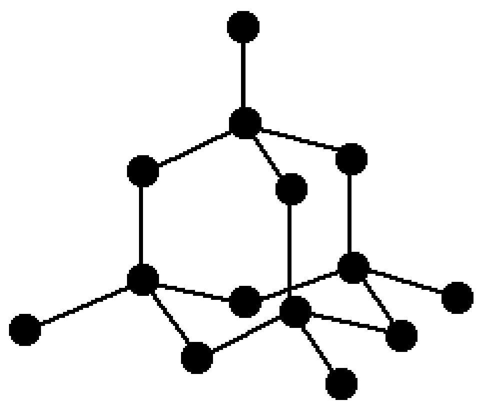
Covalent Network Solids

.

Diamond

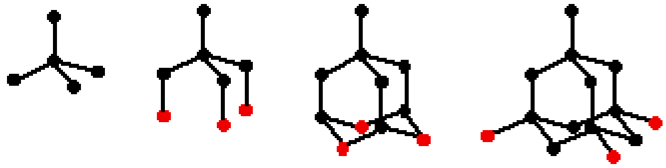
Carbon has an electronic arrangement of 2,4. In diamond, each carbon shares electrons with four other carbon atoms - forming four single bonds.



In the diagram some carbon atoms only seem to be forming two bonds (or even one bond), but that's not really the case. We are only showing a small bit of the whole structure. This is a giant covalent structure - it continues on and on in three dimensions. It is not a molecule, because the number of atoms joined up in a real diamond is completely variable - depending on the size of the crystal.

How to draw the structure of diamond

Don't try to be too clever by trying to draw too much of the structure! Learn to draw the diagram given above. Do it in the following stages:



Practice until you can do a reasonable free-hand sketch in about 30 seconds.

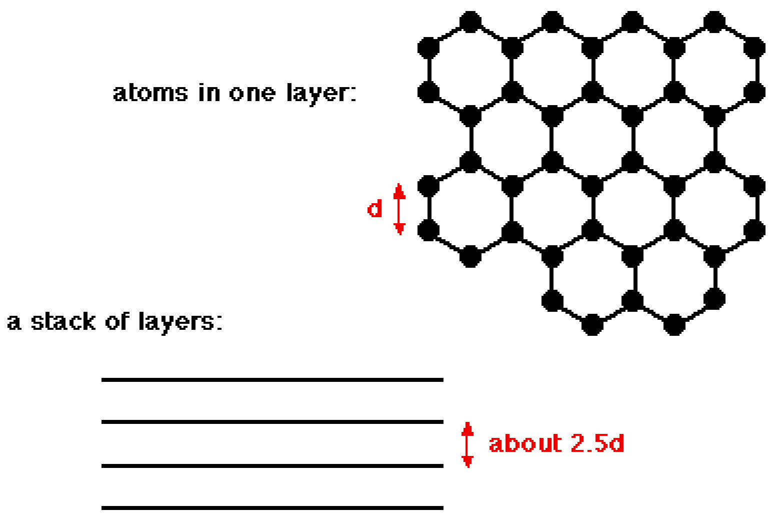
The physical properties of diamond

Diamond

- has a very high melting point (almost 4000°C). Very strong carbon-carbon covalent bonds have to be broken throughout the structure before melting occurs.
- is very hard. This is again due to the need to break very strong covalent bonds operating in 3-dimensions.
- doesn't conduct electricity. All the electrons are held tightly between the atoms, and aren't free to move.
- is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and carbon atoms which could outweigh the attractions between the covalently bound carbon atoms.

Graphite

Graphite has a layer structure which is quite difficult to draw convincingly in three dimensions. The diagram below shows the arrangement of the atoms in each layer, and the way the layers are spaced.



Notice that you can't really draw the side view of the layers to the same scale as the atoms in the layer without one or other part of the diagram being either very spread out or very squashed.

In that case, it is important to give some idea of the distances involved. The distance between the layers is about 2.5 times the distance between the atoms within each layer. The layers, of course, extend over huge numbers of atoms - not just the few shown above.

You might argue that carbon has to form 4 bonds because of its 4 unpaired electrons, whereas in this diagram it only seems to be forming 3 bonds to the neighboring carbons. This diagram is something of a simplification, and shows the arrangement of atoms rather than the bonding.

The bonding in graphite

Each carbon atom uses three of its electrons to form simple bonds to its three close neighbors. That leaves a fourth electron in the bonding level. These "spare" electrons in each carbon atom become delocalized over the whole of the sheet of atoms in one layer. They are no longer associated directly with any particular atom or pair of atoms, but are free to wander throughout the whole sheet.

The important thing is that the delocalized electrons are free to move anywhere within the sheet - each electron is no longer fixed to a particular carbon atom. There is, however, no direct contact between the delocalized electrons in one sheet and those in the neighboring sheets.

The atoms within a sheet are held together by strong covalent bonds - stronger, in fact, than in diamond because of the additional bonding caused by the delocalized electrons. So what holds the sheets together?

In graphite you have the ultimate example of van der Waals dispersion forces. As the delocalized electrons move around in the sheet, very large temporary dipoles can be set up which will induce opposite dipoles in the sheets above and below - and so on throughout the whole graphite crystal.

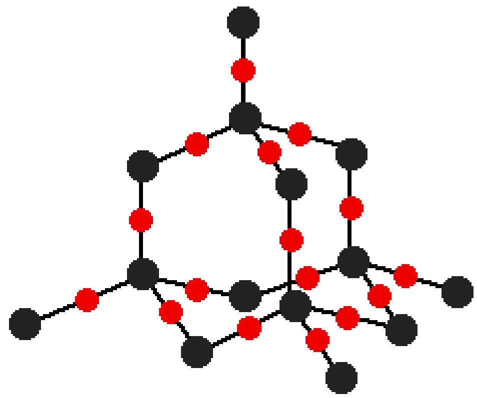
The physical properties of graphite

Graphite

- has a high melting point, similar to that of diamond. In order to melt graphite, it isn't enough to loosen one sheet from another. You have to break the covalent bonding throughout the whole structure.
- has a soft, slippery feel, and is used in pencils and as a dry lubricant for things like locks. You can think of graphite rather like a pack of cards - each card is strong, but the cards will slide over each other, or even fall off the pack altogether. When you use a pencil, sheets are rubbed off and stick to the paper.
- has a lower density than diamond. This is because of the relatively large amount of space that is "wasted" between the sheets.
- is insoluble in water and organic solvents - for the same reason that diamond is insoluble. Attractions between solvent molecules and carbon atoms will never be strong enough to overcome the strong covalent bonds in graphite.
- conducts electricity. The delocalized electrons are free to move throughout the sheets. If a piece of graphite is connected into a circuit, electrons can fall off one end of the sheet and be replaced with new ones at the other end.

Silicon dioxide: SiO_2

Silicon dioxide is also known as silica or silicon(IV) oxide has three different crystal forms. The easiest one to remember and draw is based on the diamond structure. Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, all you need to do is to modify the silicon structure by including some oxygen atoms.



Notice that each silicon atom is bridged to its neighbors by an oxygen atom. Don't forget that this is just a tiny part of a giant structure extending on all 3 dimensions.

The physical properties of silicon dioxide

Silicon dioxide

- has a high melting point - varying depending on what the particular structure is (remember that the structure given is only one of three possible structures), but around 1700°C. Very strong silicon-oxygen covalent bonds have to be broken throughout the structure before melting occurs.
- is hard. This is due to the need to break the very strong covalent bonds.
- doesn't conduct electricity. There aren't any delocalized electrons. All the electrons are held tightly between the atoms, and are not free to move.
- is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and the silicon or oxygen atoms which could overcome the covalent bonds in the giant structure.

Source: http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Lattices/Lattice_Basics/Covalent_Network_Solids