sup> L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

reacting with a positive hydrogen from water:



The lack of reactivity of germane and stannane could result from the absence of a  $M^{\delta+}-H^{\delta-}$  dipole of sufficient magnitude to induce reaction, i.e., if the electronegativities of Ge and Sn are closer to that of hydrogen than that of Si. The behavior of the reactions of the triphenyl derivatives with lithium alkyls supports a similar interpretation: When bonded to a more electronegative carbon or germanium atom,<sup>51</sup> a hydrogen atom will be more acidic than when bonded to a less electronegative silicon or tin atom.<sup>51</sup>

Finally, Allred and Rochow examined the bond energies of the Group IVA halides (see Table 17.5). They noted that although the homopolar bond energies of Si—Si and Ge—Ge are almost identical (188 and 186 kJ mol<sup>-1</sup>), Ge—X bonds are from 21 to 113 kJ mol<sup>-1</sup> weaker than Si—X bonds. This difference in energy can be assigned to differences in electronegativity *only if germanium has a higher electronegativity than silicon and when bonded to electronegative halogens yields smaller ionic resonance energies*. By a series of Pauling-type calculations<sup>52</sup> they obtained the following electronegativities for the Group IVA elements (all  $sp^3$  hybrids): C = 2.60 (assumed), Si = 1.91, Ge = 2.00, Sn = 1.94, Pb = 2.23.

Two of the Allred-Rochow experimental values<sup>53</sup> (Ge and Pb) for the electronegativities deserve special comment. That the electronegativity of germanium is greater than that of either silicon or tin is supported by three electronegativity scales: the Allred-Rochow electrostatic scale, the Sanderson relative compactness scale, and the Mulliken-Jaffé ionization energy scale.<sup>54</sup> The former two are based on size and reveal the results of the contraction across the first transition series. The latter, based on ionization and electron affinity energies, reflects the increased ionization energy resulting from poor shielding by  $d$  electrons. They are thus in essential agreement over the nature of the increase in electronegativity for germanium. This coupled with the experimental evidence given above makes most inorganic chemists accept the higher value for germanium.

The electronegativity of lead is still a matter of considerable disagreement. On all counts the data available for calculations for lead are poor. Exact values for its radius, effective atomic number, ionization energy, electron affinity, and bond energies are much more difficult to obtain than for the lighter elements. On the basis of other work, Allred and Rochow suggested an even higher value than that derived from bond energies, 2.45!

<sup>51</sup> The relative electronegativities of Ge and Sn vary somewhat but are obviously close to hydrogen and greater than silicon. Substituent effects could be responsible for these small variations.

<sup>52</sup> The interested reader is referred to the original paper for details of the calculations.

<sup>53</sup> These are the values obtained from bond energies and other experimental work described above and should not be confused with the Allred-Rochow electrostatic values. See p. 149.

<sup>54</sup> Although this scale has the soundest theoretical basis, in the present instance it is of limited usefulness since all of these elements except carbon utilize some (unknown) amount of  $d$  character and the  $d$  orbitals have low (unknown) electronegativities. The values for the  $sp^3$  hybrids are all somewhat high therefore.

Many workers, including Drago,<sup>55</sup> could not accept such a high value (yet note that even the "conservative" Pauling scale gave Au a value of 2.4, 0.5 unit higher than Ag, and both Hg and Tl were given values higher than their lighter congeners). In support of a higher value for lead (not necessarily as high as 2.45) it may be pointed out that both the ionization energy and electron affinity (see Table 2.5) of lead are relatively high as a result of the addition of 14 poorly shielded protons across the lanthanide series.<sup>56</sup>

The controversy has not as yet been completely resolved. It is interesting to note (and to oversimplify somewhat) that Drago assumed the constancy of electronegativity (Si—Pb), the concomitant constancy of ionic bonding, and hence was forced to the conclusion that something was peculiar with the overlap and/or repulsions in the bonds of Ge and Pb. On the other hand, Allred and Rochow assumed that all of the bonds were more or less normal in behavior as far as the covalent contribution was concerned—hence differences in bonding reflected differences in ionic character and higher electronegativities for Ge and Pb.<sup>57</sup> By extension, this would ascribe the "inert pair effect" to weak bonds in the heavy metals because they are not stabilized by ionic character. It is interesting to note that both points of view agree on one point, an empirical observation: Those elements such as Ga, Ge, and As that follow the first transition series and those elements such as Tl, Pb, and Bi that follow the first lanthanide or inner transition series are affected by the increased effective nuclear charge and exhibit unusual properties. When exhibited by the fourth-row elements it may be referred to as a "reluctance to exhibit the maximum oxidation state (for As, Se, and Br)," and when shown by the sixth-row elements it may be termed the "inert pair effect." In both cases it probably rests ultimately on the effects of unshielded nuclear charge.<sup>58</sup>

This behavior has been generalized as follows. Those elements that follow the first filling of a given type of sublevel (*p*, *d*, *f*, etc.) will exhibit a lowered tendency to form stable compounds in their highest oxidation states.<sup>59</sup> This correlates the behavior of the post-lanthanide (first filling of *f* levels) elements (Hf to Rn) and the postscandide (first filling of *d* levels) elements (Ga to Kr). In addition, more subtle effects can also be found: Both sodium and magnesium form less stable compounds than would be expected on the basis of the behavior of their lighter (Li, Be) and heavier (K, Ca) congeners.<sup>60</sup> These elements are those that follow immediately after the first filling of a set of *p* orbitals (Ne), and the same effects of incomplete shielding (though less pronounced to be sure) presumably are operative

<sup>55</sup> R. S. Drago, *J. Inorg. Nucl. Chem.*, **1960**, *15*, 237. This was followed by a rebuttal from Allred and Rochow, and the debate has continued. The interested reader is urged to study this controversy as an excellent example of a situation in which intelligent and knowledgeable workers can take the same data and interpret them in diametrically opposite ways! See A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **1960**, *20*, 167; R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.*, **1965**, *3*, 62.

<sup>56</sup> Unfortunately the spectroscopic data necessary to calculate promotion energies and valence state ionization energies and electron affinities are not available, so it is impossible to provide a Mulliken-Jaffé electronegativity.

<sup>57</sup> Both sets of authors have done a considerably better job of arguing their points of view than can possibly be represented in the space available here.

<sup>58</sup> For a discussion of these problems, see W. E. Dasent, "Nonexistent Compounds," Dekker, New York, **1965**, Chapters 5 and 6. For a discussion of the use of *d* orbitals in these elements, see D. S. Urch, *J. Inorg. Nucl. Chem.*, **1963**, *25*, 771.

<sup>59</sup> J. E. Huheey and C. L. Huheey, *J. Chem. Educ.*, **1972**, *49*, 227.

<sup>60</sup> R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **1970**, *32*, 777.

here as well as in the postlanthanide and postscandide elements. This principle has been used to predict some of the chemical properties of the superheavy transactinide elements.<sup>59</sup>

#### “Anomalous” ionization energies and electron affinities

Many introductory chemistry books give simple rules for remembering the periodic changes of ionization energies and electron affinities. The rules usually follow some modification of “Ionization energies and electron affinities increase as one moves to the right in the periodic chart; they decrease as one moves from top to bottom.” These generalizations, as well as the shielding rules that account for the atomic behavior, were discussed in Chapter 2, along with some of the exceptions. Unfortunately for simplicity, the exceptions are somewhat more numerous than is generally realized. Many of the problems discussed in the preceding sections result from these “exceptions.”

The horizontal behavior of atoms follows the general rule with good regularity as might be expected from adding a single proton at a time with expected monotonic changes in properties. We have already seen the exception of the inversion of the ionization potentials of the VA and VIA groups related to the stability associated with half-filled subshells. A similar inversion of electron affinities takes place, for the same reason, between groups IVA and VA.

The vertical exceptions to the generalizations are much more widespread: If we count every time that a heavier element has a higher ionization potential or higher electron affinity than its next lighter congener, we find that about one-third of the elements show “electron affinity anomalies”<sup>61</sup> and a somewhat higher fraction of the elements show “ionization energy anomalies.” With such a high fraction of exceptions, one wonders why the rules were formulated as they were originally. The answer seems to lie in the lack of data available until recently; most of the good data were for familiar elements, such as the alkali metals and the halogens. For these main-group elements, with the exception of the lower electron affinity of fluorine resulting from electron–electron repulsion (and paralleled by oxygen and nitrogen), the rules work fairly well; however, the poorer shielding *d* and *f* electrons upset the simple picture. For the transition metals, higher ionization energies with increasing atomic number in a group are the *rule*, not the exception. As we have seen in the preceding discussion, this carries over somewhat into the posttransition elements, causing some of the problems associated with families IIIA and IVA.

The increased ionization energies of the heavier transition metals should not be unexpected by anyone who has had a modicum of laboratory experience with any of these elements. Although none of the coinage metals is very reactive, gold has a well-deserved reputation for being less reactive than copper or silver;<sup>62</sup> iron, cobalt, and nickel rust and corrode, but osmium, iridium, and platinum are noble and unreactive and therefore are used in jewelry; platinum wires are the material of choice for flame tests without contamination; and one generates hydrogen with zinc and simple acids, not with mercury.

<sup>61</sup> E. C. M. Chen and W. E. Wentworth (*J. Chem. Educ.*, 1975, 52, 486) have reviewed the experimental values of atomic electron affinities and plotted them periodically.

<sup>62</sup> The legend of *aqua regia* seems to persist even in the absence of student contact with this powerful elixir.

## Conclusion

The periodic chart is the inorganic chemist's single most powerful weapon when faced with the problem of relating the physical and chemical properties of over 100 elements. In addition to knowing the general trends painted in broad brush strokes by the simple rules, the adept chemists should know something of the "fine structure" that is at the heart of making inorganic chemistry diverse and fascinating.

## PROBLEMS

- 17.1. Compare Figs. 14.28 and 14.29. The difference in P—O bond lengths in  $P_4O_{10}$  is  $162 - 139 = 23$  pm but only 13 pm in  $P_4S_{10}$ . Explain.
- 17.2. The separation of zirconium and hafnium has been of considerable interest because of the low neutron cross section of zirconium and the high neutron cross section of hafnium. Unfortunately, the separation of these two elements is perhaps the most difficult of any pair of elements. Explain why.
- 17.3. Carbon tetrachloride is inert toward water but boron trichloride hydrolyzes in moist air. Suggest a reason.
- 17.4. Discuss the possibility that there is an alternation of electronegativities in Group VA. [A. L. Allred and A. L. Hensley, Jr., *J. Inorg. Nucl. Chem.*, **1961**, *17*, 43.]
- 17.5. "Gallium dichloride,"  $GaCl_2$ , is a diamagnetic compound that conducts electricity when fused. Suggest a structure.
- 17.6. If a major breakthrough in nuclear synthesis is achieved, two elements that are hoped for are those with atomic numbers 114 and 164, both congeners of lead. Look at the periodic chart on p. 817 and suggest properties (such as stable oxidation states) for these two elements. How do you suppose their electronegativities will compare with the other Group IVA elements? [G. T. Seaborg, *J. Chem. Educ.*, **1969**, *46*, 626; also see footnote 59.]
- 17.7. The small F—S—F bond angles in  $F_3S\equiv N$  can be rationalized by
  - a. Bent's rule
  - b. Gillespie-type rules
  - c. Bent bonds
 Discuss each and explain their usefulness (or lack) in the present case.
- 17.8. One of the challenges of teaching (or text writing) is the problem of presenting material (especially to a person new to the subject) in a simplifying and nondistracting way without oversimplifying (or even falsifying) the material for the sake of "helping" the student. Read the chapter or section on periodicity in your freshman text and criticize it in light of what you now know. Could you rewrite it to improve it?
- 17.9. It is sometimes said that nitrogen cannot form a pentafluoride because it has no *d* orbitals in its valence shell. C. T. Goetschel et al., [*Inorg. Chem.*, **1972**, *11*, 1696] believe they have synthesized  $NF_5$ . Discuss the bonding and structural possibilities.

- 17.10. Either look up the article by Chen and Wentworth<sup>61</sup> or plot the electron affinities from Table 2.5 onto a periodic chart. Discuss the reasons for the “exceptions” you observe.
- 17.11. Plot the first ionization energies from Table 2.4A onto a periodic chart. Discuss the reasons for the “exceptions” you observe.
- 17.12. On p. 843 the statement is rather casually made that “ $R_2Ge$ ,  $R_2Sn$ , and  $R_2Pb$  exist as diamagnetic monomers in solution.” What experiments must an inorganic chemist do to substantiate these statements? [See footnote 45.]
- 17.13. The compound  $R_4Sn_2$  shown on p. 843 is diamagnetic. Draw out the most reasonable electronic structure for it, and compare it with the geometric structure. Discuss.
- 17.14. Lithium carbonate is often administered orally in the treatment of mania or depression or both. From what you have learned of the diagonal relationship of the periodic chart, predict one possible unpleasant side effect of lithium therapy.
- 17.15. Zinc is a much more reactive metal than cadmium, as expected from the discussion on pp. 847–848. Yet *both* are used to protect iron from rusting. How is this possible?
- 17.16. Sodium hypophosphite,  $Na\dot{H}_2PO_2$ , has been suggested as a replacement of sodium nitrite,  $NaNO_2$ , as a meat preservative to prevent botulism. Draw the structure of each anion.
- 17.17. The simplest relationship between electronegativity and dipole moments is a linear one: The greater the difference in electronegativity, the greater the dipole. How can you reconcile this with the N—O and P—O dipoles cited in this chapter (p. 826)?