

## 12.6: Network Covalent Atomic Solids: Carbon and Silicates

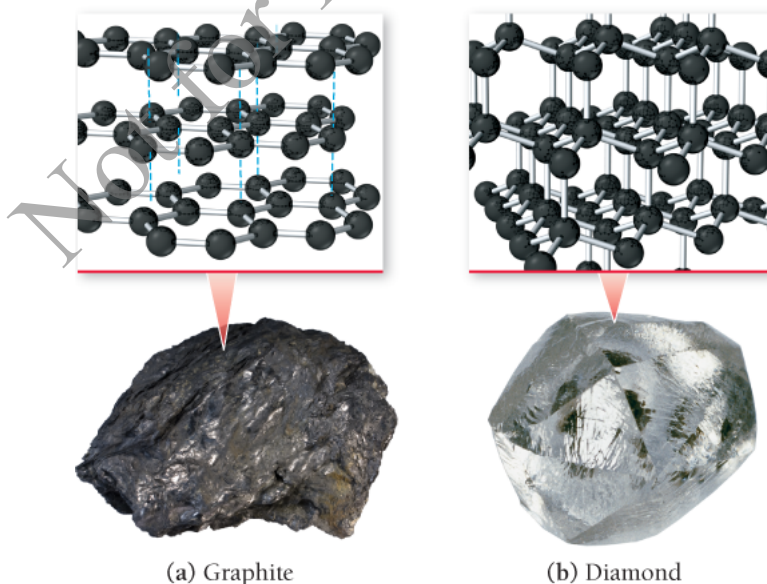
As we saw in [Section 12.4](#), network covalent atomic solids are composed of atoms held together by covalent bonds. Network covalent atomic solids have some of the highest melting points of all substances. In this section, we examine two different families of network covalent atomic solids: carbon and silicates.

### Carbon

Elemental carbon exists in several different forms or **allotropes** including graphene, which we discussed in [Section 12.1](#). Each form has a different structure and therefore different properties. Two well-known naturally occurring crystalline forms of carbon are **graphite** and **diamond**. Graphite's structure, shown in [Figure 12.16a](#), consists of flat sheets of carbon atoms covalently bonded together as interconnected hexagonal rings. The bond length between carbon atoms *within a sheet* is 142 pm. In contrast, the forces *between* sheets are much different than the bonds within sheets. There are no covalent bonds between sheets, only relatively weak dispersion force, and the separation between sheets is 341 pm. Consequently, the sheets slide past each other relatively easily, which explains the slippery feel of graphite and its extensive use as a lubricant. The electrons in the extended pi bonding network (see [Section 6.3](#)) within a sheet make graphite a good electrical conductor in the direction of the plane of the sheets. Because of its relative stability and electrical properties, graphite is used for electrodes in electrochemical applications and for heating elements in furnaces.

**Figure 12.16 Network Covalent Atomic Solids**

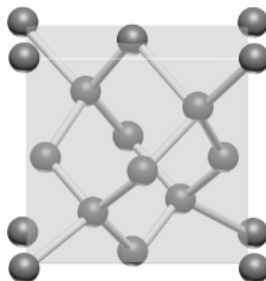
(a) In graphite, carbon atoms are arranged in sheets. Within each sheet, the atoms are covalently bonded to one another by a network of  $\sigma$  and  $\pi$  bonds. Neighboring sheets are held together by dispersion forces. (b) In diamond, each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry.



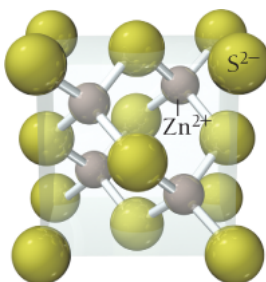
The density of graphite is  $2.2 \text{ g/cm}^3$ . Under higher pressure, the carbon atoms in graphite rearrange to form diamond, which has a higher density of  $3.5 \text{ g/cm}^3$ . Diamond forms naturally when carbon is exposed to high pressures deep underground. Through movements in Earth's crust, diamond rises toward the surface. Most diamond is found in Africa, mainly in the Congo region and in South Africa. The first synthetic diamonds were

produced in the 1940s, using pressures of 50,000 atm and a temperature of 1600 °C.

The unit cell for diamond is shown here:



Diamond Unit Cell



Zinc Blende (ZnS) Unit Cell

You can imagine the unit cell as a face-centered cubic structure with an additional carbon atom in half of the eight tetrahedral holes located directly in each corner atom. Notice the similarity between the diamond unit cell and the zinc blende unit cell that we discussed in [Section 12.5](#). Notice also that each carbon atom is covalently bonded to four other carbon atoms at the corners of a tetrahedron ([Figure 12.16b](#)). This structure extends throughout the entire crystal, so that a diamond crystal can be thought of as a giant molecule, held together by these covalent bonds.

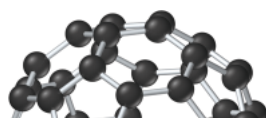
Because covalent bonds are very strong, diamond has a very high melting point (it is estimated to melt at about 3550 °C). The electrons in diamond are confined to the covalent bonds and are not free to flow. Therefore, diamond does not conduct electricity. However, because the bonds are strong and the connectivity between atoms so extensive, diamond is an excellent conductor of heat. Consequently, the largest use of diamonds is for abrasives and cutting tools. Small diamonds are used at the cutting edge of tools, making the tool edges much harder and giving them a longer life. Natural diamonds are valued as gems for their brilliance and relative inertness.

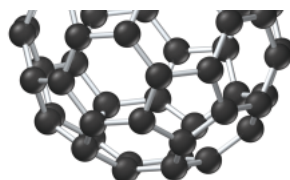
#### Conceptual Connection 12.4 Phase Changes and Pressure

In the 1980s, researchers discovered a new form of carbon when they aimed a powerful laser at a graphite surface. This new form of carbon occurs as soccer-ball-shaped clusters of 60 carbon atoms ( $C_{60}$ ). The atoms form five- and six-membered carbon rings wrapped into a 20-sided icosahedral structure ([Figure 12.17](#)). The compound was named *buckminsterfullerene*, honoring R. Buckminster Fuller (1895–1953), a twentieth-century engineer and architect who advocated the construction of buildings using a structurally strong geodesic dome shape that he patented.

**Figure 12.17**  $C_{60}$  and a Geodesic Dome

The  $C_{60}$  structure resembles Buckminster Fuller's geodesic dome.



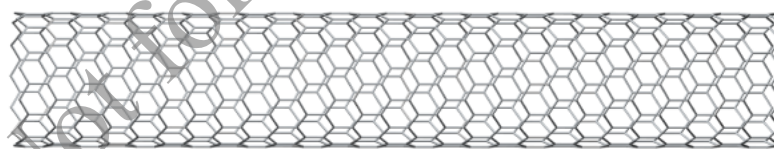
 $C_{60}$ 

Researchers have since identified carbon clusters similar to  $C_{60}$  containing from 36 to over 100 carbon atoms. As a class, these carbon clusters are called **fullerenes** and nicknamed *buckyballs*. At room temperature, fullerenes are black solids—the individual clusters are held to one another by dispersion forces. Fullerenes are somewhat soluble in nonpolar solvents, and the different fullerenes form solutions of different colors.

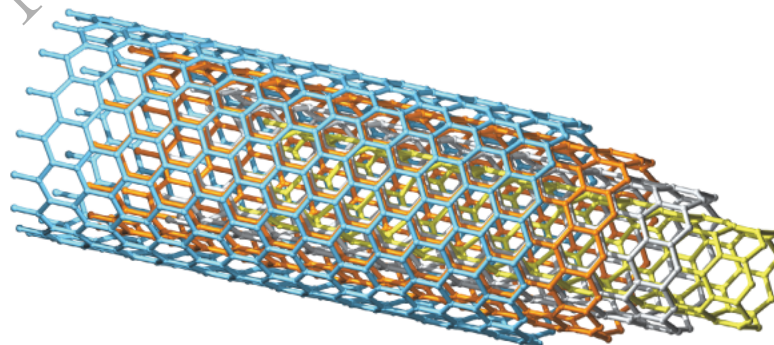
Researchers have also synthesized long carbon structures called **nanotubes**, which consist of sheets of interconnected  $C_6$  rings that assume the shape of a cylinder (like a roll of chicken wire). The first nanotubes discovered consisted of tubes with double walls of  $C_6$  rings with closed ends. The ends of the tubes can be opened when they are heated under the proper conditions. Today, two general types of nanotubes can be produced: (1) *single-walled nanotubes* (SWNT) that have one layer of interconnected  $C_6$  rings forming the walls, and (2) *multiwalled nanotubes* (MWNT) that have concentric layers of interconnected  $C_6$  rings forming the walls. In addition, researchers have been able to form *nanoribbons* by slicing open nanotubes. As we saw in [Section 12.1](#), carbon can also form graphene, long extended sheets of carbon atoms just one atom thick. These carbon structures are illustrated in [Figure 12.18](#).

**Figure 12.18 Novel Carbon Structures**

(a) Single-walled nanotube (SWNT)



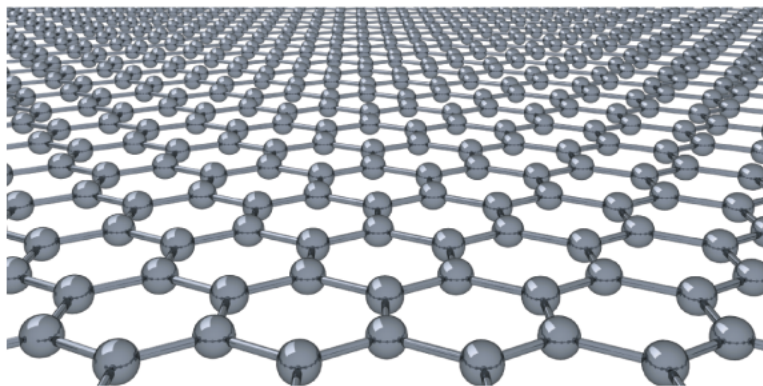
(b) Multiwalled nanotube (MWNT)



(c) Graphene nanoribbon



(d) Graphene sheet



Nanotubes are 100 times stronger than steel and only one-sixteenth as dense. Consequently, we use carbon nanotubes commercially for lightweight applications that require strength, such as golf clubs and bicycle frames. When the nanotubes are lined up parallel to one another, a bundle of the tubes forms a “wire” with very low electrical resistance. These tiny wires raise the possibility of making incredibly small electronic devices.

## Silicates

The **silicates** (extended arrays of silicon and oxygen) are the most common network covalent atomic solids. Geologists estimate that 90% of Earth’s crust is composed of silicates. Silicon and oxygen form a network covalent structure in which a silicon atom bonds to four oxygen atoms, resulting in a tetrahedral shape with the silicon atom in the middle and the four oxygen atoms at the corners of the tetrahedron (Figure 12.19). In this structure, the silicon atom bonds to each oxygen atom with a single covalent sigma bond. In contrast to carbon, which often bonds to oxygen with a double bond (one  $\pi$  and one  $\sigma$  bond), silicon forms only a single bond with oxygen because the silicon atom is too large to allow substantial overlap between the  $p$  orbitals on the two atoms. The silicon atom in this structure, by bonding to four oxygen atoms, obtains a complete octet. However, each oxygen atom is one electron short of an octet. Therefore, each O atom forms a second covalent bond to a different Si atom, forming the three-dimensional structure of **quartz**. Quartz has a formula unit of  $\text{SiO}_2$ , and is generally called **silica**. In silica, each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom acts as a bridge connecting the corners of two tetrahedrons (Figure 12.20).

Figure 12.19  $\text{SiO}_2$  Tetrahedron

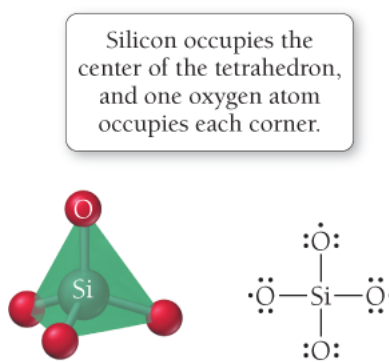
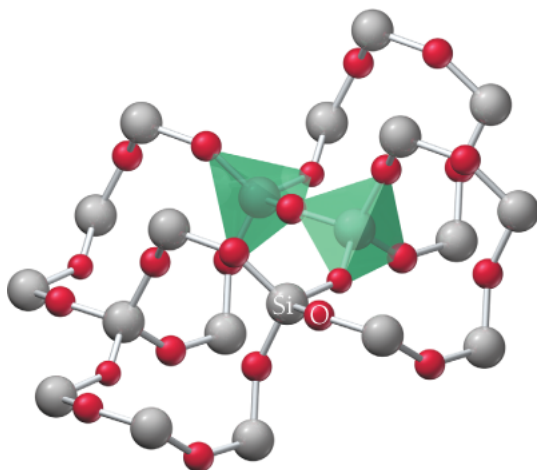


Figure 12.20 Structure of Quartz

Each O atom in each tetrahedron is a bridge connecting the corners of two tetrahedra.



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