Chem Factsheet

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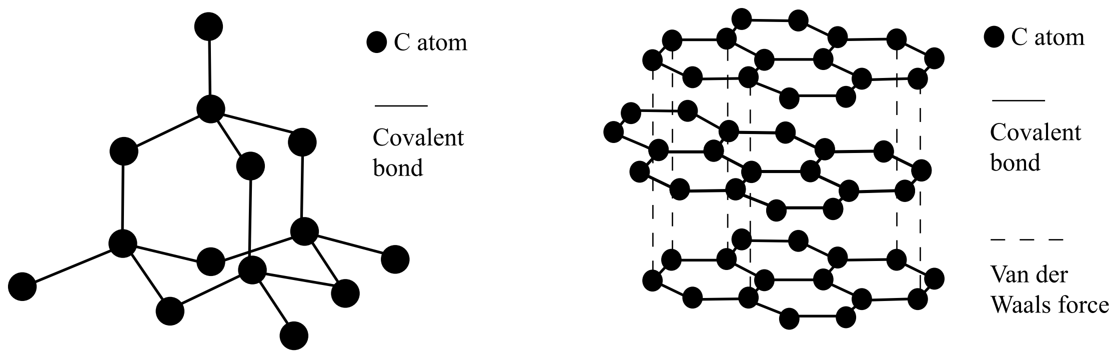
Diamond, Graphite and Graphene

Diamond and Graphite

Carbon is the fifteenth most abundant element in the Earth's crust and has been known of for a very long time. The ancient Egyptians used it in about 3750 BCE but it was only confirmed as an element by Antoine Lavoisier in 1789. Furthermore, carbon has been known to exist in nature in two very distinctly different crystalline forms (known as allotropes) for a long time. These are the familiar diamond and graphite, the structures of which are shown in Fig. 1.

Fig. 1



Diamond Structure Graphite Structure

Note: There are several other forms of carbon but they do not occur naturally on earth. They can be produced under the extreme conditions experienced when graphite containing meteorites strike the earth (e.g. lonsdaleite) or they can be manufactured (e.g. graphene, fullerenes, glassy carbon and carbon nanofoam).

Considering that they are both made only from carbon atoms, diamond and graphite have remarkably different *physical* properties. These are summarised in the following table.

Note: Since they are both composed of carbon atoms, the chemical properties of diamond and graphite are *identical*. For example, both will burn in excess oxygen to form carbon dioxide – although diamond will react significantly slower.

Physical Property	**Diamond**	**Graphite**
Melting point	Very high	Very high
Density	3.5 gcm^{-3}	2.1 gcm^{-3}
Hardness	Very hard	Soft and lubricating
Electrical conductivity	Very low	Very high
Thermal conductivity	Very high	Very high
Transparency	Transparent	Opaque

Note: The possibly unexpected similarity in thermal conductivity is accounted for by their similar abilities to allow increased vibrations of covalent bonds (see below) to transit thermal energy. However, diamond conducts heat equally well in all directions (3D) through its crystal, whereas graphite conducts only along the planes (2D) of atoms.

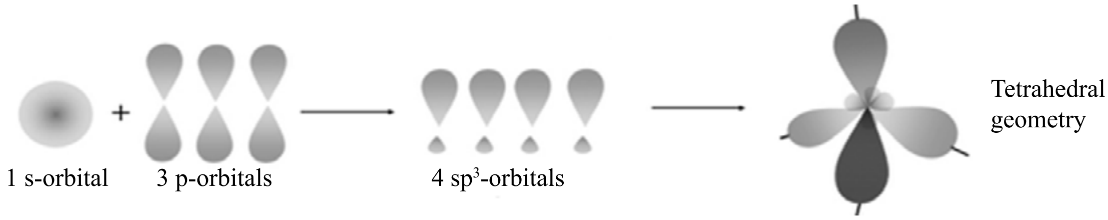
These fundamental differences in properties can be explained in terms of differences in bonding and structure.
Both forms of carbon are composed of atoms which have a $1s^2\ 2s^2\ 2p^2$ electron configuration as their ground state.

C (Z=6)	1s	2s	3p		
	↑↓	↑↓	↑	↑	

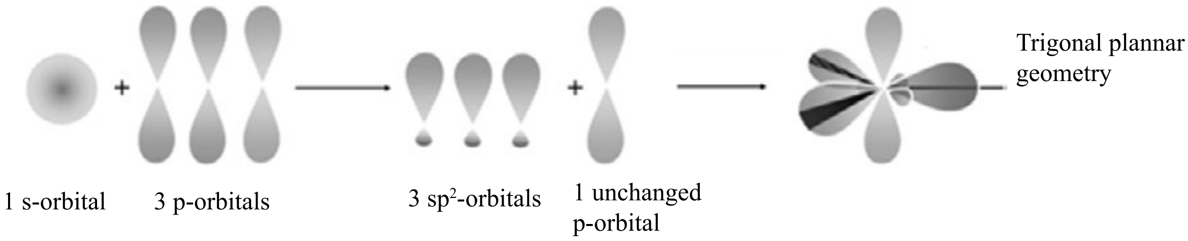
During bonding, one of the 2s electrons is excited to the vacant 3p orbital to give four unpaired electrons available for bonding.

C (Z=6)	1s	2s	3p		
	↑↓	↑	↑	↑	↑

In diamond, the 2s and three 3p orbitals "blend together" (hybridise) to form four tetrahedral sp^3 orbitals per carbon atom, each containing one electron. Each carbon can bond by sharing a pair of electrons (single covalent bond) with four neighbouring carbon atoms to form a giant covalent structure and give diamond its tetrahedral geometry.



In graphite, the 2s and just two of the three 3p orbitals "blend together" (hybridise) to form three trigonal planar sp^2 orbitals. Each carbon can bond by sharing a pair of electrons with three neighbouring carbon atoms to form a giant covalent structure to give graphite its trigonal planar geometry which arrange to give an overall planar hexagonal geometry.



This means there is an unchanged (unhybridised) p-orbital containing one electron on each atom. These overlap sideways to create a delocalized Pi orbital which extends over the whole plane of carbon atoms. Furthermore, the planes are held "loosely" together by van der Waals forces.

Hence:
1. The "loose", mobile delocalised electrons in graphite allow it to conduct electricity. However, diamond has no "loose" charged particles, making it an insulator.
2. The weak van der Waals forces between layers of carbon atoms allow those layers to slide over each other giving graphite a "soft" texture. However, diamond's 3D tetrahedral giant structure gives rigidity in all directions and results in it being an extremely hard substance.
3. The electrons in the delocalised Pi orbital of graphite allow it to absorb all the frequencies of visible light resulting in it being a black substance. However, diamond does not absorb any part of the visible spectrum resulting in it being transparent.

Uses of diamond
Diamond is used extensively in more expensive jewellery because, when cut properly, it sparkles and reflects light in such a way as to give a very attractive appearance.
Diamond's extreme hardness and high melting point make it very useful for cutting tools. Diamond-tipped discs are used to cut bricks and concrete and heavy-duty drill bits are used to drill through metres and metres of rocks in the oil exploration industry.

Uses of graphite
Graphite has many and very varied applications. Apart from its use in pencils, it is used as a refractory material in furnaces where its thermal conductivity allows it to keep an even temperature throughout a furnace. However, it eventually burns away!

Graphite is also used as the anode in many different types of battery because of its electrical conductivity.
The tendency of its layers to slide over each other leads to its uses a lubricant. These include mould linings to allow finished products to be removed easily from the moulds without damage, protection of moving parts in mine machinery (where oil based lubricants would be hazardous) and lock mechanisms.

Graphite has many other applications such as electrodes during various electrolytic manufacturing processes (e.g. aluminium), as neutron moderators in nuclear reactors and as reinforcing material in plastic based products such as golf clubs and fishing rods.

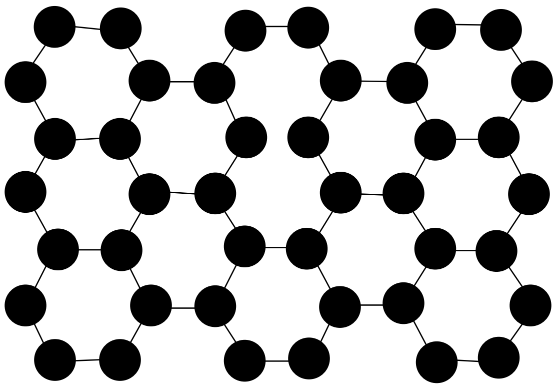
Graphene

Graphene is a form of carbon which was isolated and first investigated in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester. They were subsequently awarded the Nobel Prize in Physics in 2010 for their initial work and the development of applications for graphene. Indeed, it has been called one of the most exciting and useful materials ever produced!

Graphene's structure is very closely related to that of graphite and, in fact, was derived first of all from the graphite found in a "lead" pencil – it was peeled off a graphite crystal using the stickiness of Scotch tape (i.e. Sellotape)! The layer was then transferred to a silica (SiO_2) supporting base because such a thin 2-dimensional structure cannot be self-supporting – it would naturally bend into a 3D shape if left unsupported. More efficient and larger scale methods of preparation are being developed.

As shown in Fig. 2, it consists of just one of the layers of carbon atoms which would "normally" stack together to form graphite. The layer is only 3.35×10^{-10} m thick.

Fig. 2



As in graphite, each atom has three planar sp^2 hydridised orbitals which form three sigma bonds per carbon atom in the same plane resulting in the planar hexagonal geometry shown. As in graphite, the fourth electron of each carbon atom is found in a delocalized Pi orbital which covers the entire sheet of atoms.

Some properties of graphene are summarized in the following table.

Property	Comments
Chemical reactivity	Much higher than diamond or graphite because all atoms are exposed to potential reagents in its 2D structure. For example, graphene will burn at about 350°C.
Thermal conductivity	It has a thermal conductivity which is almost three time greater than graphite.
Mechanical strength	As quoted in the original Nobel Prize publication, "a one square meter graphene hammock would support a 4 kg cat but would weigh only as much as one of the cat's whiskers, at 0.77 mg".
Electrical conductivity	The resistivity of graphene sheets is less than the resistivity of silver, the lowest otherwise known at room temperature.

Uses of graphene?

The answer to this is probably "watch this space" at present. Its remarkable properties have made it the subject of considerable speculation as to how it can be used.

Many uses for graphene have been proposed or are under development, in areas including electronics, biological engineering, filtration, lightweight but very strong composite materials, photovoltaic cells and energy storage.

Graphene in powder form and then dispersed in a polymer matrix finds applications in paints, coatings, lubricants, capacitors, batteries, solar cells and inks to mentions a few.

Question

Compare and contrast the structures and bonding in diamond, graphite and graphene.

Answer

Property	**Diamond**	**Graphite**	**Graphene**
Bonding type	Covalent	Covalent	Covalent
Hybridisation	sp^3	sp^2	sp^2
Bonding geometry	Tetrahedral	Trigonal planar	Trigonal planar
Bond angles	109.5^o	120^o	120^o
Dimensionality	3D structure	3D structure	2D structure
Layering	None	Multiple layers with van der Waals' forces between layers	Single layer
Pi electrons	None	Delocalised over each layer	Delocalised over the layer

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