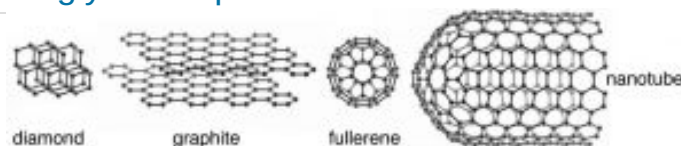
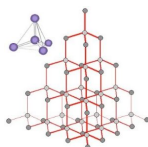


3.3: Carbon: An Amazingly Allotropic Element



To give you an idea of some of the different types of bonds that form between elements, we are going to consider several representative elements from different areas of the periodic table. For starters, let us take a look at carbon. Carbon (C) belongs to the family of elements known as non-metals. The bonding between C atoms (and to other types of atoms) is typically described as covalent bonding where each bond involves two electrons (one from each of the bonded atoms). Although this is the most common model we will see that it is not the only possible one; we will introduce other models as they are needed. Diamond is the name given to one of the naturally occurring forms (known as allotropes) of pure C; the other allotropes of carbon are graphite, graphene, and various fullerenes (↓), which we will return to later. **The important question is: How can these substances have such different properties, yet be composed of the same types of atoms?** For example: diamond is hard, colorless, sparkly and do not conduct electricity, but graphite is soft, grey, shiny, and does conduct electricity. The answer lies in the molecular level structure of these allotropes of carbon.

Diamonds form from carbon-rich materials subjected to very high pressure (45,000–60,000 atmospheres) but relatively low temperatures (900–1300°C).^[12] Such conditions can be found about 100 miles under the Earth's crust, the region known as the lithosphere. Diamonds have also been found in asteroids, which originate from outside of the Earth. Diamonds are so valued because they are rare, sparkly, hard, and almost completely inert. It is very hard to make diamonds do anything at all except sit there and sparkle; they don't dissolve in water and they melt only at very high temperatures (mp = 3330°C). Diamond has the highest melting point of any known substance, so high that these measurements are actually done under high pressure and then calculated to estimate what the value would be at atmospheric pressure. In addition, when diamond is melted it decomposes. When it is heated in an atmosphere of oxygen it reacts to produce carbon dioxide; when oxygen is absent it transforms into graphite. There is no such thing as molten diamond. Diamonds are extremely hard (the hardest naturally occurring substance) and do not conduct electricity at all (as we will see, to conduct electricity, electrons must be able to flow through the material). This suggests that the molecular-level structure of diamond is quite different from that found in metals (which we will see are malleable and conduct electricity). Any useful model of diamond's structure must explain how these properties arise from atomic interactions.

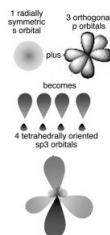


Let us step back and look at the properties of diamond and see if we can make sense of them. To be so stable (chemically inert) diamond must have very strong bonds that take a lot of energy to break. The fact that it does not conduct electricity indicates that the electrons must not be free to move around within a diamond. A polished diamond is sparkly because some light is reflected from the surface and some light passes through it, making it transparent. If the diamond were not cut with so many facets it would allow most light to pass through it.

When we look at an X-ray diffraction-based structure^[13] of diamond we find that each carbon atom is surrounded by four other carbon atoms situated at equal distances and equal angles from each other. In this context, the most useful model of bonding involves thinking of each carbon atom as forming four covalent (electron-sharing) bonds, all arranged so that the electron pairs are as far apart as possible. This places the four bonded atoms at the corners of a tetrahedron, with a central carbon atom. Each of these corner atoms is itself at the center of a similar tetrahedron of carbons (see Figure). Experimental evidence indicates that all the bonds, bond lengths, and bond angles in diamond are identical; the C–C–C bond angles are $\sim 109^\circ$. A diamond can be considered as one huge molecule connected by a network of carbon–carbon bonds.

How do we explain this arrangement in terms of what we know about the electronic structure of carbon atoms? The answer is that the electronic structure of the carbon atoms is reorganized to form bonding orbitals. In the case of carbon, each atom can form four bonding orbitals that are oriented as far apart as possible. There are several models to explain how this occurs, but it is important to remember that they are all models, designed to help us understand the properties of diamond.

The Hybrid Orbital Model



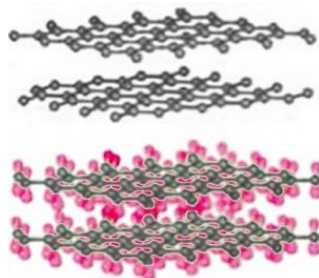
In this model the orbitals involved in carbon–carbon bonding are considered to be hybrids or mixtures of atomic orbitals. If carbon forms four bonds (and it does) then four bonding orbitals are needed. Carbon has available orbitals in the second ($n = 2$) quantum shell: the $2s$, $2p_x$, $2p_y$, and $2p_z$. In an isolated carbon atom there is a full $2s$ orbital and two half-filled p orbitals. When the carbon atoms form a bond, these orbitals are somehow mysteriously transformed into four new bonding orbitals, which are called sp^3 hybrid orbitals because they are a mixture of an s and three p orbitals. These sp^3 orbitals exist only in the context of bonded carbon; they are not present in isolated carbon atoms. They spring into existence when one carbon atom interacts with another atom to form a bond; they are generated through the interaction. In the case of carbon the four electron clouds (bonds) move as far apart as possible to minimize the repulsions between them, adopting a tetrahedral configuration (\rightarrow).

The Molecular Orbital Model

Another way to consider how these bonds form is similar to the way we approached molecular hydrogen. That is, we consider that when carbon–carbon ($C-C$) bonds form, atomic orbitals are transformed into molecular orbitals (MOs). For each stabilizing bonding orbital, a destabilizing antibonding orbital is also formed. Using the molecular orbital approach, we can model the bonding in diamond as carbon atoms forming a three-dimensional network held together by these molecular bonding orbitals. $C-C$ bonds are very stable because there is a large energy gap between the bonding orbitals and the high-energy antibonding orbitals. The bonding molecular orbitals are occupied while the antibonding molecular orbitals are unoccupied. Because of this large gap between the filled bonding and empty antibonding orbitals it is hard to remove an electron from a $C-C$ bonding MO. The electrons are not free to move between energy levels. Given that electrical conduction depends upon the relatively free movement of electrons it is not surprising that diamonds do not conduct electricity. But why, you might ask, is a diamond transparent, rather than opaque, like a block of graphite, which is also composed of only carbon atoms? For an object to be transparent most of the light that hits it must pass through it; the light can be neither reflected or absorbed. For a diamond to absorb light a photon would need to move an electron from a low-energy bonding MO to a high-energy antibonding orbital. However, visible light does not have enough energy to bridge the energy gap between the bonding and antibonding orbitals. Based on this thinking we conclude that there is something different between bonds holding C atoms together in diamond from the bonds holding C atoms together in graphite even though we do not know, at this point, what it could be.

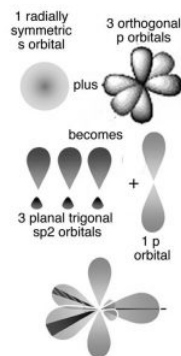
An important point to consider here is that we have described the bonding in carbon using two different models: the hybrid orbital (valence bond) and molecular orbital models. Although this may be (a bit!) confusing, and may take some getting used to, it is quite common to describe chemical and physical phenomena using different models. Typically we use the simplest model that will allow us to explain and predict the phenomenon we are interested in. Usually the bonding in carbon is described using the hybrid orbital model, because it is highly predictive and easier to use in practice.

Graphite



As we have already mentioned, different allotropes (different forms of the same element) can have quite different properties. The carbon allotrope graphite is soft, grey/black, opaque, conducts electricity, and slippery – it makes a good lubricant.^[14] Diamond is hard, transparent, and does not conduct electricity. How can this be possible if both are pure carbon? The answer lies in how the

carbon atoms are organized with respect to one another. Whereas the carbon atoms in diamond form a three-dimensional network, in graphite, the atoms are organized in two-dimensional sheets that stack one on top of the other. Within each two-dimensional sheet the carbon atoms are linked by covalent bonds in an extended array of six-membered rings. This means that the carbon sheets are very strongly bonded, but the interactions between sheets are much weaker. Although there are no covalent bonds between the sheets, the atoms of the sheets do interact through London dispersion forces, very much like the interactions that hold helium atoms together. Because the sheets interact over very much larger surface areas (\searrow), however, these interactions are much stronger than those in helium. Yet another allotrope of carbon, graphene, consists of a single sheet of carbon atoms.^[15] These sheets can be rolled into tubes to form nanotubes that are the subject of intense research interest because of their inherently high tensile strength. Carbon atoms can also form spherical molecules, known as buckminsterfullerenes or buckyballs.^[16]



The obvious question is, why don't covalent bonds form between graphite sheets? Why are the patterns of covalent bonding so different: three-dimensional (tetrahedral) in diamond, with each carbon bonded to four others, and two-dimensional (planar) in graphite and graphene, with each carbon atom bonded to only three others? One way to describe the molecular structure is to use the hybrid orbital bonding model. As we discussed previously, to form the four bonds attached to each carbon atom in diamond, we needed to hybridize four atomic orbitals to form four bonding orbitals. We might think we only need three bonds in graphite/graphene because each carbon is only connected to three others. This is not exactly true. In graphite and graphene we use a model in which only three atomic orbitals are hybridized—an s and two 2p orbitals in order to form three sp² bonding orbitals. These orbitals attach each carbon atom to three other atoms. Just like in diamond the three bonds associated with each carbon atom in graphite/graphene move as far apart as possible to minimize electron pair repulsion; they lie at the points of a triangle (rather than a tetrahedron). This geometry is called trigonal planar and the C–C–C bond angle is 120° (\rightarrow).

All well and good, but this does not really explain why the carbons in graphite/graphene are attached to three other carbon atoms, whereas in diamond each carbon is attached to four others. Perhaps surprisingly there is no good answer for why carbon takes up different forms—except that it can. But in fact carbon does form four bonds in graphite (carbon almost always forms four bonds—a central principle of organic chemistry). The trick is that the four bonds are not always equivalent; in graphite the fourth bond is not formed by the sp² bonding orbitals but rather involves an unhybridized 2p atomic orbital. These p orbitals stick out at right angles to the sheet and can overlap with p orbitals from adjacent carbons in the same sheet (see Figure). Remember that p orbitals have two regions of electron density. To explain the fact that graphite conducts electricity, we use an idea from molecular orbital (MO) theory, namely that bonding and antibonding MOs are formed from the adjacent p orbitals that extend over the sheet surface. The energy difference between these orbitals is not large and electrons can move from one to the other, allowing the movement of electrons throughout the whole sheet of graphite, which gives it many of the properties that we associate with metals. Note that we use both the hybridization model, which explains the planar framework of C–C bonds in graphite, and molecular orbital theory, which explains graphite's electrical conductivity. So before we delve further into the properties associated with graphite, let us take a look at bonding in metals.

? Questions

Questions to Answer

- Diamond and graphite appear to be quite different substances, yet both contain only carbon atoms. Why are the observable properties of diamond and graphite so different when they are made of the same substance?
- The electron configuration of C is 1s²2s²2p². Using the idea that each atom provides one electron to a bond, if carbon used atomic orbitals to bond, how many bonds would it form? Would they all be the same? What would be the bond angles if this were to happen? (Draw a picture of what this might look like.)

- The electron configuration of C is $1s^2 2s^2 2p^2$ this means that carbon has 6 electrons. Why doesn't it form 6 bonds?
- We have seen that carbon can form materials in which it bonds to 4 other atoms (sp^3 hybridization) or three other atoms (sp^2 hybridization). What would be the hybridization for a carbon that was only bonded to two atoms? How would the other (unhybridized) p orbitals influence the behavior of such material (assuming that it could form)?

Questions to Ponder

- Could carbon form a three-dimensional structure by linking to two other carbon atoms?
- Do you think diamonds are transparent to all forms of light, such as X-rays?
- What does the color of graphite imply about the energies of the photons it absorbs?

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