Introduction

- Silicon is the most abundant element after oxygen in the earth's crust occurring mostly as the silicates and quartz (SiO2).
- The other elements are actually quite rare (\(\sim 10^{-3}\%\)) but tin and lead are found in concentrated pockets of their ores (cassiterite, SnO2 and galena, PbS2) from which they are easily obtained, so they have been known and used since antiquity.
- The existence of germanium ("ekasilicon") was predicted by Mendeleev when he constructed the first reasonably complete periodic table. It was isolated in 1886 from coal and zinc ores.
- The main uses of tin and lead are as the metals and as synthetic reagents as their organo compounds. Silicon and germanium are the basis of the semiconductor industry.

Multiple Bonding

Because of the great versatility of carbon, it is interesting to compare the other members of group 14.

- Carbon dioxide is molecular gas whereas silicon dioxide is a network solid (in all its forms several forms).
- Dehydration of alcohols, ROH yields both alkenes and ROR depending on the conditions, but dehydrating R3SiOH yields only R3SiOSiR3.
- Multiple p-p bonding between silicon atoms and other first row elements was thought not to exist until the '60's when the first Si=C bonds were observed as transient species, and then isolated in heavily sterically hindered compounds:

Replacement of the hydrogen with tertiary butyl groups allows the isolation of similar compounds of silicon, germanium and tin.

- Silicon can use empty d-orbitals for p-p - d-p bonding. Examples are planar (H3Si)3N vs pyramidal (H3C)3N and linear H3SiNCO vs H3CNCO which is bent at the nitrogen. In both cases the nitrogen lone pair is delocalized by p-bonding with the silicon(s).

In CR3OCR3 the Si-O-Si angle is around 109 ^\circ\text{O} whereas in R3SiOSiR3 the angles range from 140 to 180 ^\circ\text{O} indicative of Si=O d-p - p-p bonding.

(CH3)3COH is a very weak acid but (CH3)3SiOH is stronger because the ion (CH3)3SiO^- is stabilized by d-p - p-p bonding.
Stereochemistry

See Table 15-1 for summary information about the tetravalent state:

- All show tetrahedral coordination.
- Five coordinate complexes e.g. MX₅⁻ or MnX₅₋₅ can be trigonal bipyramids or rarely square pyramidal if a constraining chelating ligand is used, e.g. [XSi(O₂C₂H₄)₂]⁻.
- 6-coordinatate complexes are normally octahedral.

See Table 15-2 for summary information about divalent states.

- Very often, but not always, the lone pair is stereochemically active and influences the molecular shape. F₂Pb is bent and so is SiCl₃⁻.

Isolation and Properties of the Elements

- Silicon and germanium can be made by reduction of their dioxides by carbon or calcium carbide in an electric furnace, and then purified further by zone-refining.
- Tin and lead are obtained by carbon reduction of their oxides or sulphides. Further purification is necessary they can be dissolved in acid and redeposited electrolytically.
- Silicon and germanium are relatively inert but the following reactions occur:
  \[ \text{Si} + 2X_2 \rightarrow \text{SiX}_4 \text{ (}X_2\text{ is a halogen)} \]
  \[ \text{Si} + \text{excess OH}^- \rightarrow \text{silicates} \]
  \[ \text{Si} + \text{excess } X \rightarrow \text{no reaction except HF will give SiF}_6^{2-} \]

Germanium is somewhat more reactive and will dissolve in sulphuric or nitric acids.

Tin and lead dissolve in several acids, hot alkalis and also react with halogens.

Hydrides

Compounds MH₄ all exist as spontaneously flammable gases and are not very important.
Chlorides

Compounds MCl_4 are all colourless liquids except PbCl_4 which is yellow. They are hydrolysed easily to give hydrous oxides. In hydrochloric acid the lower members, tin and lead, give MCl_6^{2-} ions in aqueous solution. The compounds are intermediates in the synthesis of organo compounds for example the infamous tetraethyl lead.

Oxygen Compounds

- Silica comes on three forms: quartz and cristobalite which are both crystalline, and silica glass. The glass has a very low coefficient of expansion and high melting point so it is relatively resistant to heat and sudden temperature changes. It is also transparent to a large part of the ultraviolet spectrum and therefore used in cells for spectrophotometry in that region.
- There are several important oxides of lead: PbO exists in a red form, litharge, and a yellow form, massicot. It is the most used Pb source of lead for synthesis. Pb_2O_3 which behaves like a mixture of PbO and PbO_2 although it is a well defined structure is called "red lead". It is used as an anti-rust coating for steel. Lead dioxide, PbO_2 is maroon in colour and has a structure similar to rutile (TiO_2). It is one of the electrode materials in lead/acid batteries.
- The oxides vary from acidic for SiO_2 to basic for tin and lead.

Complex Compounds

Anionic Complexes

Silicon forms a very stable fluoroanion:

\[
\text{SiO}_2(s) + 6\text{HF}(aq) \rightarrow 2\text{H}^+(aq) + \text{SiF}_6^{2-}(aq) + 2\text{H}_2\text{O}
\]

The same anion is formed by the incomplete hydrolysis of SiF_4:

\[
\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + \text{SiF}_6^{2-} + 2\text{H}^+ + 2\text{HF}
\]

The other MF_6^{2-} ions are hydrolysed by bases or even water in the case of the lead complex ion. All the elements give analogous chloroanions, except silicon. The other fairly important anionic complex is obtained with oxalate, [M(ox)_3]^{2-}.

Cationic Complexes and Neutral Adducts

Can be formed with chelating uninegative oxygen donor ligands, e.g. [Pb(acac)_3]^+.

The MX_4 compounds are Lewis acids and can form adducts which are sometimes neutral MX_4L or MX_4L_2 molecular compounds but can also be ionic [MX_2L_2]X_2.
Alkoxides, Carboxylates and Oxo Salts

Typical preparative routes are, for alkoxides:

\[
\begin{align*}
MCl_4 + 4ROH + 4(\text{Et})_3N & \quad \rightarrow \quad M(OR)_4 + 4(\text{Et})_3NHCl \\
\end{align*}
\]

Note the use of the triethylamine to "remove" the HCl which would be formed in its absence.

Carboxylates can be made by direct reaction:

\[
\begin{align*}
PbO_4 + 8\text{CH}_3\text{COOH} & \quad \rightarrow \quad \text{Pb(CH}_3\text{COO)}_4 + 2\text{Pb(CH}_3\text{COO)}_2 + 8\text{H}_2\text{O} \\
\end{align*}
\]

Lead tetraacetate is used as an oxidizing agent in certain organic reactions.

Tin and Lead (IV) salts are hydrated e.g Pb(SO_4)_2.2H_2O and subject to extensive hydrolysis in aqueous solution.

The Divalent State

- This oxidation state becomes more and more stable down the group.
- Silicon dihalides are only transient species. GeF_2 and GeCl_2 can be isolated.
- Tin II fluoride and chloride are well known and useful. (SnF_2 is the active ingredient in many fluoridated toothpastes.) In solution, tin II is easily oxidized by air. The sulphates and nitrates are heavily hydrolysed: Sn_3(OH)_4(NO_3)_2 and Sn_3(OH)_2SO_4.
- Lead II is the best defined divalent state. Most lead II salts are not very water soluble. The exception are the nitrate and the acetate. The solid halides are always anhydrous.

Silenes and Other Organic Compounds

It is possible to make some compounds containing a Si=Si or Ge=Ge double bonds.

The earliest attempts tried the reaction:

\[
\begin{align*}
2R_2\text{SiCl}_2 + \text{Na/K in THF} & \quad \rightarrow \quad R_2\text{Si}=\text{SiR}_2 + 4\text{K/NaCl} \\
\end{align*}
\]

Without the bulky R groups cyclic polymers are generated typically with 6 silicons in a ring. By using sufficiently bulky organic groups, it was possible to prepare transient dimers, R_2Si=SiR_2, or monomers R_2Si. The first silene stable enough to isolate was prepared by the photochemical decomposition of (mes)_2Si(SiMe_3)_2:
Unlike the carbon analogs, the molecule is not perfectly flat. The Si=Si double bond is 9% shorter than a normal Si-Si single bond, c.f. 13% in an olefin.