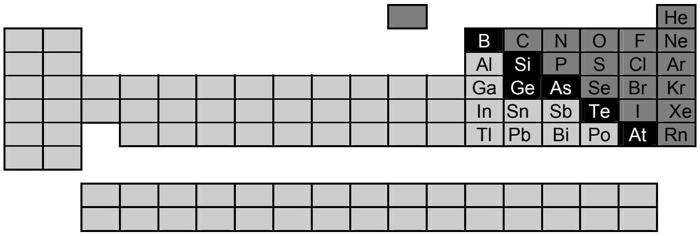
8. *p*-Block Elements

We have now arrived in our journey across the periodic table to that section which has the most variation in chemical properties. This is reflected in the large range of electronegtivities that is observed for this range of elements, from a low of 1.61 for Al to a high of 3.98 for F (and even higher for the noble gases, although Pauling values are not available for these systems in that they don't all form chemical bonds.

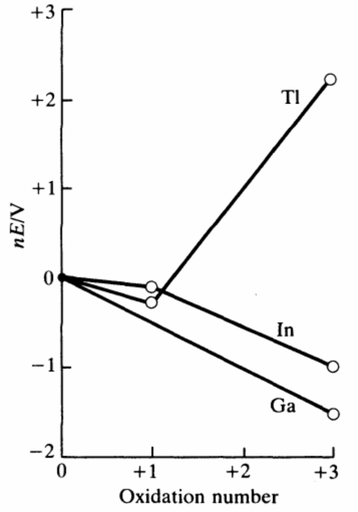
8.1 Metals, metalloids and non-metals



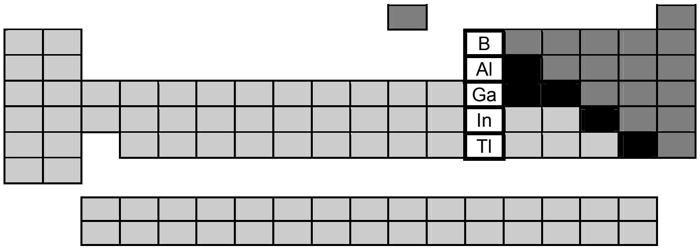
One example of the variation in chemical properties through the *p*-block is in element properties. Thus Al, Ga, In, Tl, Sn, Pb, Sb, Bi and Po are metals, although in their highest oxidation states they have some metalloid properties. Note that *all* the metalloids (with the possible exception of Be) are found in the *p*-block. Thus B, Si, Ge, As, Te and At have these very important properties which are of the utmost technological importance. Si and Ge are the two most important materials for all types of semiconductors used in the electronic industries. Thus electrical conductivity is another physical property whereby the metals, metalloids and non-metals can be distinguished: the metals tend to be good conductors, the metalloids *intrinsic* semiconductors, and the non-metals insulators. This trend is seen clearly within a single group such as 14, where carbon (diamond) is an excellent insulator, Si and Ge are semiconductors, and Sn and Pb are conductors.

We will not say a lot about the metallic *p*-block elements, except to mention that In and especially Tl, Sn and especially Pb, Sb and especially Bi can exist in two oxidation states. Thus we have Tl^+ and Tl^{3+}. By contrast, Al and Ga are only found as the element or as the 3+ ion. Why is this? Consider the electron configurations of the thallium ions already mentioned:
Tl^+ [Xe]$4f^{14}5d^{10}6s^2$ Tl^{3+} [Xe]$4f^{14}5d^{10}$ These differ by the presence and absence of the 6*s* electrons.

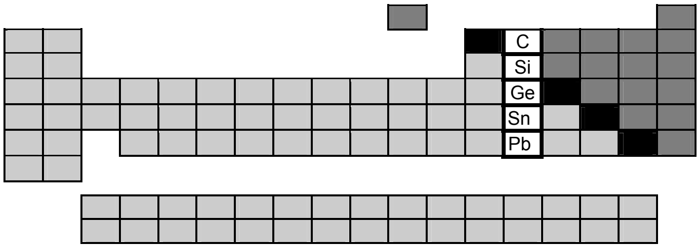
This is also the origin of the 2+ difference in oxidation states for the other metals, i.e. Sn^{2+} and Sn^{4+}, etc. If we remember that the 4f electrons are especially poor at shielding, we recognize that these elements will experience an unusually high effective nuclear charge. This has the effect of causing the 6s electrons to be particularly strongly bound to the nucleus, and therefore harder to oxidize. The full explanation of this behavior involves **relativistic** behavior of the electrons in these heavy atoms, and we will not treat it further in this course.



8.2 Group 13 elements - Boron

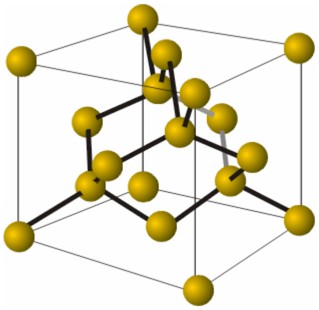


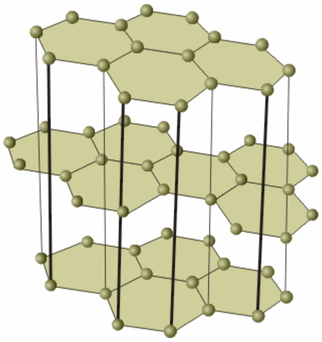
8.3 Group 14 elements; silicones; silicate minerals



Element	Electronic structure	mp, °C	1st I.E., kJ mol^{-1}	Electronegativity	Covalent radius
C	$[He]2s^2 2p^2$	3550	1086	2.50	0.77
Si	$[Ne]3s^2 3p^2$	1410	786.3	1.74	1.17
Ge	$[Ar]3d^{10} 4s^2 4p^2$	937	760	2.02	1.22
Sn	$[Kr]4d^{10} 5s^2 5p^2$	232	708.2	1.72	1.40
Pb	$[Xe]4f^{14} 6s^2 5d^{10} 6p^2$	328	715.3	1.8	1.44

The elemental forms of carbon are graphite (thermodynamically the most stable at room temperature) and diamond. These two forms could not be more different! Graphite is a soft, black, conducting solid, which is used in many commercial applications, including their use as electrodes in many important electrochemical processes (e.g. the 1.5 V dry cell, electrolysis of bauxite/cryolite in the manufacture of aluminum.) Diamond is a clear colourless insulator, and is the hardest substances known. These differences are due entirely to the physical structure of these important structures. We have already dealt with the diamond structure and the graphite structure.


Diamond


Graphite

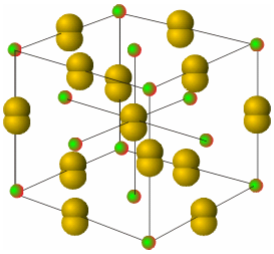
In diamond, all the carbon atoms are sp^3 hybridized, and therefore four coordinate. The whole crystal is one large molecule. This is what gives it its immense hardness.

Elemental silicon and germanium have the diamond structure. It is a fascinating fact that silicon, with its diamond structure, is actually a semiconductor! So is germanium. Tin (β-tin, white tin) and lead have close-packed metallic structures, but tin has an allotrope called ‘grey tin’ which has the diamond structure. Grey tin (α-tin) is more stable below 13.2 °C,

$$\alpha\text{-Sn} \rightleftarrows \beta\text{-Sn}$$

however, the interconversion is very slow. β-tin has to be below 13.2 °C for a long time to be converted to the less dense α-tin; usually the surface of tin becomes ‘infected’ by regions of powdery tin which serve as nucleation points. Then the transition spreads rapidly like a contagious disease (‘tin plague’ or ‘tin pest’).

Direct combination of carbon with metallic elements results in the formation of metal carbides. Probably the most famous of these is calcium carbide, CaC_2. This material is an example of a saline carbide, consisting of Ca^{2+} and C_2^{2-} ions. It is a colourless solid when pure, but is usually discoloured or grey. Its crystal structure is based on that of NaCl, except that at each Cl site, a C_2 unit is located. All the C_2 molecules are oriented in the same direction, and the expanded unit cell is tetragonal. Figure 8-1 illustrates the CaC_2 structure.

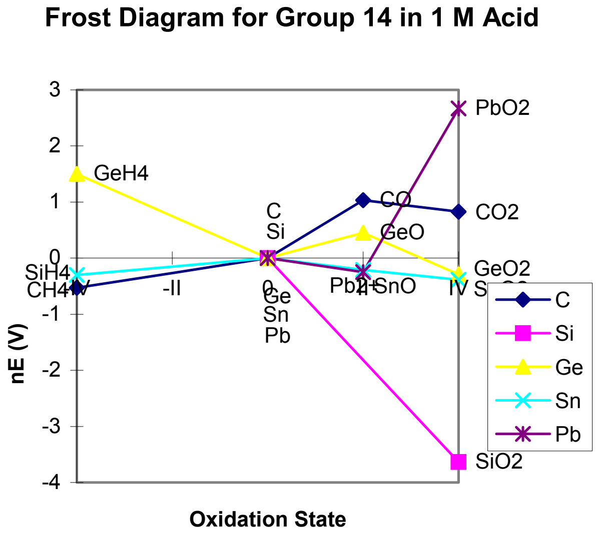


A hint about the chemical structure of the carbide ion in calcium carbide is provided by the reaction the ion undergoes with water:

$$CaC_{2(s)} \quad + \quad H_2O_{(l)} \quad \rightarrow \quad Ca(OH)_{2(aq)} \quad + \quad H\text{-}C{\equiv}C\text{-}H_{(g)}$$

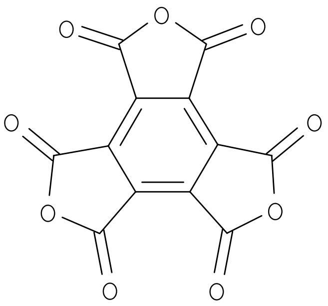
This result, the generation of acetylene, suggests that the carbide ion in saline carbides has a triple bond. Try and write a Lewis structure for C_2^{2-} using this hint. In the early years of this century, this reaction was used in a practical application as a source of fuel for lamps. Early motorcars invariably had carbide headlamps. It is from the manufacture of this product that the giant multinational chemical conglomerate Union Carbide gets its name.

Frost diagram for Group 14:

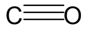


They have the general valence configuration ns^2np^2, and thus commonly have the oxidation state of 4. Carbon has essentially no chemistry in the divalent state. Certain carbenes, especially CF_2, are stable but very reactive species. These are true divalent carbon compounds, but they are extremely rare. Silicon and germanium are also primarily tetravalent in their compounds. But for the heaviest members of the group, Sn and Pb, the oxidation state +2 is quite common, (electron configuration s^2d^{10}). The stability of the tetravalent state decreases down the group as well, so that while CCl_4 and $SiCl_4$ are extremely easy to make from the elements and chlorine, $PbCl_4$ can only be made under forcing conditions, and decomposes readily to $PbCl_2$.

You may be surprised to see carbon on the agenda of an inorganic chemistry course! In fact, though the vast majority of carbon compounds are hydrocarbon derivatives (and hence the proper subject of organic chemistry), there is also and important inorganic chemistry of carbon. Remember that these artificial sub-disciplines of our convenience make absolutely no impression on Nature! In this laboratory we consider two important inorganic carbon compounds, carbon dioxide and calcium carbide.

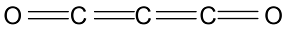


mellitic anhydride



carbon monoxide

carbon dioxide



carbon suboxide

Carbon has four thermodynamically stable oxides: CO, CO_2, C_3O_2 and $C_{12}O_9$. The latter is the anhydride of mellitic acid, hence is best considered an organic derivative. Carbon suboxide is and evil-smelling gas, which is stable at low temperatures, but polymerizes when warmed to room temperature. The two important oxides are the monoxide and dioxide.

CO is formed when carbon is burned in a deficiency of oxygen. It is a significant component of automobile exhaust fumes. Industrially it is produced on a huge scale by the reaction of steam with coke to give hydrogen and carbon monoxide (syngas):

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

These products form the feedstocks of some petrochemical processes. They can also be combined with the water gas shift reaction to maximize hydrogen production and produce CO_2:

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$$

Carbon monoxide is very toxic. It replaces oxygen on the O_2 carrier complex hemoglobin, blocking the transfer of oxygen from the lungs to the rest of the body. CO also reacts with many metals to form organometallic compounds in which carbon is bound to transition metals. An example is the compound $Ni(CO)_4$, which is an intermediate in the **Mond process** for the purification of nickel.

Carbon dioxide is the main product of the combustion of fossil fuels, as well as many natural processes such as respiration. In the laboratory it is most commonly prepared by the controlled addition of HCl(aq) to $CaCO_3$ in the form of marble chips. CO_2 is denser than air, so it can be collected directly in containers by upward displacement of the air.

CO_2 does not support combustion, and is used as the compressed liquid in many fire extinguishers. However, although it is one of the most versatile extinguishing materials, it cannot be used on all fires. An example is afforded in this laboratory by demonstrating that magnesium "burns" in a CO_2 environment. This is the exact reverse of obtaining the element by coke reduction of magnesium oxide.

CO_2 is present in the atmosphere in large quantities, and it is feared by many that the huge scale of human activity in the past century has raised the total level of CO_2 in the atmosphere. This may lead to global warming under the so-called "greenhouse effect." CO_2 is also intimately connected with plant and animal life. Photosynthesis in plants is the only known way to get usable forms of carbon compounds back from CO_2.

CO_2 dissolves in water to give a solution of carbonic acid:

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+$$

This is why water in contact with the atmosphere is usually found to be slightly acidic. Carbon dioxide has a very high solubility in water. The true pK_a of carbonic acid is -3.7, a figure which takes into consideration that much of the CO_2 in water is simply solvated, and is not in the form of H_2CO_3. Thus solutions of $CO_2$are less acidic than expected based on the quantity of CO_2dissolved.