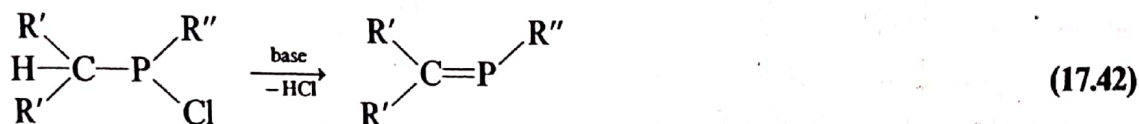


The isolation of compounds containing simple C=P double bonds parallels the triple-bond work. The first stable phosphalkene was synthesized but five years ago. Again, base-induced dehydrohalogenation and stabilization by bulky groups is important.<sup>41</sup>



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

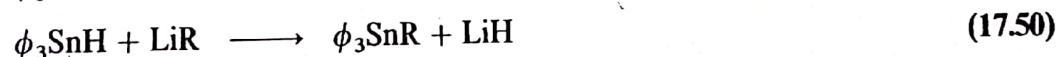
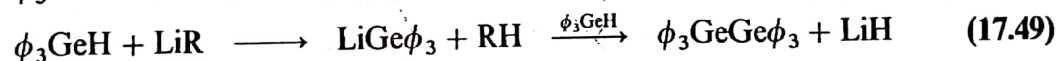
Before seeking an explanation of the reluctance of As, Se, and Br to exhibit maximum oxidation states, a related phenomenon will be explored. This involves a tendency for germanium to resemble carbon more than silicon. Some examples are:<sup>43</sup>

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.

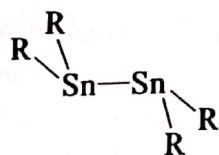
<sup>44</sup> R. T. Sanderson, *J. Am. Chem. Soc.*, 1952, 74, 4792. This was the first paper to call attention to the anomalies discussed in this chapter and may be consulted for further details on several of the topics.

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  $\text{SbBr}_6^{-3}$ ,  $\text{TeCl}_6^{-2}$ , and  $\text{TeBr}_6^{-2}$  (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

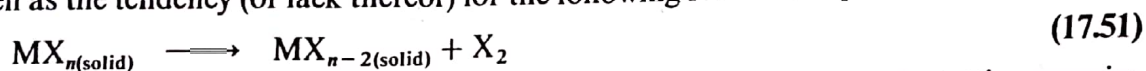
<sup>45</sup> M. F. Lappert, in "Inorganic Compounds with Unusual Properties," R. B. King, ed., *Advances in Chemistry Series*, No. 150, American Chemical Society, Washington, D.C., 1976, pp. 256–265. Also see P. J. Davidson et al., *J. Chem. Soc., Dalton*, 1976, 2268.

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.

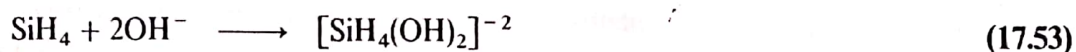
Table 17.5 Bond energies of some group IVA halides in kJ mol<sup>-1</sup>

Element	MF <sub>2</sub>	MF <sub>4</sub>	MCl <sub>2</sub>	MCl <sub>4</sub>	MBr <sub>2</sub>	MBr <sub>4</sub>	MI <sub>2</sub>	MI <sub>4</sub>
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.