13.7: Network Covalent Atomic Solids- Carbon and Silicates

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 13.7.1, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.
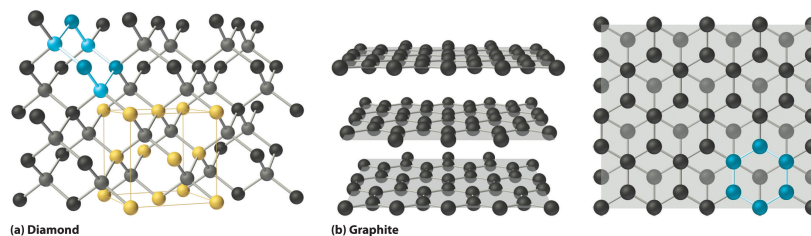

(a) Diamond   (b) Graphite

Figure 13.7.1: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure 13.7.1. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the "lead" in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons. Table 13.7.2 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 13.7.2: A Comparison of Intermolecular (ΔHsub) and Intramolecular Interactions

Substance	ΔH$_{sub}$ (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.
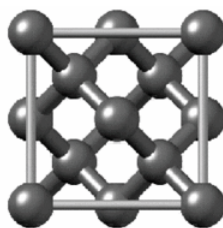

Figure 13.7.2: Rotating model of diamond cubic. Figure used with permission from Wikipedia

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider:
- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure 13.7.3 shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.
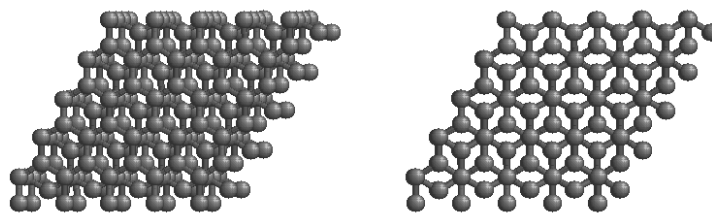
Figure 13.7.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider:

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoretians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.
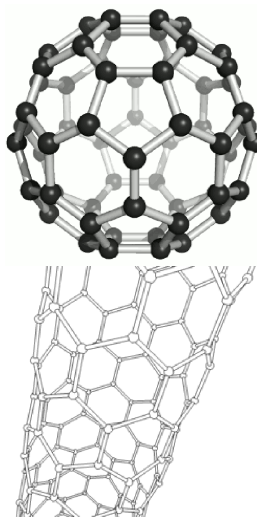

Figure 13.7.4: Example of fullerenes: a buckyball (C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.

The C_{60} molecule (Figure 13.7.4; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure 13.7.4; right). All of these substances are pure carbon.

to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?