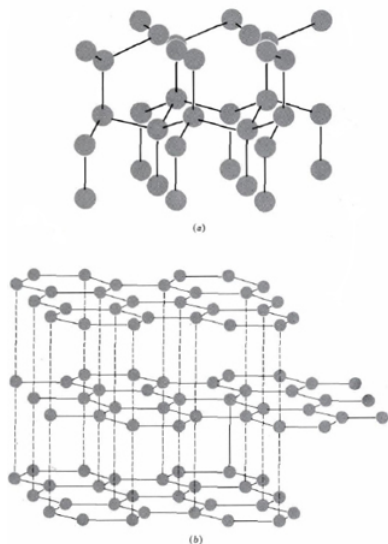


12.5: Group IVA

Near the middle of the periodic table there is greatest variability of properties among elements of the same group. This is certainly true of group IVA, which contains carbon, a nonmetal, silicon and germanium, both semi- metals, and tin and lead, which are definitely metallic. Elemental carbon exists in two allotropic forms, diamond and graphite, whose structures are shown below.



The crystal structure of (a) diamond and (b) graphite.

In diamond there is a three-dimensional network of covalent bonds, while graphite consists of two-dimensional layers covalently bonded. Silicon, germanium, and one allotrope of tin (gray tin) also have the diamond structure—each atom is surrounded by four others arranged tetrahedrally. White tin has an unusual structure in which there are four nearest-neighbor atoms at a distance of 302 pm and two others at 318 pm. Only lead has a typical closest-packed metallic structure in which each atom is surrounded by 12 others.

Properties of the Group IVA Elements

| Element | Symbol | Electron Configuration | Usual State | Oxidation | Radius/pm | |
|-----------|--------|-------------------------------------|-------------|-----------|-----------|--------------------|
| | | | | | Covalent | Ionic (M^{2+}) |
| Carbon | C | $[\text{He}]2s^22p^2$ | +4, +2 | | 77 | - |
| Silicon | Si | $[\text{Ne}]3s^23p^2$ | +4, +2 | | 117 | - |
| Germanium | Ge | $[\text{Ar}]4s^23d^{10}4p^2$ | +4, +2 | | 122 | - |
| Tin | Sn | $[\text{Kr}]5s^24d^{10}5p^2$ | +2, +4 | | 141 | 122 |
| Lead | Pb | $[\text{Xe}]6s^24f^{14}5d^{10}6p^2$ | +2, +4 | | 146 | 131 |

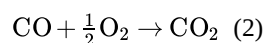
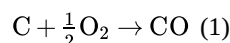
| Symbol | Ionization Energy/MJ mol ⁻¹ | | | | Density/ g cm ⁻³ | Electro- negativity | Melting Point (in °C) |
|--------|--|--------|-------|--------|--------------------------------|------------------------|--------------------------|
| | First | Second | Third | Fourth | | | |
| C | 1.093 | 2.359 | 4.627 | 6.229 | 3.51 | 2.5 | 3550 |
| Si | 0.793 | 1.583 | 3.238 | 4.362 | 2.33 | 1.8 | 1410 |
| Ge | 0.768 | 1.544 | 3.308 | 4.407 | 5.35 | 1.8 | 937 |
| Sn | 0.715 | 1.418 | 2.949 | 3.937 | 7.28 | 1.8 | 232 |

| | | | | | | | |
|----|-------|-------|-------|-------|-------|-----|-----|
| Pb | 0.722 | 1.457 | 3.088 | 4.089 | 11.34 | 1.8 | 327 |
|----|-------|-------|-------|-------|-------|-----|-----|

Some properties of the group IVA elements are summarized in the table. As in the case of group IIIA, there is a large decrease in ionization energy and electronegativity from carbon to silicon, but little change farther down the group. This occurs for the same reason in both groups, namely, that elements farther down the group have filled *d* subshells. Note also that ionization energies, especially the third and fourth, are rather large. Formation of true +4 ions is very difficult, and in their +4 oxidation states all group IVA elements form predominantly covalent bonds. The +2 oxidation state, corresponding to use of the *np*², but not the *ns*², electrons for bonding, occurs for all elements. It is most important in the case of tin and especially lead, the latter having an inert pair like that of thallium. In the +4 oxidation state lead is a rather strong oxidizing agent, gaining two electrons (6s²) and being reduced to the +2 state.

Chemical Reactions and Compounds

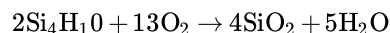
Carbon's ability to form strong bonds with other carbon atoms and the tremendous variety of organic compounds have already been discussed extensively in the section on organic compounds. You may want to review the subsections dealing with hydrocarbons and the other organic compounds. The most important inorganic carbon compounds are carbon monoxide and carbon dioxide. Both are produced by combustion of any fuel containing carbon:



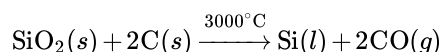
The triple bond in $\text{C}\equiv\text{O}$ is the strongest chemical bond known, and $\text{O}=\text{C}=\text{O}$ contains two double bonds, and so both molecules are quite stable. Equations (1) and (2) occur stepwise when a fuel is burned, and the strong $\text{C}\equiv\text{O}$ bond makes Eq. (2) slow unless the temperature is rather high. If there is insufficient O_2 or if the products of combustion are cooled rapidly, significant quantities of CO can be produced. This is precisely what happens in an automobile engine, and the exhaust contains between 3 and 4% CO unless pollution controls have been installed.

CO is about 200 times better than O_2 at bonding to hemoglobin, the protein which transports O_2 through the bloodstream from the lungs to the tissues. Consequently a small concentration of CO in the air you breathe can inhibit transport of O_2 to the brain, causing drowsiness, loss of consciousness, and death. (After a few minutes of breathing undiluted auto exhaust, more than half your hemoglobin will be incapable of transporting O_2 , and you will faint.) CO in automobile exhaust can be used to put animals to sleep. Because CO is colorless and odorless, your senses cannot detect it, and people must constantly be cautioned not to run cars in garages or other enclosed spaces. With the large number of cars and the great number of miles driven, it is important to limit CO emissions from automobiles. In the early 1970s new EPA standards led to the adoption of catalytic converters, which convert the poisonous CO into CO_2 ^[1]. Implementation and increasing effectiveness of these converters has caused CO levels to drop since the 1970s, despite the increase in automobiles on the road^[2].

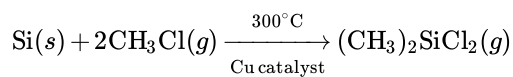
Like the organic compounds of carbon, the oxygen compounds of silicon which make up most of the earth's crust have already been described. These substances illustrate a major contrast between the chemistry of carbon and silicon. The latter element does form a few compounds, called silanes, which are analogous to the alkanes, but the Si—Si bonds in silanes are much weaker than Si—O bonds. Consequently the silanes combine readily with oxygen from air, forming Si—O—Si linkages. Unlike the alkanes, which must be ignited with a spark or a match before they will burn, silanes catch fire of their own accord in air:



Another important group of silicon compounds is the **silicones**. These polymeric substances contain Si—O—Si linkages and may be thought of as derived from silicon dioxide, SiO_2 . To make silicones, one must first reduce silicon dioxide to silicon. This can be done using carbon as the reducing agent in a high-temperature furnace:



The silicon is then reacted with chloromethane:

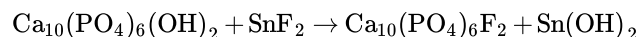


The dichlorodimethylsilane obtained in this reaction polymerizes when treated with water:

$$n(\text{CH}_3)_2\text{SiCl}_2 + n\text{H}_2\text{O} \rightarrow \left(\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{CH}_3 \end{array} \right)_n + 2n\text{HCl}$$

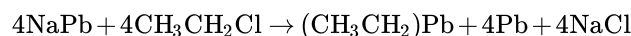
The silicone polymer consists of a strongly bonded —Si—O—Si—O—Si—O chain, called a **siloxane** chain, with two methyl groups (or other organic groups) on each silicon atom. The strong backbone of a silicone polymer makes it stable to heat and difficult to decompose. Silicone oils make good lubricants and heat-transfer fluids, and rubber made from silicone remains flexible at low temperatures.

Besides the metals themselves, some tin and lead compounds are of commercial importance. Tin(II) fluoride (stannous fluoride), SnF_2 , is added to some toothpastes to inhibit dental caries. Tooth decay involves dissolving of dental enamel [mainly $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] in acids synthesized by bacteria in the mouth. Fluoride ions from SnF_2 inhibit decay by transforming tooth surfaces into $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, which is less soluble in acid:



Since F^- is a weaker base than OH^- , the F^- compound has less tendency to react with acids. Note that when tin or lead are in the +2 oxidation state and are combined with a highly electronegative element like fluorine, the compounds formed are rather ionic.

Lead is found in two main commercial applications. One, the lead-acid storage battery is used to start cars and power golf carts. The other is the lead found in automobile fuel. In the +4 oxidation state lead forms primarily covalent compounds and bonds strongly to carbon. The compound tetraethyllead may be synthesized by reacting with a sodium-lead alloy:



Sodium dissolved in the lead makes the latter more reactive. Tetraethyl-lead prevents gasoline from igniting too soon or burning unevenly in an automobile engine, circumstances which cause the engine to “knock” or “ping.” This is where the term leaded gasoline comes from. A major problem connected to using tetraethyl-lead is the introduction of lead into the atmosphere. Lead is toxic, and thus use of TEL as an antiknock agent has been phased out in favor of other agents less dangerous to public health.

References

1. ↑ "Automobiles and Carbon Monoxide." Environmental Protection Agency. January 1993. <http://www.epa.gov/oms/consumer/03-co.pdf>
2. ↑ "Air Trends-Carbon Monoxide." Environmental Protection Agency. 4 June 2009. <http://www.epa.gov/airtrends/carbon.html>

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