

Chapter 15

THE GROUP IVB(14) ELEMENTS: SILICON, GERMANIUM, TIN, AND LEAD

15-1 Introduction

Silicon is second only to oxygen in its natural abundance (~28% of the earth's crust) and occurs in a great variety of silicate minerals and as quartz (SiO_2).

Germanium, tin, and lead are rare elements (~ $10^{-3}\%$). Tin and lead have been known since antiquity because of the ease with which they are obtained from their ores.

Cassiterite (SnO_2) occurs mixed in granites, sands, and clays. Lead occurs mainly as *galena* (PbS).

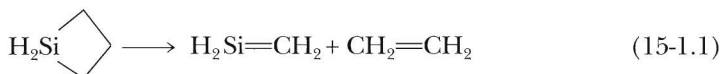
Germanium was discovered in 1886 following the prediction of its existence by Dimitri Mendeleev. It occurs widely but in small amounts and is recovered from coal and zinc ore concentrates.

The main use of Ge, Sn, and Pb is as the metals, but alkyltin and alkyllead compounds are made on a large scale (Chapter 29).

The position of the elements in the periodic table and some general features, including the reasons for the existence of the lower II oxidation state, were discussed in Section 8-11. Some properties of the elements were given in Table 8-4.

Multiple Bonding

It was earlier thought that silicon and the remainder of the Group IVB(14) elements did not form stable $p\pi-p\pi$ multiple bonds, as is common for carbon. Beginning in the 1960s, however, transient intermediates with $\text{Si}=\text{C}$, $p\pi-p\pi$ bonding were discovered in thermal decomposition reactions such as 15-1.1, which takes place at 560 °C.



Numerous such compounds ($\text{R}_2\text{Si}=\text{CR}'_2$ and $\text{R}_2\text{M}=\text{MR}'_2$) for Si, Ge, and Sn are now known to be isolable, provided that bulky groups are used, as discussed in Section 15-7.

Although stoichiometric similarities exist between the compounds of carbon and those of the remaining elements of Group IVB(14) [e.g., the pairs CO_2 and SiO_2 , as well as $(\text{CH}_3)_2\text{CO}$ and $(\text{CH}_3)_2\text{SiO}$], there is no structural or chemical similarity between them. Carbon dioxide is a gas, properly written $\text{O}=\text{C}=\text{O}$, whereas SiO_2 is a giant molecule, or network substance, with each Si atom singly bonded to four adjacent oxygen atoms, giving linked SiO_4 tetrahedra, as discussed in Section 5-4. Also, reactions of the compounds of silicon and the lower elements of the group do not give products analogous to those for carbon. For example, the dehydration of alcohols gives alkenes, but the dehydration of silanols, $\text{R}_2\text{Si}(\text{OH})_2$, is accompanied by condensation, giving $(\text{R}_2\text{SiO})_n$ and $\text{R}_2(\text{OH})\text{SiOSi}(\text{OH})\text{R}_2$.

Whereas multiple bonds to carbon involve overlap of the $p\pi$ - $p\pi$ variety, multiple bonding for silicon and germanium (and to a lesser extent for tin) usually arise from a $p\pi$ - $d\pi$ component, especially in bonds to O and N. It is important to note that this does not usually lead to conjugation, as is so prevalent for carbon. The following structural and chemical features of silicon and germanium compounds are best explained by some degree of $p\pi$ - $d\pi$ double-bond character.

1. Trisilylamine, $(\text{H}_3\text{Si})_3\text{N}$, differs from trimethylamine, $(\text{CH}_3)_3\text{N}$, being planar rather than pyramidal, and being a very weak base. Disilylamine is also planar. These observations can be explained by supposing that nitrogen forms dative π bonds to the silicon atom, as shown in Fig. 15-1. We assume that the central nitrogen atom is sp^2 hybridized, leaving a filled $2p_z$ orbital, which overlaps appreciably with an empty silicon $3d_{xz}$ (or $3d_{yz}$) orbital. Thus a dative $p\pi \rightarrow d\pi$ bond is established, which provides additional bond strength in each Si-N linkage of the molecule. It is this additional bond strength that stabilizes the NSi_3 skeleton in a planar configuration. In contrast, for $\text{N}(\text{CH}_3)_3$, since carbon has no low-lying d orbitals, σ bonding alone determines the configuration at the AB_3E carbon atom, which is pyramidal. As an interesting comparison, consider trisilylphosphine, $(\text{H}_3\text{Si})_3\text{P}$, which is pyramidal. Evidently phosphorus is less able than nitrogen to form a $p\pi \rightarrow d\pi$ dative bond to silicon.

2. In the vapor phase, H_3SiNCO is linear (hydrogen atoms excepted). This can be explained by the formation of a $p\pi \rightarrow d\pi$ bond between nitrogen and silicon ($\text{H}_3\text{Si}=\text{N}=\text{C}=\text{O}$). The corresponding carbon compound (H_3CNCO) is not linear, since carbon has no vacant, low-lying d orbitals. Interestingly, H_3GeNCO is not linear in the gas phase. Evidently, effective $p\pi$ - $d\pi$ bonding occurs for Si-N, but not for Ge-N.

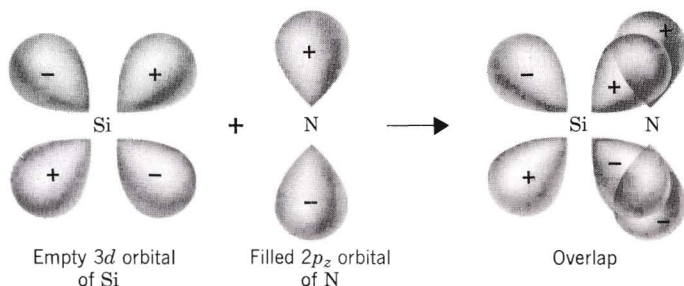


Figure 15-1 The formation of a $d\pi$ - $p\pi$ bond between Si and N atoms in trisilylamine.

3. The disilyl ethers, $(R_3Si)_2O$, all have large angles at oxygen ($140\text{--}180^\circ$), and both electronic and steric explanations have been suggested. Electronically, overlap between filled oxygen $p\pi$ orbitals and empty silicon $d\pi$ orbitals would improve with increasing Si—O—Si angles, and might be most effective for a linear Si—O—Si group. There may also be very strong steric factors favoring more linear structures, especially for large R groups. For instance, the angle at oxygen is 180° for $(Ph_3Si)_2O$.

4. Silanols such as $(CH_3)_3SiOH$ are stronger protonic acids than their carbon analogs, and form stronger hydrogen bonds. This is due to stabilization of the conjugate base anion by $O(p\pi) \rightarrow Si(d\pi)$ bond formation. A similar stabilization of the conjugate base anion can be invoked to explain the order of acidities ($M = Si > Ge > C$) in the series R_3MCO_2H .

Stereochemistry

The stereochemistry of silicon compounds and the lower members of Group IVB(14) depend on the oxidation state. Also, unlike carbon, certain compounds of these elements have five, six, seven, and eight or higher coordination.

Compounds having *oxidation state IV* are listed in Table 15-1. All of the elements form tetrahedral compounds, some of which are chiral, for example, $GeH(CH_3)C_6H_5$ (α -naphthyl). Since valence shell expansion by use of outer d orbitals can occur, giving hybridizations (such as dsp^3 and d^2sp^3), five- and six-coordinate compounds are common, as shown in Table 15-1. Pentacoordination is found mainly in

- Anions such as MX_5^- and $MR_nX_{n-5}^-$, which are usually trigonal bipyramidal, and are stabilized in the solid state by large cations.
- Adducts of donor ligands with halides or substituted halides of the elements, such as $L \rightarrow MX_4$.
- For Sn, polymeric compounds R_3SnX , where X acts as a bridge in the solid state structure.

Octahedral coordination is common for all of the elements, although for ions and adducts, the preference for five or six coordination depends on delicate energy balances, and cannot be predicted.

Table 15-1 Coordination Number and Geometry of Tetravalent Compounds of the Group IVB(14) Elements

Coordination Number	Geometry	Examples
3	Trigonal (AB_3)	$(C_6H_5)_3Si^+$
4	Tetrahedral (AB_4)	SiO_2 , $SiCl_4$, GeH_4 , $Pb(CH_3)_4$
5	Trigonal bipyramidal (AB_5)	$(CH_3)_3SnCl(py)$, $SnCl_5^-$, SiF_5^- , $RSiF_4^-$
5	Square pyramidal (AB_5)	$[XSi(O_2C_6H_4)_2]^-$
6	Octahedral (AB_6)	SiF_6^{2-} , $[Si(acac)_3]^+$, $[Si(ox)_3]^{2-}$, GeO_2 , $PbCl_6^{2-}$, <i>trans</i> - $GeCl_4(py)_2$, $Sn(S_2CNEt_2)_4$
7	Pentagonal bipyramid	$Ph_2Sn(NO_3)_2(OPPh_3)$
8	Dodecahedral	$Sn(NO_3)_4$, $Pb(O_2CCH_3)_4$

Table 15-2 Coordination Number and Geometry of Divalent Compounds of the Group IVB(14) Elements

Coordination Number	Geometry	Examples
2	Angular (AB_2E)	$Ge(N-tBu_2)_2$, $Pb(C_6H_5)_2$
3	Pyramidal (AB_3E)	$SnCl_2 \cdot 2H_2O$, $SnCl_3^-$, $Pb(SC_6H_5)_3^-$
4	"Seesaw" (AB_4E)	Pb^{II} in Pb_3O_4 $Sn(S_2CNR_2)_2$
5	Square pyramidal (AB_5E)	SnO (blue-black form), PbO
6	Octahedral	PbS (NaCl type) GeI_2 (CaI_2 type)
7	Complex	(18-C-6) $SnCl^+$
9, 10	Complex	$Pb(NO_3)_2$ (semicarbazone) $Pb(O_2CCH_3)_2 \cdot 3H_2O$

Compounds having *oxidation state II* are listed in Table 15-2. In many of the compounds of Sn^{II} , and to a lesser extent Ge^{II} and Pb^{II} , the lone pair of electrons on the metal atom has important structural and stereochemical consequences. First, the structures are such that the lone pairs, unlike the so-called "inert pairs," appear to occupy a bond position. Thus the $SnCl_3^-$ ion is pyramidal with a lone pair, as in NH_3 . According to the AB_xE_y scheme, which was discussed in Chapter 3, we would therefore consider this Sn atom to fall into the AB_3E classification. The lone pair not only has structural consequences, but chemical ones as well; $SnCl_3^-$ can act as a donor toward transition metals, as in the complex $[Pt^{II}(SnCl_3)_5]^{3-}$. Consider also $SnCl_2 \cdot 2H_2O$, which contains a pyramidal $SnCl_2OH_2$ molecule; the second water molecule is not coordinated, and is readily lost at 80 °C. Other Sn^{II} compounds, such as $SnCl_2$ and SnS , accomplish three coordination in the solid by use of a bridging group between the metal atoms. The $Sn_2F_5^-$ ion consists of two SnF_3 groups sharing a fluorine atom.

In Ge_5F_{12} , the Ge^{II} atoms fall into the AB_5E classification, being square pyramidal with the lone pair occupying the sixth position. The same is true of SnO (the blue-black form) and of PbO , in which there are MO_5E metal atoms.

15-2 Isolation and Properties of the Elements

Silicon is obtained in the ordinary commercial form by reduction of SiO_2 with carbon or CaC_2 in an electric furnace. Similarly, Ge is prepared by reduction of GeO_2 with C or H_2 . Silicon and Ge are used as semiconductors, especially in transistors. For this purpose, exceedingly high purity ($<10^{-9}$ atom % of impurities) is essential, and special methods are required to obtain usable materials. The element is first converted to the tetrachloride, which is reduced back to the metal by hydrogen at high temperatures. After casting into rods it is *zone refined*. A rod of metal is heated near one end so that a cross-sectional wafer of molten silicon is produced. Since impurities are more soluble in the melt than they are in the solid they concentrate in the melt, and the melted zone is then caused to move slowly along the rod by moving the heat source. This carries impurities to the end. This process may be repeated. The impure end is then removed. Super-pure Ge is made in a similar way.

Tin and lead are obtained by reduction of the oxide or sulfide with carbon. The metals can be dissolved in acid and deposited electrolytically to effect further purification.

Silicon is ordinarily rather unreactive. It is attacked by halogens giving tetrahalides, and by alkalis giving solutions of silicates. Silicon is not attacked by acids except hydrofluoric; presumably the stability of $[SiF_6]^{2-}$ provides the driving force here.

Germanium is somewhat more reactive than silicon and dissolves in concentrated H_2SO_4 and HNO_3 . Tin and lead dissolve in several acids and are rapidly attacked by halogens. These elements are slowly attacked by cold alkali, and rapidly by hot, to form stannates and plumbites. Lead often appears to be more noble and unreactive than would be indicated by its standard potential of -0.13 V. This low reactivity can be attributed to a high overvoltage for hydrogen and also, in some instances, to insoluble surface coatings. Thus lead is not dissolved by dilute H_2SO_4 and concentrated HCl.

15-3 Hydrides: MH_4

These are colorless gases. Only *monosilane* (SiH_4) is of any importance. This spontaneously flammable gas is prepared by the action of $LiAlH_4$ on SiO_2 at 150 – 170 °C or by reduction of $SiCl_4$ with $LiAlH_4$ in an ether. Although stable to water and dilute acids, rapid base hydrolysis gives hydrated SiO_2 and H_2 .

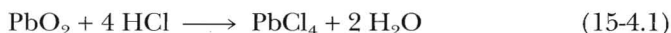
Substituted silanes with organic groups are of great importance, as are some closely related tin compounds (Chapter 29). The most important reaction of compounds with Si—H bonds, such as $HSiCl_3$ or $HSi(CH_3)_3$, is the Speier or hydrosilation reaction of alkenes.



This reaction, which employs chloroplatinic acid as a catalyst, is commercially important for the synthesis of precursors to silicones.

15-4 Chlorides: MCl_4

Chlorination of the hot Group IVB(14) elements gives colorless liquids (MCl_4), except $PbCl_4$, which is yellow. The compound $PbCl_4$ may also be prepared by Reaction 15-4.1.



The tetrachlorides are eventually hydrolyzed by water to hydrous oxides, but limited hydrolysis may give oxochlorides. In aqueous HCl, the tetrachlorides of Sn and Pb give chloroanions, $[MCl_6]^{2-}$.

The compound $GeCl_4$ differs from $SiCl_4$ in that the former can be distilled and separated from concentrated HCl, whereas silicon tetrachloride is immediately hydrolyzed by water.

The principal uses of $SiCl_4$ and $GeCl_4$ are in the synthesis of pure Si and Ge. Additional uses of $SiCl_4$ and $SnCl_4$ are in syntheses of organometallic compounds (Chapter 29).

15-5 Oxygen Compounds

Silica

Pure SiO_2 occurs in two forms, *quartz* and *cristobalite*. The Si is always tetrahedrally bound to four oxygen atoms but the bonds have considerable ionic character. In cristobalite the silicon atoms are placed as are the carbon atoms in diamond, with the oxygen atoms midway between each pair. In quartz, there are helices so that enantiomorphic crystals occur, and these may be easily recognized and separated mechanically.

Quartz and cristobalite can be interconverted when heated. These processes are slow because the breaking and re-forming of bonds is required and the activation energy is high. However, the rates of conversion are profoundly affected by the presence of impurities, or by the introduction of alkali metal oxides.

Slow cooling of molten SiO_2 or heating any solid form to the softening temperature gives an amorphous material that is glassy in appearance and is indeed a glass in the general sense, that is, a material with no long-range order but, instead, a disordered array of polymeric chains, sheets, or three-dimensional units.

Silica is relatively unreactive towards Cl_2 , H_2 , acids, and most metals at 25°C or even at slightly elevated temperatures but is attacked by F_2 , aqueous HF, alkali hydroxides, and fused carbonates.

Aqueous HF gives solutions containing fluorosilicates (e.g., $[\text{SiF}_6]^{2-}$). The *silicates* have been discussed in Section 5-4. The fusion of excess alkali carbonates with SiO_2 at about 1300°C gives water-soluble products commercially sold as a syrupy liquid that has many uses. Aqueous sodium silicate solutions appear to contain the ion $[\text{SiO}_2(\text{OH})_2]^{2-}$ but, depending on the pH and concentration, polymerized species are also present. In weathering of rocks and soils, "silicic acid," $\text{Si}(\text{OH})_4$, is released in addition to $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, and it appears that soluble silica can thereby reduce the Al levels, through formation of aluminosilicates (Chapter 5).

The basicity of the dioxides increases, with SiO_2 being purely acidic, GeO_2 less so, SnO_2 amphoteric, and PbO_2 somewhat more basic. When SnO_2 is made at high temperatures or by dissolving Sn in hot concentrated nitric acid, it is, like PbO_2 , remarkably inert to attack.

Only lead forms a stable oxide containing both Pb^{II} and Pb^{IV} , namely, Pb_3O_4 , which is a bright red powder known commercially as red lead. It is made by heating PbO and PbO_2 together at 250°C . Although it behaves chemically as a mixture of PbO and PbO_2 , the crystal contains $\text{Pb}^{\text{IV}}\text{O}_6$ octahedra linked in chains by sharing opposite edges. The chains are linked by Pb^{II} atoms each bound to three O atoms.

There are no true hydroxides and the products of hydrolysis of the hydrides or halides, and the like, are best regarded as hydrous oxides.

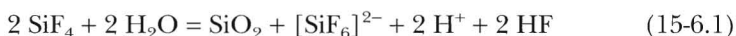
Among the most interesting and commercially valuable of silicon-oxygen compounds are the aluminosilicates, which have been mentioned earlier (Section 5-4).

15-6 Complex Compounds

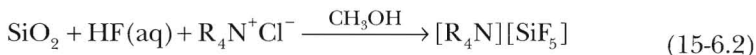
Most of the complex species contain halide ions or donor ligands that are O, N, S, or P compounds.

Anionic Complexes

Silicon forms only fluoroanions, normally $[\text{SiF}_6]^{2-}$, whose high formation constant accounts for the incomplete hydrolysis of SiF_4 in water, according to Reaction 15-6.1.



The ion is usually made by dissolving SiO_2 in aqueous HF and is stable even in basic solution. Under selected conditions and with cations of the right size, the $[\text{SiF}_5]^-$ ion can be isolated, for example,



By contrast with $[\text{SiF}_6]^{2-}$, the $[\text{GeF}_6]^{2-}$ and $[\text{SnF}_6]^{2-}$ ions are hydrolyzed by bases; $[\text{PbF}_6]^{2-}$ ion is hydrolyzed even by water.

Although Si does not, the other elements give chloroanions, and all the elements form oxalato ions $[\text{M}(\text{ox})_3]^{2-}$.

Cationic Complexes

The most important are those of chelating uninegative oxygen ligands, such as the acetylacetonates. An example is $[\text{Ge}(\text{acac})_3]^+$.

The tetrahalides act as Lewis acids; SnCl_4 is a good Friedel–Crafts catalyst. The *adducts* are 1:1 or 1:2 but it is not always clear in the absence of X-ray evidence whether they are neutral, that is, MX_4L_2 , or whether they are salts, for example, $[\text{MX}_2\text{L}_2]\text{X}_2$. Some of the best defined are the pyridine adducts, for example, *trans*-(py)₂SiCl₄.

Alkoxides, Carboxylates, and Oxo Salts

All four elements form alkoxides. Those of silicon [e.g., $\text{Si}(\text{OC}_2\text{H}_5)_4$] are the most important; the surface of glass or silica can also be alkoxyated. Alkoxides are normally obtained by the standard method, solvolysis of chlorides, as in Eq. 15-6.3.



Silicon alkoxides are hydrolyzed by water, eventually to hydrous silica. Of the carboxylates, *lead tetraacetate* is the most important, as it is used in organic chemistry as a strong but selective oxidizing agent. It is made by dissolving Pb_3O_4 in hot glacial acetic acid or by electrolytic oxidation of Pb^{II} in acetic acid. In oxidations the attacking species is probably $\text{Pb}(\text{OOCCH}_3)_3^+$, which is isoelectronic with the similar oxidant, $\text{Tl}(\text{OOCCH}_3)_3$, but this is not always so, and some oxidations are free radical in nature. The trifluoroacetate is a white solid, which will oxidize even heptane to give the ROOCCF_3 species, whence the alcohol ROH is obtained by hydrolysis; benzene similarly gives phenol.

Tin(IV) sulfate, $\text{Sn}(\text{SO}_4)_2 \cdot 2 \text{H}_2\text{O}$, can be crystallized from solutions obtained by oxidation of Sn^{II} sulfate; it is extensively hydrolyzed in water.

Tin(IV) nitrate is a colorless volatile solid made by interaction of N_2O_5 and SnCl_4 ; it contains bidentate NO_3^- groups giving dodecahedral coordination. The compound reacts with organic matter.

15-7 The Divalent State

Silicon

Divalent silicon species are thermodynamically unstable under normal conditions. However, several species, notably SiO and SiF₂, have been identified in high temperature reactions and trapped by chilling to liquid nitrogen temperatures. Thus at about 1100 °C and low pressures, the following reaction goes in about 99.5% yield:



Silicon difluoride (SiF₂) is stable for a few minutes at 10⁻⁴ cm pressure; the molecule is angular and diamagnetic. When the frozen compound warms, it gives fluorosilanes up to Si₁₆F₃₄.

Germanium

Germanium dihalides are stable. Germanium difluoride (GeF₂) is a white crystalline solid obtained by the action of anhydrous HF on Ge at 200 °C; it is a fluorine bridged polymer with approximately tbp coordination of Ge. Germanium dichloride (GeCl₂) gives salts of the GeCl₃⁻ ion similar to those of Sn noted in the next subsection.

Tin

The most important compounds are SnF₂ and SnCl₂, which are obtained by heating Sn with gaseous HF or HCl. The fluoride is sparingly soluble in water and is used in fluoride-containing toothpastes. Water hydrolyzes SnCl₂ to a basic chloride, but from dilute acid solutions SnCl₂·2H₂O can be crystallized. Both halides dissolve in solutions containing an excess of halide ion, thus



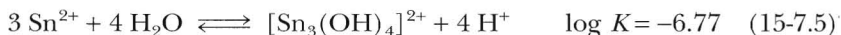
In aqueous fluoride solutions SnF₃⁻ is the major species, but the ions SnF⁺ and Sn₂F₅⁻ can be detected.

The halides dissolve in donor solvents such as acetone, pyridine, or DMSO, to give pyramidal adducts, for example, SnCl₂OC(CH₃)₂.

The very air-sensitive tin(II) ion (Sn²⁺) occurs in acid perchlorate solutions, which may be obtained by reduction of copper(II) perchlorate as in Reaction 15-7.4.

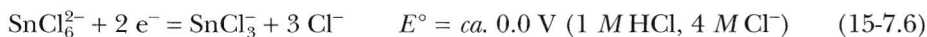


Hydrolysis gives [Sn₃(OH)₄]²⁺, with SnOH⁺ and [Sn₂(OH)₂]²⁺ in minor amounts.



The trimeric, probably cyclic, ion appears to provide the nucleus of several basic

tin(II) salts obtained from aqueous solutions at fairly low pH. Thus the nitrate appears to be $\text{Sn}_3(\text{OH})_4(\text{NO}_3)_2$ and the sulfate, $\text{Sn}_3(\text{OH})_2\text{OSO}_4$. All Sn^{II} solutions are readily oxidized by oxygen and, unless stringently protected from air, normally contain some Sn^{IV} . The chloride solutions are often used as mild reducing agents.

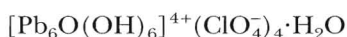


Lead

Of the four elements, only lead has a well-defined low-valent cationic chemistry. The lead(II) ion (Pb^{2+}) is partially hydrolyzed in water.



In concentrated solutions and on addition of base, polymeric ions that contain three, four, and six Pb atoms are formed. The crystalline "basic" salt



has the cluster structure in Fig. 15-2. The O atom lies at the center of the middle tetrahedron, while the OH groups lie on the faces of the outer tetrahedra.

Most lead salts are only sparingly soluble in water and some (e.g., PbSO_4 or PbCrO_4) are insoluble. The common soluble salts are $\text{Pb}(\text{NO}_3)_2$ and $\text{Pb}(\text{CO}_2\text{CH}_3)_2 \cdot 2 \text{H}_2\text{O}$, which is incompletely ionized in water. The halides are always anhydrous and in solution they form complex species PbX^+ , PbX_3^- , and so on, except for the fluoride where only PbF^+ occurs.

Silenes and Other Organo Compounds

Although for many of the elements, discussion of organo chemistry has been reserved for later chapters, it is now appropriate to mention the recent developments in divalent organo chemistry for silicon, germanium, and tin. Compounds of stoichiometry GeR_2 or SnR_2 , which were known for a long time, proved to be cyclogermanes or stannanes such as $(\text{Me}_2\text{Sn})_6$ (where $\text{Me} = \text{CH}_3$), or various other polymers with $\text{M}^{\text{II}}-\text{M}^{\text{II}}$ bonds. Also, the silicon compounds made by the reduction of R_2SiCl_2 with Li or Na/K in THF, where R is *not* a bulky ligand, are

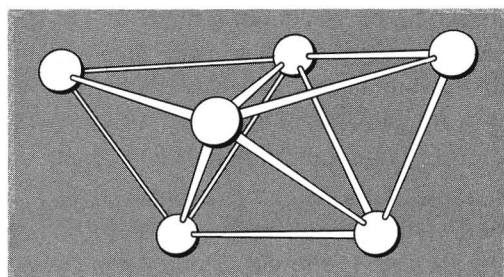


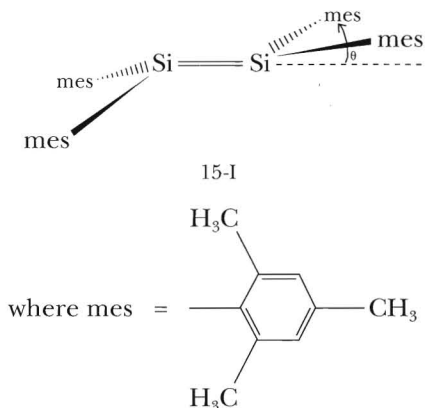
Figure 15-2 The three face-sharing tetrahedra of Pb atoms in the $\text{Pb}_6\text{O}(\text{OH})_6^{4+}$ cluster.

cyclic polymers. These compounds are often similar to hydrocarbons, but differ in having large ($\sim 115^\circ$) Si—Si—Si angles.

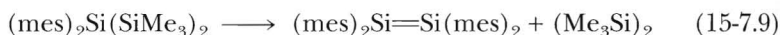
However, when the alkyl or aryl R groups are very bulky, monomers (MR_2) or dimers ($\text{R}_2\text{M}=\text{MR}_2$) can be isolated. The simplest silene (Me_2Si) can be obtained only in the gas phase or in solution by thermal decomposition of the cyclic hexamer, as in Reaction 15-7.8.



The first isolable *silene*, the yellow tetramesityl disilene, Structure 15-I



can be made photochemically according to Reaction 15-7.9.



This compound is an air sensitive, but thermally stable solid, with a slightly bent trans structure, the angle θ being 18° . In this respect, this silene differs from typical alkenes, which are planar. The Si=Si bond (2.16 Å) is about 9% shorter than a Si—Si single bond. Many other disilenes can be made by the reduction of R_2SiCl_2 with Li, and some compounds have sufficiently strong double bonds to permit the existence of cis and trans isomers. There are similar $\text{R}_2\text{Si}=\text{CR}_2$ compounds containing Si=C bonds. A good example is $\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)(\text{SiMe}_2\text{-}t\text{-Bu}_2)_2$, where the $\text{C}_2\text{Si}=\text{CSi}_2$ skeleton is planar, with a C=Si bond distance of 1.702 Å. Finally, compounds with Si=N, Si=P, and Si=O bonds are known, for example, $t\text{-Bu}_2\text{Si}=\text{NSi-}t\text{-Bu}_3$.

The *germenes*, which can be made by the action of Grignard reagents on $\text{GeCl}_2 \cdot \text{dioxane}$ in ether, and stannenes, are less stable than silenes. Distortions from planar geometry are larger than is found among the silenes. Tin and lead form highly colored monomers or dimers, but in Sn_2R_4 the Sn—Sn distance is 2.76 Å, a value closer to that of a Sn—Sn single bond.

15-8 Summary of Group Trends for the Elements of Group IVB(14)

Using the list of periodic chemical properties listed in Section 8-11, as well as properties mentioned in Chapters 14 and 15, we can now summarize the periodic trends in the properties of the elements of Group IVB(14).

1. Carbon

- (a) Is completely nonmetallic.
- (b) Has a strong tendency for catenation among its compounds.
- (c) Forms molecular (covalent) substances almost exclusively (carbides excepted).
- (d) Obeys the octet rule, the maximum covalence being four.
- (e) Forms divalent (lower valent) compounds that are unstable (as in reactive intermediates), or that exist as such only as a formality (e.g., CO).
- (f) Forms hydrides that are stable, molecular substances that are difficult to hydrolyze, but oxidize readily.
- (g) Forms stable, molecular halides that are not readily oxidized or hydrolyzed.
- (h) Forms oxides (CO and CO₂) that are acidic anhydrides.
- (i) Forms multiple bonds of the $p\pi-p\pi$ variety, which can be conjugated.

2. Silicon

- (a) Is a nonmetal.
- (b) Displays little or no tendency for catenation among its compounds.
- (c) Forms mostly covalent substances, as well as polyatomic ions and oxoanions containing covalent bonds.
- (d) Readily undergoes coordination number expansion to a maximum covalence of six, namely, SiF₅⁻ and SiF₆²⁻.
- (e) Forms divalent (lower valent) compounds only rarely, an example being the unstable SiF₂.
- (f) Forms hydrides that are reactive and unstable, an example being SiH₄, which is readily hydrolyzed.
- (g) Forms molecular halides that are readily hydrolyzed.
- (h) Forms an oxide (SiO₂) that is an acidic, covalent-network substance.
- (i) Forms strong, but unconjugated multiple bonds of the $p\pi-d\pi$ variety, especially to O and N.

3. Germanium, Tin, and Lead

- (a) Are increasingly metallic on descent of the group, Ge being most like Si.
- (b) Display little catenation, since in general bond strength decreases on descending the group.
- (c) Form both covalent and ionic substances.
- (d) Form compounds with a variety of coordination numbers, six or eight being common.
- (e) Form divalent (lower valent) compounds that are increasingly stable upon descending the group.
- (f) Do not form any important covalent hydrides.
- (g) Form both high-valent (MX₄) and low-valent (MX₂) molecular halides, which are readily hydrolyzed and undergo coordination number expansion to produce, for instance, SnCl₆²⁻ or PbCl₆²⁻.
- (h) Display increasingly metallic character on descent of the group, as

demonstrated by the following. Whereas SiO_2 is acidic and SnO_2 is amphoteric, PbO_2 is purely a basic anhydride.

- (i) Form multiple bonds of the $p\pi-d\pi$ variety, but less effectively on descent of the group.

STUDY GUIDE

Study Questions

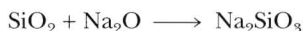
A. Review

1. Why is CO_2 a gas and SiO_2 a giant molecule?
2. Explain what is meant by $d\pi-p\pi$ bonding.
3. Why does tin form divalent inorganic compounds more easily than silicon?
4. How is super pure Ge made from GeO_2 ?
5. Write balanced equations for the synthesis of SiH_4 and for its hydrolysis by aqueous KOH.
6. Why is CCl_4 unreactive to H_2O , whereas SiCl_4 is rapidly hydrolyzed?
7. Why is SiF_4 incompletely hydrolyzed by water?
8. Explain the nature of zeolites and of molecular sieves.
9. Why does silicon have much less tendency to form bonds to itself than does carbon?
10. How is lead tetraacetate made?
11. What is red lead?
12. What is the nature of Sn^{II} in aqueous chloride solution?

B. Additional Exercises

1. Explain why H_3SiNCS has a linear SiNCS group, whereas in H_3CNCS the CNC group is angular.
2. Why are silanols, such as $(\text{CH}_3)_3\text{SiOH}$, stronger acids than their carbon analogs?
3. List the various types of geometries among the compounds of the tetravalent Group IVB(14) elements and give examples. For each example, give the structural classification for the Group IVB(14) atom, according to the AB_xE_y scheme of Chapter 3.
4. What methods could one use to determine the nature of 1:1 and 1:2 adducts of SnCl_4 with neutral donors?
5. Why can Sn^{II} compounds, such as SnCl_3^- , act as donors (ligands) to transition metals?
6. The single-bond energies for the elements of the first and second short periods follow the trends $\text{C} > \text{Si}$; $\text{N} < \text{P}$; $\text{O} < \text{S}$; $\text{F} < \text{Cl}$. Why is the first pair in the list apparently anomalous?
7. Predict the relative π -bond strength between B and N in the two compounds bis(trimethylsilyl)aminoborane and bis(*tert*-butyl)aminoborane. Explain your answer in terms of the π orbitals that are involved.
8. Draw the π -bond system that is responsible for the planarity of trisilylamine.
9. Draw the Lewis diagrams and discuss the geometries of SnCl_2 , SnCl_3^- , and $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$.
10. Balance the equation for the reaction of SiCl_4 with LiAlH_4 .
11. Use valence shell electron-pair repulsion (VSEPR) theory to compare the bond angles in the pyramidal ions SnF_3^- , SnCl_3^- , and GeCl_3^- .

12. Review the material of Section 8-11 plus the material of this chapter, and summarize the facts concerning the low-valent state for the elements of Group IVB(14), citing specific compounds as examples to illustrate each point.
13. Compare the reactivities of the divalent chlorides (GeCl_2 , SnCl_2 , and PbCl_2) with chlorine, and use this information to arrive at the correct order of stabilities of the divalent state for these elements.
14. Diagram the apparent extent of the π -bonding systems in H_3SiNCO and in H_3GeNCO , taking into consideration the geometries of the two.
15. Explain the planarity of disilylamine using an orbital overlap approach.
16. Offer an explanation for the relative extent of N-to-M π bonding in H_3SiNCO versus H_3GeNCO .
17. The compound $\text{SnCl}_2(\text{C}_2\text{H}_5)_2$ crystallizes as long needles, in which there are Sn—Cl—Sn bridges in one plane and ethyl groups in coordination positions perpendicular to that plane. The effective coordination number of Sn in the solid is six, but there are two Sn—Cl distances in the structure. Propose a solid state structure.
18. Choose the correct answer from among the following possibilities:
 - (a) The most stable low-valent halide:
 GeCl_2 SnCl_2 PbCl_2
 - (b) A nonexistent halide:
 SnCl_4 PbCl_4 PbI_4
 - (c) A purely acidic oxide:
 PbO_2 SnO_2 SiO_2
 - (d) Forms an oxoacid on treatment with HNO_3 :
 P_4 Sb_4 Bi
 - (e) The most stable hydride:
 NH_3 PH_3 AsH_3
 - (f) The substance that is coordinatively saturated:
 CCl_4 SiCl_4 PbCl_4
 - (g) The substance that is not coordinatively saturated:
 SnF_5^- CH_4 PCl_6^-
19. Explain how the following reaction demonstrates the acidity of SiO_2 :



20. List and explain three ways in which the chemistry of carbon differs from that of the other members of the group.
21. Give balanced equations for each of the following:
 - (a) Production of Ge from the oxide.
 - (b) Oxidation of Si by chlorine.
 - (c) Dissolution of SnCl_2 in pyridine.
 - (d) Hydrolysis of GeCl_4 .
 - (e) Hydrolysis of Sn^{2+} solutions.
 - (f) Hydrolysis of SiF_4 .
22. Why does the tendency towards catenation decrease on descent of Group IVB(14)? Illustrate your answer with some examples.
23. Suggest a synthesis, starting from elemental silicon and fluorine, of SiF_6^{2-} .
24. What is the main product on reaction of lead with chlorine, PbCl_4 , PbCl_2 , or PbOCl ?
25. Suggest a synthesis of lithium bis(dimethylsilyl)amide.
26. Sketch the structures of SnCl_2 , SnCl_3^- , SnF_4 , and SnF_5^- .

C. Questions from the Literature of Inorganic Chemistry

- Let the paper by R. H. Nielson and R. L. Wells, *Inorg. Chem.*, **1977**, *16*, 7–11, serve as a basis for the following questions:
 - What typical values for B—N rotational barriers does one expect for mono-, bis-, and tris-aminoboranes?
 - Why should studies of rotational barriers in these aminoboranes indicate the relative extent of π bonding between boron and an *N*-trimethylsilyl, an *N*-trimethylgermyl, and an *N*-trimethylstannyl substituent?
 - Both a steric and a competitive π -bonding argument can be given to explain the trends reported here. Elaborate.
- Consider the paper by D. Kummer and T. Seshadri, *Angew. Chem. Int. Ed. Eng.*, **1975**, *14*, 699–700.
 - Determine the oxidation state of Si and draw the Lewis diagram for each of the Si-containing compounds mentioned in this article.
 - Predict the geometry for each of these compounds.
- Compare and contrast the structure of and the bonding in two different classes of Sn^{IV} compounds as presented in
 - R_2SnX_2
N. W. Alcock and J. F. Sawyer, *J. Chem. Soc., Dalton Trans.*, **1977**, 1090–1095.
 - $\text{SnCl}_4(\text{PR}_3)_2$
G. G. Mather, G. M. McLaughlin, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, **1973**, 1823–1827.
- Consider the compounds $\text{M}[\text{CH}(\text{Me}_3\text{Si})_2]_2$, where M = Ge, Sn, or Pb, as described by J. D. Cotton, P. J. Davidson, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1976**, 2275–2285.
 - Draw the Lewis diagram of these substances.
 - Explain (and give an example of) each of the four types of reactions mentioned for these substances.
- Look up the structure of PbO (*Acta Crystallogr.*, **1961**, *14*, 1304) and describe the geometry at lead. What structural role does the “lone pair” play?
- The structure of the $[\text{K}(18\text{-C}-6)]^+$ salt of $[(t\text{-Bu})_3\text{C}_6\text{H}_2\text{—SiF}_4]^-$ was reported by S. E. Johnson, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **1989**, *28*, 3182. What unusual bond angles are there in this anion, and what is the apparent cause?
- Read the first report on the structure of two stable disilenes by M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, and J. Michl, “X-ray Structure of Two Disilenes,” *Organometallics*, **1984**, *3*, 793–800.
 - Which of these two disilenes has a structure most like an alkene?
 - What two principle deviations from planarity are noted for Compound *1a*?
 - What explanations do the authors give for the pyramidalization at Si in Compound *1a*?
 - Why do these distortions from planarity not occur for Compound *1b*?

SUPPLEMENTARY READING

Breck, D. W., *Molecular Sieves*, Wiley, New York, 1973.

Burger, H. and Eugen, R., “The Chemistry of Lower-Valent Silicon,” *Topics in Current Chemistry*, No. 5, Springer-Verlag, Berlin, 1974.