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Carbon – Element of Many Faces

The sixth in the periodic table of elements is, at the same time, among the most important ones. With about 180 ppm, carbon is only 17th on the list of terrestrial elements' frequency, situated even after barium or sulfur—for comparison, the second-most frequent element, silicon, is about 1300 times as abundant as carbon. Still the latter is essential for the assembly of all organic matter. It is predestined for this central role especially due to its mid position in the periodic system and its associated ability to form stable substances with more electropositive and more electronegative reaction partners. Yet in the present text the organic chemistry resulting from these various bonding possibilities will only be mentioned if it is employed to modify carbon materials or, to put it in other words, the element itself as a material will be in the focus.

Another feature that gave reason to write this book was the occurrence of various allotrope modifications with in parts completely opposite properties. For the time being, this renders carbon one of the most interesting topics in materials science and research. Be it fullerenes, nanotubes or nanocrystalline diamond phases—they all are subject to intensive investigation and promise a multitude of applications, for example, in electronics, medicine, and nanotechnology.

Nevertheless, it is hardly possible to assess the development within the last two decades and to perceive its impact on the multitalented carbon's perspectives in chemistry, material science, and physics, without an understanding of its long-known modifications, mainly graphite and diamond. Hence, the first chapter summarizes the essential facts on the “classical” modifications and their properties, for only a solid comprehension of basic concepts and principles enables us to understand the properties of “new” carbon materials and to develop new ideas.

1.1

History

Elemental carbon in different shapes played a role in human life long before the term “element” was even coined. Charcoal and soot have been known and utilized for various purposes since ~5000 BC. They were mainly obtained from wood and employed, for example, for metallurgic processes such as the production of iron.

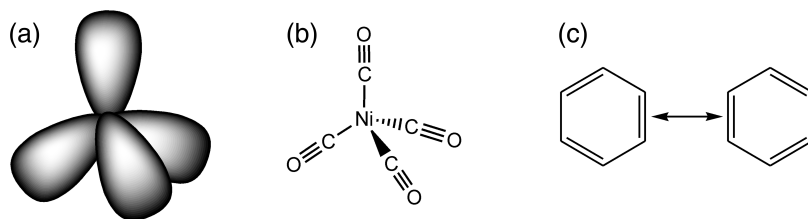


Figure 1.1 (a) sp^3 -Hybrid orbitals of carbon, (b) nickel tetracarbonyl, (c) mesomerism of the aromatic compound benzene.

The first application of graphite is documented from the late central European Iron Age (La Tène period). It was excavated near Passau (Bavaria) and employed to blacken pottery. Further examples of carbon being used for artistic purposes include pigment black from charcoal for cave painting, for example, as seen in the caves of Rouffignac (France).

The term “graphite” reflects its use as a pigment: it is derived from the Greek word *graphein*, meaning *to write*. Pencils, that became fashionable in the Middle Ages, originally were made from graphite, and ancient Egyptian papyri bear hieroglyphs written with ink were made from soot. The latter also became important for written records and works of art in East Asia from the beginning of modern times. Moreover, carbon in the shape of medicinal charcoal is employed in therapeutics to treat gastrointestinal diseases by its degassing and adsorbing effects. Charcoal is also a constituent of black powder—it is mainly black alder wood (*frangula alnus*) being charred at relatively low temperatures for this purpose.

In the 19th century, the exploration of the element took a rapid progress, and many important insights were obtained. Shortly after Berzelius made a distinction between inorganic and organic matter in 1807, it became obvious that carbon played a central role in organic substances. His definition of organic compounds only to occur in living organisms had to be revised soon (Wöhler conducted his important experiments to synthesize organic urea from definitely inanimate ammonium acetate in 1828 already). Nevertheless, his work laid the path for extensive research that largely influenced the development of bonding theories for complex molecules.

F. v. Kékulé interpreted benzene to be a cyclic entity in 1865. The concept of carbon as a tetrahedrally, four-fold coordinated atom was presented independently by J. H. van t’Hoff and J. A. Le Bel in 1874 and revolutionized the interpretation of the element’s chemical activity (Figure 1.1). Since then, fundamental discoveries on this ubiquitous element multiplied. L. Mond and co-workers published the first metal carbonyls in 1890, and in 1891, E. G. Acheson for the first time achieved artificial graphite via intermediate silicon carbide (*carborundum*), which itself had been unknown then, too.

The development proceeded in the early 20th century. Next to the first preparation of a graphite-intercalation compound (C_8K , 1928), A. S. King and R. T. Birge found the element’s composition from the isotopes ^{12}C and ^{13}C in 1929. Radioac-

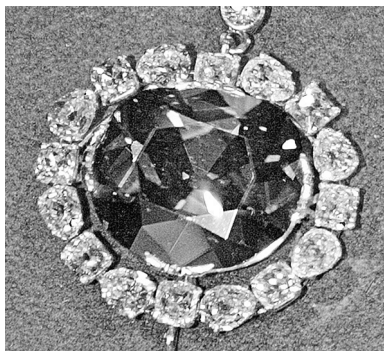


Figure 1.2 The blue *Hope* diamond kept in the National Museum of Natural History in Washington counts among the world's most famous diamonds (© Kowloonese 2004).

tive ^{14}C was detected in 1936 by W. E. Burcham and M. Goldhaber. This enabled the development of radiocarbon dating for the age determination of the organic matter by Libby, who was awarded a Nobel prize for that discovery in 1960. One year later, the mass of isotope ^{12}C was established as basis for the standard atomic masses ($^{12}\text{C} = 12.0000$ amu). When NMR spectrometers with ^{13}C -Fourier transformation became widely available in the 1970s, structural analysis of organic molecules was immensely facilitated.

From 1985 on, the research on carbon gained new impetus from the first observation of fullerenes, and in 1991, carbon nanotubes were presented as another new allotrope modification. The whole field has been in a very dynamic state ever since, and the number of publications has grown to more than 50000 in the meantime, demonstrating the large interest of specialists from various areas of research.

Diamond, whose name is derived from the Greek words *diaphanes* (translucent) and *adamas* (invincible), has also been known for long (Figure 1.2). It was first discovered in India around 4000 BC. The oldest, and at the same time one of the biggest diamonds surviving to our days (186 carat) is the *Kooh-i-Noor*. It was presumably found in India about 3000 BC and is kept in the Tower of London today. From about 600 BC on, diamonds from India came to Europe. As early as that, magical powers were ascribed to the stone due to its distinct appearance and resistant nature. Diamond as a decorative gem did appear later, though. In ancient Rome, the stone was known and appreciated as well, and Pliny the Elder (23–79 A.C.) already did mention its use as a tool. Still, the stones had to be imported from southeast Asia, which made them an extremely rare material, and even after reports on the first finding of diamonds on the island of Borneo (Indonesia today), India for its favorable situation remained the most important source until modern times.

It was only when the Indian mines were exhausted in the 18th century that new sources of the coveted stone had to be found. In the year 1726, diamond for the first time was found out of Asia while searching for gold in the then Portuguese colony of Brazil. This caused a veritable “diamond rush” that lasted for several years. But after some time, these sources began to run dry as well (today, there

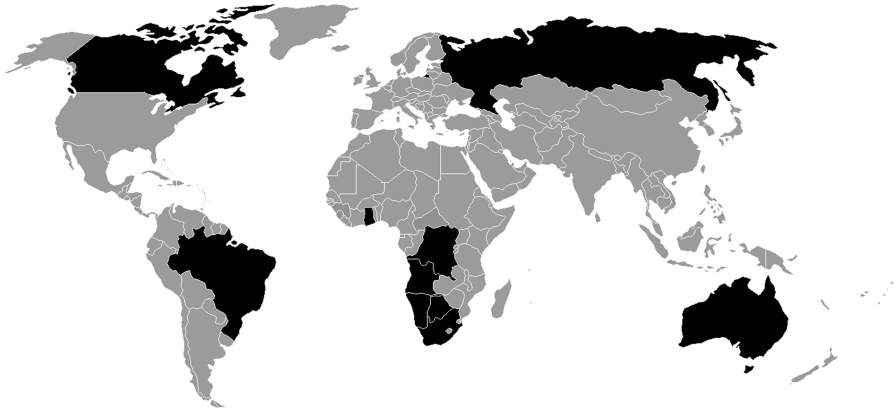


Figure 1.3 World-wide deposits of diamond (dark shading: countries with diamond resources). The classical African export countries experience increasing competition from discoveries in Canada and Australia.

are still black diamonds, so-called *carbonados*, mainly processed to be tools for oil drilling). Then, in 1870, the first so-called *Kimberlite* pipe was found near the town of Kimberley in South Africa, which within shortest time turned that country into the world's main supplier of diamond.

Discoveries of diamond increased in other African countries too. From the beginning of the 20th century, partly copious deposits were found, for example, in Congo, Namibia, Ghana, Guinea, Sierra Leone, and the Ivory Coast, which made Africa the virtually sole source of diamonds until the 1950s. It was not before 1950 that the large-scale exploitation of Siberian mines began and the former Soviet Union started supplying the world market with big amounts of diamond. Mainly the deposits in Jakutia near the city of Mirny, 4000km east of the Ural Mountains, furnish good yields of jewelry and industrial grade diamonds to the present days (Figure 1.3).

Today, more or less abounding deposits have been found on all continents including Europe, for example, near Arkhangelsk (Russia). Especially the Kimberlite pipes discovered in northwestern Australia in the 1970s were very yielding, and by now, Australia is among the world's biggest suppliers. In recent years, also Canada became a big player on the world market after having prospected diamond sources and starting their exploitation (Figure 1.4).

However, a part of the diamonds offered today does not originate from the production controlled by a few big companies. These so-called blood diamonds are hauled in central Africa under inhumane and degrading conditions, and the money from their sale serves local warlords to subsidize a multitude of civil wars. In 2001, a treaty under the auspices of the UN was signed to make the raw material's origin traceable and thus prevent the selling of conflict diamonds, but despite this certification, the source of many stones remains unclear because documents are frequently faked and the diamond itself does not give information on its place of discovery.

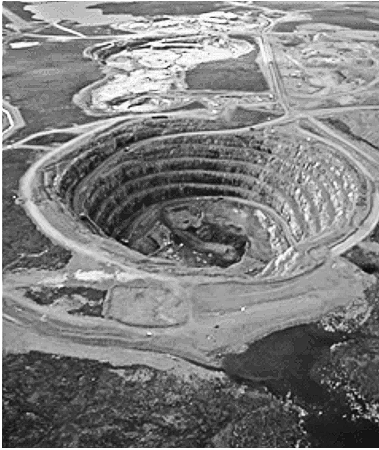


Figure 1.4 The Ekati-Billiton mine in Canada
(© Billiton Corp.).

Another milestone in the history of diamond was its first synthetic production. A team of Swedish researchers of the ASEA Corp. first succeeded in this task by using a pressure chamber, but their work did not obtain wide attention (refer to Section 1.3.2). A lot of attempts had been made before to produce the coveted stone in the lab, with approaches ranging from alchemistic folly to serious experiment. Among the noteworthy attempts there is the work of the French chemist H. Moissan (awarded the Nobel prize in 1906 for the discovery of fluorine). He saturated liquid iron with carbon and precipitated parts of the carbon as small, colorless crystals on shock-cooling. Nevertheless, diamond formation could not doubtlessly be proven. In 1880, J. B. Hannay published his work on heating a mixture of hydrocarbons and lithium in a closed iron container, which resulted in crystals with a density of 3.5 g cm^{-3} and a carbon content of 98%. However, doubts on whether these samples really originated from his decomposition experiment could never be cleared out. C. Parsons experimented for more than 30 years on the manufacture of synthetic diamond. He failed to reproduce the experiments of Moissan and Hannay, but he also tested the addition of iron to a mixture according to Hannay. Although convinced at first to have made diamond, he later retracted this thesis after further, thorough investigation. He even doubted that it had then (1943) ever been possible to make synthetic diamond. Yet there had been experiments by C. V. Burton in 1905, consisting in the precipitation of carbon from oversaturated lead–calcium alloys by removing the calcium. Eighty years later, these experiments could be reproduced, and at least in the X-ray powder diffractogram, the product did show signs of a diamond-like crystal structure.

In 1955, the age of industrial diamond began when General Electric started the first large-scale production in the United States. Six years later, P. S. DeCarli and J. C. Jamieson introduced a method employing the shock-wave energy of an explosion to generate pressure and thus to change graphite into diamond. From the mid-1960s on, an entirely new type of material became available besides the classical, more or less bulky diamond. Obtained by chemical vapor deposition, it does exist in the shape of thin films and serves, for example, as surface coating. Today,

several other diamond materials are known which will be discussed in Chapters 5 and 6.

It was not before the end of the 18th century that the fact of diamond, graphite and soot being the very same element was acknowledged. The German chemist C. W. Scheele demonstrated graphite to be a kind of carbon, known in his mother tongue as Kohlenstoff (*coal-matter*). The french name *carbone* for the element was coined in 1789 by A. L. Lavoisier, who deduced it from the latin *carbo*, meaning *charcoal*. And only in 1796, S. Trencant could prove that diamond as well is a form of carbon.

By now, the phase diagram of carbon has grown out to be rather complex, with a multitude of allotrope modifications which in their turn are surrounded by additional high-pressure and high-temperature phases. All of them have distinct, and in parts even opposite properties, which put carbon among the most versatile and many-sided of elements in materials science.

1.2 Structure and Bonding

The carbon atom bears six electrons—two tightly bound, close to the nucleus, and the remaining four as valence electrons. The electronic configuration is $1s^2$, $2s^2$, $2p^2$, accordingly (Figure 1.5). This implies a bivalence, which in fact does only exist in a few structures (carbenes), though. In the vast majority of its compounds, carbon is tetravalent. Yet in more recent times, even higher coordination numbers were found in a series of molecules, for example, in Al_2Me_6 , in different carbaboranes, or in the octa-coordinated carbon atom in $[Co_8C(CO)_{18}]^{2-}$ (Figure 1.6).

The preferred tetravalence may be explained with the hybridization model: the energetic difference between $2s$ - and $2p$ -orbitals is rather low compared to the energy released in chemical bonding. Therefore, it is possible for the wavefunc-

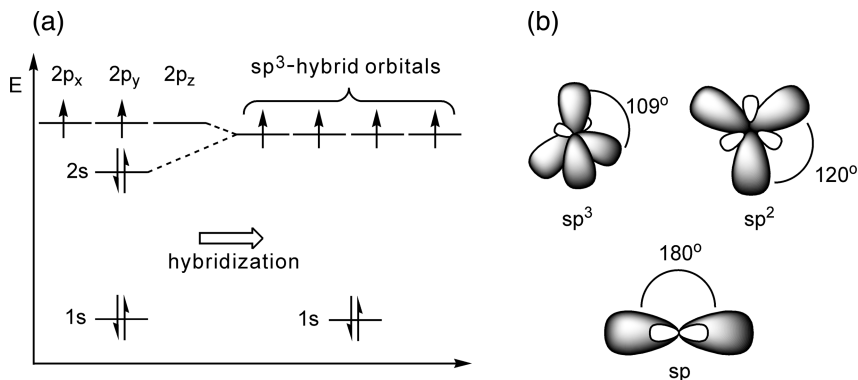


Figure 1.5 (a) Diagram of atomic orbitals and sp^3 -hybridization, (b) hybrid orbitals of carbon.

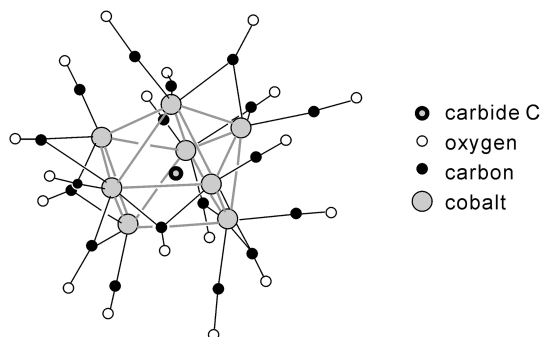


Figure 1.6 Hypervalent carbon. In the complex $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$ the isolated carbon atom has eight coordinating neighbors.

tions of these orbitals to mix and form four equivalent hybridized orbitals. These sp^3 -hybrid orbitals are directed toward the four corners of a tetrahedron circumscribed to the carbon atom. Likewise, the $2s$ -orbital may mix with a lower number of $2p$ -orbitals to form sp^2 - or sp -hybrid orbitals, respectively. Figure 1.5b displays the hybrid orbitals and their spatial arrangement. A carbon atom may accordingly form bonds with one to four partners. Depending on the degree of hybridization, the resulting compounds show different structural features: sp -hybridized C-atoms form linear chains, whereas sp^2 - and sp^3 -hybridization give rise to planar structures and to three-dimensional tetrahedral networks, respectively. In sp - or sp^2 -hybridized C-atoms there are two or one p -orbitals not taking part in hybridization. These can form additional π -bonds that, in contrast to the aforementioned σ -bonds, do not exhibit rotational symmetry. Their existence shows in the bond lengths and enthalpies. For example, the C–C distance in a double or triple bond is 133.4 or 120.6 pm, respectively, as compared to 154.4 pm in a single C–C- σ -bond. An analogous trend is observed for bonding enthalpies.

1.2.1

Graphite and Its Structure

The structure of graphite had been elucidated from 1917 on by Debye, Scherrer, Grimm, Otto, and Bernal. It is characterized by a succession of distinct so-called graphene layers that spread over an xy -plane. They are stacked in a z -direction, and there are only weak van der Waals interactions among them (Figure 1.7).

Within one graphene layer, the carbon atoms are situated at the corners of regular hexagons that constitute a two-dimensional lattice. From each C-atom there are three σ -bonds leading along the hexagons' edges, which correspond to sp^2 -hybridization. As a consequence, only three out of four valence electrons participate in hybridization. The remaining electrons, contained in the p_z -orbitals, do also interact: they form a π -cloud that is delocalized over the entire graphene layer. The π -electrons thus behave like a two-dimensional electron gas, and by their

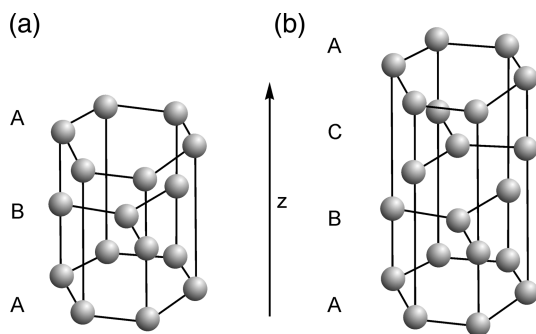


Figure 1.7 The sequence of layers in hexagonal (a) and rhombohedral graphite (b).

mobility, they cause material properties like an anisotropic electrical conductivity (Section 1.4.1). Within one graphene plane, the distance between adjacent atoms is 141.5 pm. This corresponds to a bond order of 1.5 and twice the covalence radius of an aromatic carbon atom (C–C distance in benzene: 139 pm), and it is a clear indication of the π -bond contribution. The distance between adjoining graphene sheets, on the other hand, is 335.4 pm (about twice the van der Waals radius) because there is only weak van der Waals interaction. That is why the planes of graphite are easily shifted in parallel against each other.

There are two different modifications, the hexagonal (“normal”) or α -graphite, and the rhombohedral β -graphite. The latter is quite frequent in natural graphites and may be transformed into the thermodynamically more stable hexagonal form by the action of heat. The individual graphene layers in the hexagonal structure are stacked according to a sequence ABAB with the atoms of a layer B being situated above the centers of the hexagons in a layer A, and vice versa (Figure 1.7a). The third layer is congruent with the z -projection of the first one. The hexagonal unit cell, containing four carbon atoms, has a $P6_3/mmc$ (D_{6h}^4) symmetry and the dimensions $2.456 \times 2.456 \times 6.708 \text{ \AA}$. In rhombohedral graphite, the layers are stacked in an ABCABC order (Figure 1.7b), giving rise to a bigger unit cell ($2.456 \times 2.456 \times 10.062 \text{ \AA}$) that also contains four carbon atoms nevertheless. Rhombohedral material is converted into the α -form above 1025°C , whereas the reverse transformation may be achieved by milling. The enthalpy of formation is just about 0.06 kJ mol^{-1} higher for rhombohedral than for hexagonal graphite.

In reality, however, there is a wide range of graphitic materials apart from these ideal manifestations. They feature a perfect arrangement of carbon atoms within single graphene sheets, but the interplanar distance is about 344 pm due to stacking disorders. As a consequence, there is virtually no more interaction between the layers, and the orientation of individual planes no longer has an influence on the effective forces. Usually, the layers are irregularly turned around the z -axis and shifted against each other in the xy -direction. These structures are called *turbostratic*.

1.2.2

Diamond and Its Structure

In diamond, each carbon atom has four immediate neighbors situated at the corners of a tetrahedron that is circumscribed to the atom in question. All carbon atoms are sp^3 -hybridized, and the bond length uniformly is 154.45 pm.

There are two modifications of diamond, the cubic and the hexagonal type (*Lonsdaleite*), with the first being the more abundant one. Another structural distinction of diamonds is made by their content of nitrogen: type Ia contains nitrogen as platelets with an approximate composition of C_3N . Type Ib, on the other hand, has nitrogen evenly distributed throughout the crystal. Diamond virtually void of nitrogen is classified as type IIa, but it rarely ever occurs naturally. Type IIb, which in contrast to the other variants is semiconducting, does not contain nitrogen either, but it bears a certain concentration of aluminum.

The crystal lattice of “normal” diamond is face-centered cubic with a lattice constant of 356.68 pm and eight atoms contained in the unit cell (Figure 1.8). The structure is not densely packed, but of the *sphalerite* kind, which is a penetration of two face-centered cubic lattices shifted against each other along the unit cell’s space diagonal. An analogous structure is found in zincblende (ZnS). Upon heating to more than 3750 °C under a pressure of 1840 psi, cubic diamond turns into graphite.

Hexagonal diamond (*Lonsdaleite*) is extremely rare in nature. It was first discovered in a meteorite from Arizona in 1967. Still it is possible to obtain *Lonsdaleite* from graphite by exposing the latter to extreme pressure along the z -axis at ambient temperature. The hexagonal lattice (*Wurtzite* type) like its cubic relative is built from tetrahedrons of carbon, but these are arranged in a different way (Figure 1.9). The unit cell contains four atoms, and the lattice parameters are $a_0 = 252$ pm and $c_0 = 412$ pm.

As a visualization, starting from hexagonal graphite, one may fancy the freely mobile π -electrons alternately to form upward and downward σ -bonds with the respective atoms of adjacent layers. This causes a formal compression and undulation of the lattice (change of hybridization), but conserves the ABAB stacking of the imaginary planes. For the formation of cubic diamond, on the other hand, a slight

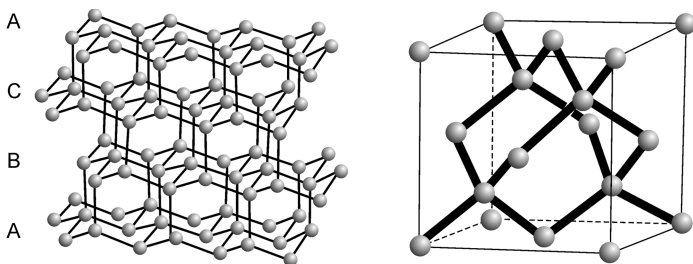


Figure 1.8 The lattice structure of cubic diamond and its elementary cell.

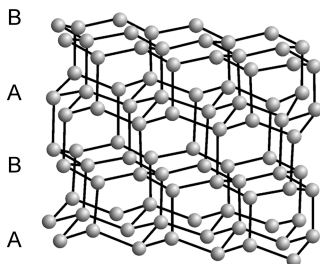


Figure 1.9 The lattice structure of hexagonal diamond. The arrangement of atoms in the horizontal crystal plane somewhat resembles a “wavy” graphite structure.

displacement of the third layer is required, which causes an ABCABC sequence and the interplanar distance of only 205 pm. To be sure, all of this is only a model made up to illustrate the lattice relation of the different carbon modifications. Actually, both cubic and hexagonal diamonds are isotropic, three-dimensional structures with every atom tetrahedrally surrounded by four neighbors.

1.2.3

Structure of Other Carbon Allotropes

There are a number of further carbon phases besides the “classics” graphite and diamond. In the 1960s, a white allotrope was found that was named *chaoite*. It was discovered in the Bavarian Ries (northeast of Ulm) in graphite gneiss that had molten under pressure. It may further be generated by heating pyrolytic graphite to about 2000 °C *in vacuo* (about 1.9×10^{-6} psi). The resulting hexagonal crystals grow as dendrites, the lattice parameters are $a_0 = 894.5$ pm and $c_0 = 1407.1$ pm, and the material’s density of 3.43 g cm^{-3} is quite similar to that of diamond. However, the actual crystal structure has not yet been fully elucidated, but carbyne units ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$) are assumed to be at least partial constituents.

The so-called carbon(IV) does also seem to contain such carbyne structures. It may be obtained by heating graphite, preferably with a laser under argon at a pressure between 1.5×10^{-6} and 1.5 psi. The unit cell is of hexagonal shape with the parameters $a_0 = 533$ pm and $c_0 = 1224$ pm. The density of 2.9 g cm^{-3} is markedly higher than that of graphite. Further carbynoid allotropes are assumed to exist between ca. 2300 °C and the melting point of carbon.

While for the time being it is unclear for the aforementioned allotropes whether they are more of a graphitic or a diamond-like crystal structure, soot (or carbon black) definitely is a graphitic phase with an expanded interplanar distance of about 344 pm. Electron micrographs (Figure 1.10) show soot particles to be more or less spherical structures that form loose, grape-like aggregates. Within the individual particles there are very small domains (up to 3 nm along the hexagon planes and 2 nm perpendicular to them) that are graphitically crystallized. These are stacked in the manner of roof tiles, with a dominant turbostratic order in the piles. The particles’ centers contain structures arising from polycyclic aromatic hydrocarbons (PAHs) attached to nucleation centers during formation of the soot

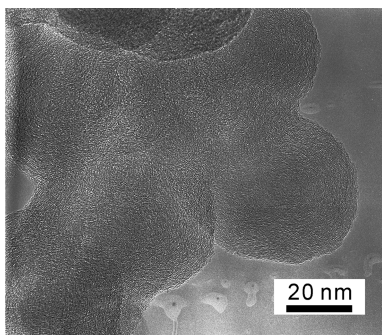


Figure 1.10 HRTEM image of soot particles (© M. Ozawa).

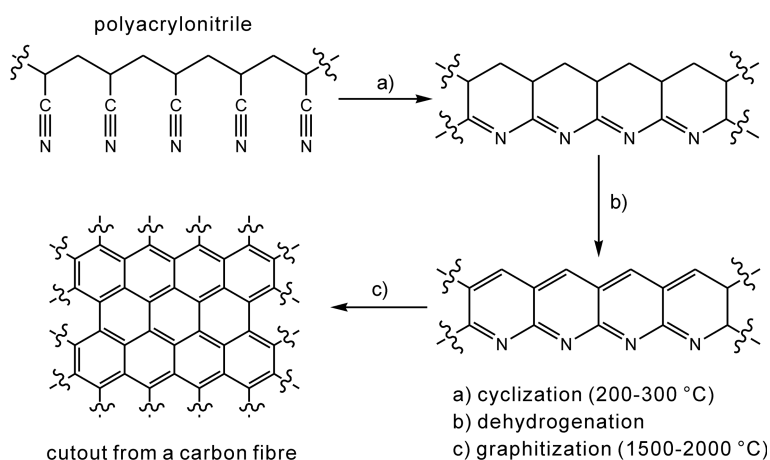


Figure 1.11 Conversion of polyacrylonitrile fibers into carbon fibers.

particles. By arranging with their molecular planes, they form the first pile, which is the starting point for particle growth. The lower the pressure during soot formation, the bigger the particles grow due to a then diminished number of condensation nuclei. Common sizes of soot particles range from 20 to 300 nm, which gives carbon black a considerable outer surface of about $100 \text{ m}^2 \text{ g}^{-1}$, and additional activation by heat may increase this value to even $1000 \text{ m}^2 \text{ g}^{-1}$. Owing to the loose stacking of subdomains, soot only has a low density of about 1.85 g cm^{-3} .

Carbon fibers are another graphitic manifestation of carbon; they only differ from the bulk material in the arrangement of graphitic elements that follow the fibrous habit here. The latter is caused by the manufacturing process: starting from polyacrylonitrile (PAN), an initially nitrogen-rich, fibroid structure is obtained by heating. This loses the nitrogen and graphitizes on further heating. The mechanism of this transformation is illustrated in Figure 1.11. Not only

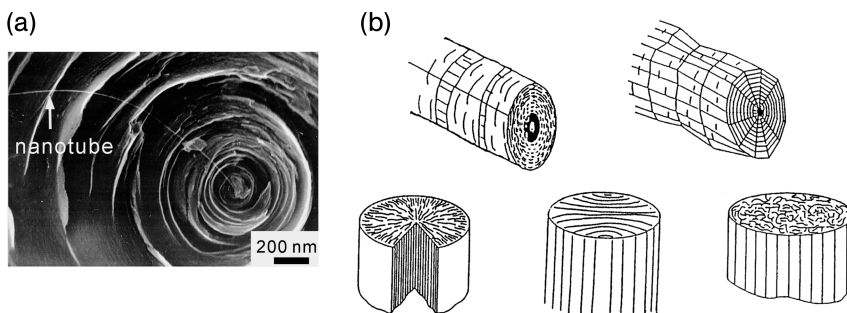


Figure 1.12 Carbon fibres; (a) microscopic image from out of the core protrudes a multi-walled carbon nanotube (bright line) (© Elsevier 1995), (b) schematic view of possible fiber structures (© Springer 1988).

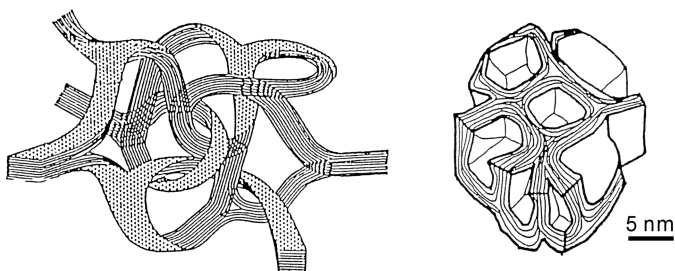


Figure 1.13 The structure of glassy carbon. The entangled graphitic ribbons give rise to extraordinary rigidity and isotropic materials properties (© Cambridge University Press 1976).

PAN, but also cellulose acetate or the tarry residues of oil refining (mesophase pitch) may serve as starting material. In the center of carbon fibres, structural elements that resemble multiwalled carbon nanotubes are frequently observed (see Chapter 3). Around these, graphitic domains are arranged in parallel with the fiber's axis with their specific structure depending on the temperature during preparation. Further thermal treatment after manufacture may change the respective morphology, but the orientation of the graphene layers in parallel with the fiber's axis is largely conserved. Figure 1.12 gives some examples of possible structures.

The so-called *glassy carbon* also bears some interesting structural features. It does contain ribbon-like graphitic domains of sp^2 -hybridized carbon atoms stacked in layers, but these are irregularly twisted and entangled, resulting in a mechanically and chemically very resistant material. Figure 1.13 illustrates the respective structures. In contrast to graphite, glassy carbon is a material of low density (1.5 g cm^{-3}) with isotropic thermal and electrical properties.

1.2.4

Liquid and Gaseous Carbon

The melting point of graphite at ambient pressure of about 4450 K is extremely high—in fact it is the highest value measured for an element so far. Accordingly, its determination was anything but trivial as crucibles of any conceivable material would have molten before their content under examination. Eventually crucibles made from graphite itself were employed. Their center then was heated, for example, by means of a laser. The melting point of diamond slightly deviates from that of graphite, but the resulting liquid phase presumably is the same.

The boiling point of carbon is close to the melting point, so there is a considerable vapor pressure over the liquid phase. It is not single atoms evaporating, though, but small carbon clusters of up to several tens of atoms (a magnitude comparable to fullerenes). The most abundant species have structures of C_n with $n = 3, 2, 4$. The release of single atoms is restrained by the coincidence of high vapor pressure and the high C–C-bonding energy.

1.3

Occurrence and Production

1.3.1

Graphite and Related Materials

Above all, graphite is found in places where igneous rock (e.g., gneiss) and stratified rock border on each other. The graphitization of coal present in the stratified material was presumably initiated by ingressing magma and the corresponding high temperatures (300–1200 °C). There are different kinds of deposits bearing graphite in big pieces (lump and chip), in flakes, or as microcrystalline powder. The latter is frequently (and falsely) called “amorphous” due to its small particle size and the related aspect. For big, coherent lumps there is also a hydrothermal formation being discussed. Some of the deposits got a lenticular shape, and usually there are layers or pouches in the surrounding rock, which is another sign of the generation from coal seams.

China, India, Brazil, Korea, and Canada are the main suppliers, besides further sources of high-quality graphite like Sri Lanka or Madagascar. The overall production was about 742.000 t of natural graphite in 2003 (Table 1.1). It has also been

Table 1.1 Annual production of natural graphite in 2003 (according to US Geological Survey).

| | China | India | Brazil | North Corea | Canada | Mexico | Czech Republic |
|---------------------------------------|---------|---------|--------|----------------|--------|--------|-------------------|
| Annual production of graphite in tons | 450.000 | 110.000 | 61.000 | 25.000 | 25.000 | 15.000 | 15.000 |

mined in Germany of old, for example, in the Passau area (Bavaria), with an annual output of about 300 t.

The concentration of graphite in the deposits ranges from 20 to 50%. Depending on this content, there are different ways of processing. The crushed and milled rock is separated from the graphite by several steps of oil floatation. In some cases, there is also work-up with hydrofluoric or hydrochloric acid. Raw material from Sri Lanka, however, does not require floatation. It is simply sorted into graphite-containing and dead fractions before the muddy parts are washed away. The graphite portion is then treated with molten soda. The products obtained make different prices on the world market depending on their degree of crystallization and their purity (the latter usually is higher for well crystallized flaky graphite than for powdered graphite).

Yet the amounts from natural sources are far too low to cover the overall demand of graphitic carbon, and so a lot of the material is obtained synthetically. The world production is in the range of two-digit gigatons per year, with coal, oil or natural gas serving as carbon sources. Various graphitic materials such as soot, activated carbon, artificial graphite or carbon fibers, etc. are obtained by thermal decomposition of the starting materials at 600 to 3000 °C.

The properties of these graphitic products, such as degree of crystallization, particle size, or layer structure, depend on the manufacturing process and the kind of source material. Some products of low crystallinity exhibit a turbostratic structure of the graphene sheets. The higher the temperature during the decomposition of the primary material, the bigger domains of graphitic order are obtained, and the products' properties approximate those of original graphite. The individual products and the ways of their production are presented below.

Coke The annual production is in the range of hundreds of megatons as big amounts of this energy source are required to feed blast furnaces and for heating. It contains about 98% of carbon. Coke is obtained by strong heating of pit-coal (coking) with the specific kind of starting material leading to either *gas coke* or *metallurgical coke*. The latter is obtained by coking coal with a low content of gas. It is harder and more suitable for the furnace process than gas coke. In addition, there is *petrol coke* from the residues of distillation in oil refining. In comparison to other types of coke, this variant is well graphitized and hence employed to make *artificial graphite*.

Artificial Graphite This type of carbon is quite close to the natural material. It is formed by pyrolysis of carbon compounds at extremely high temperatures. In large-scale production, it is mainly petrol coke being graphitized at 2600–3000 °C. The process starts by preheating to about 1400 °C to rid the petrol coke of volatile components. Subsequently, molded parts bound with pitch are made and preburned at 800–1300 °C. This *artificial carbon* is then embedded in coke in an electric furnace and graphitized by resistant heating. The molded parts are covered with sand in this step, which is not only for thermal reasons: the silicon contained therein obviously has a catalytic effect on the formation of graphite by forming intermediate silicon carbide. At the prevailing temperatures, the latter has a considerable vapor pressure of silicon, and the carbon formed during the consequent

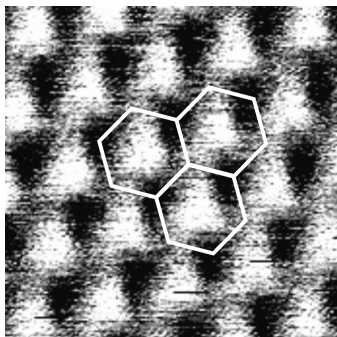


Figure 1.14 Atomic force microscopic image of highly ordered pyrolytic graphite (HOPG). The graphene lattice is indicated by the white lines. The different shading of carbon atoms results from the different situation in the atomic layer underneath (© A. Schwarz).

decomposition of carbide is obtained as graphite due to its lower chemical potential ($C_{\text{microcryst.}} + \text{Si} \rightarrow \text{SiC} \rightarrow \text{Si} + C_{\text{graphitic}}$).

Pyrolytic Carbon Depending on the manufacturing conditions, a highly parallel order of graphene layers may be obtained here. Common pyrolytic carbon is made by thermolysis of hydrocarbons at about 700 °C and low pressure (about 0.15 psi). The product precipitates on a plain surface so that the graphene layers align with it. Thermolysis at 2000 °C and postgraphitization at 3000 °C yield a material called *pyrolytic graphite* that virtually matches natural graphite in its anisotropy of thermal and electrical conductivity. When, in addition to extreme temperatures, also shear forces are applied to the precipitated carbon, the almost completely parallel *highly ordered pyrolytic graphite (HOPG)* is obtained (Figure 1.14). The deviation from perfect parallel order is less than 1% here.

Carbon Fibers Pyrolysis of organic fibers under tension yields the aforementioned carbon fibers (Section 1.2.3), the hexagonal planes of which are oriented in parallel to the initial strain. The most common starting material is polyacrylonitrile (PAN). The covalent connection of atoms along the fiber's axis provides the material with high strain resistance and a large modulus of elasticity.

Glassy Carbon If unfoamed organic polymers are employed instead of PAN fibers, another variant of graphitic carbon is obtained. It is characterized by an entanglement of graphitic ribbons (Figure 1.13) that confer extreme hardness to the material. Furthermore, its physical properties are isotropic on a macroscopic scale as there is no preferred spatial order of the graphitic domains—they are rather arranged at random. The term *glassy carbon* originates from its aspect that resembles black glass. It can only be processed with diamond tools, and also chemically it is very stable. It may be applied, for example, as material for electrodes or crucibles.

Activated Carbon With a surface of 300–2000 m² g⁻¹ and a pore diameter of 1–5 nm, activated carbon is an outstanding adsorbent for a multitude of substances. It is produced by gentle heating of organic precursors like wood, turf or coconut peel, but also of pit-coal etc. The activation (to obtain the required porous structure) results either from hydrothermal surface reaction with water vapor or from impregnating the starting material with agents that cause oxidation and

dehydration (e.g., ZnCl_2 , H_3PO_4 , or NaOH). Their residues are washed from the pores after charring. The annual production is some 100.000t worldwide.

Soot (Carbon Black) Gigatons of carbon black are made each year mainly because it is required as filling agent by the tire industry. Several kinds of soot are distinguished depending on the respective starting material. In general, there are combustion soot from incomplete combustion and split soot obtained by thermal decomposition. The most important among the combustion soots are *furnace black* (95% of C), that is produced by burning mineral oil and chilling the resultant gases with water, and *channel black* obtained by precipitating on cooled iron surfaces the carbon from a shining flame of anthracene oil. Split soot can be made starting from natural gas, methane or acetylene, the latter yielding *acetylene black* with its particularly high content of carbon (98–100%). Soot like activated carbon possesses a high specific surface due to its particle structure (Figure 1.10). The small and irregularly arranged graphitic domains cause the material to be practically isotropic.

Natural Deposits of Carbon-Containing Materials Anthracite, pit-coal, brown coal, turf, wood, mineral oil, and natural gas are possible natural sources for the production of carbon materials. They all have different carbon contents and partly result from a long-lasting series of geological events. Within millions of years, a process called carbonization first changed organic matter to humic acids by anaerobic decomposition, later to turf, and then, under elevated pressure and exclusion of air, to brown or pit-coal. The carbon content increased in the course of this process, and the content of water concomitantly was reduced. Brown coal was mainly formed during oligocene and miocene (Figure 1.15) and contains up to 45% of water. The carbon content of the dehydrated material is about 70%. Pit-coal usually originates from the older age of *Carboniferous*; it bears less than 20% of water and about 90% of carbon after drying. The coal of highest quality, called anthracite, is a very hard, shiny gray material with less than 15% of residual water and more than 90% of carbon when dried. The different percentages of carbon correspond to the respective temperature and pressure during formation; the progressing coalification does not reflect the geological age—some of the oldest coals known are pieces of brown coal poor in carbon.

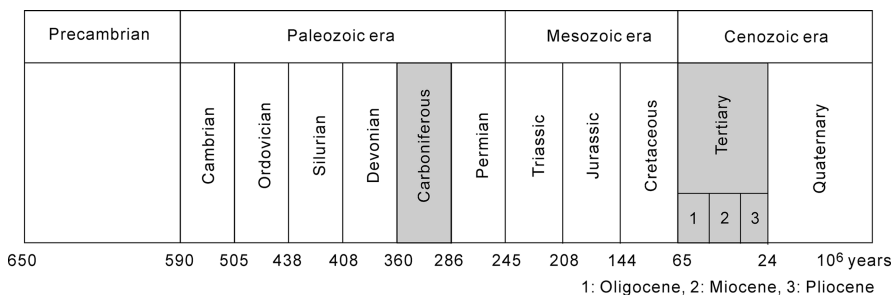


Figure 1.15 Chronological table of geological ages. The periods of coal formation are shaded gray.

1.3.2

Diamond

Natural deposits were the sole source of diamond until the mid-1950s as there was no synthesis of artificial material available—despite a variety of approaches.

The geological process of diamond formation has not been fully elucidated to the present day, but it usually is thought to be a transformation product of other carbons, for example, graphite. At a depth of more than 150 km from the earth's surface, at a pressure of more than 4.5 GPa and temperatures between 900 and 1300 °C, these change into the then-stable diamond. In volcanic eruptions several hundreds of millions of years ago the material was carried from the upper earth's mantle to the surface through chimneys of molten rock, reaching a speed of up to Mach 2 (700 m s^{-1}). The eruptive process was too fast for the retransformation into graphite to take place in spite of the reduced pressure and the lasting high temperature. The magma cooled down in the volcanic chimneys and formed igneous rock (Figure 1.16). The transporting rock of magmatic origin most frequently bearing diamond is *Kimberlite*, thus called after the South African town of Kimberley where the first of such chimneys was detected. But diamond is also found in sedimentary rock that was formed by withering of the original stone—it simply escaped erosion due to its hardness. Subsequent washout carried it away and deposited it at the future site of detection. Off the coast of Namibia, there are even marine deposits resulting from such transport processes.

Diamond is won either by washing it out of the sedimentary parent rock or by exploiting the Kimberlite pipes. The latter produces gigantic craters in the former volcanic chimneys that are dug continually deeper into the ground (Figure 1.4). In some mines also underground working takes place. The crushed and not-too-finely ground rock is washed out and the fraction holding diamond is led over

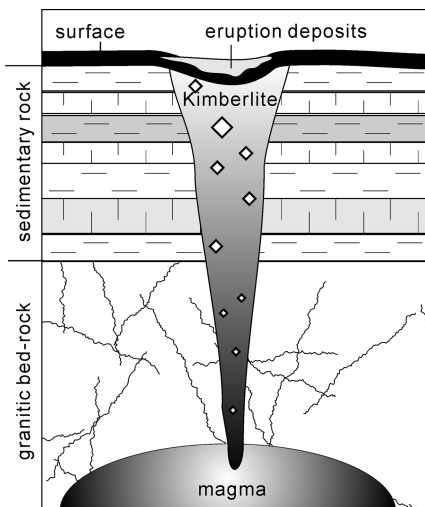


Figure 1.16 Scheme of a Kimberlite pipe. Due to the fast cooling of molten rock, carbon is conserved in the shape of diamond and conveyed to the earth's surface as such.

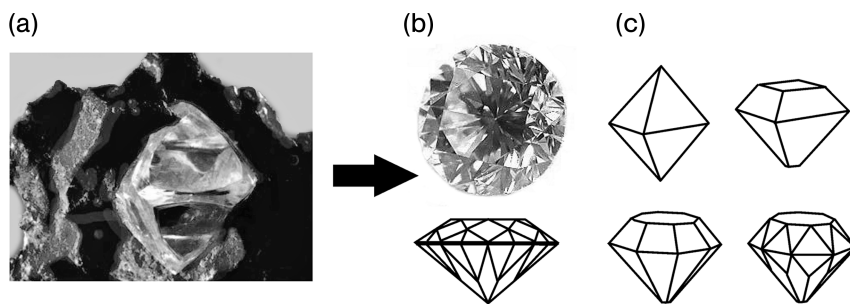


Figure 1.17 (a) Raw diamond in parent rock (© US Geological Survey), (b) jewelry diamond in brilliant cut and (c) evolution of cut types from simple octahedral stones to brilliants.

conveyor belts covered with a layer of fat. The diamond adheres to it, while other rock is carried on and discarded. Especially in large-scale industrial exploitation, there are also X-ray sorters in use. The current annual production is about 150.2 megacarat (30t) with Australia (6.6t), Africa (16t in total), and Russia (4.8t) being the main suppliers. Stones of gem quality are obtained from the respective diamond-rich fractions by assessing the raw diamonds' color, crystallinity and distribution of inclusions. Still a big part (an average of 50%, depending on the site of exploitation) does not fulfill the requirements for jewelry and thus is employed to make cutting and abrading tools. However, this amount is far from sufficient to satisfy the demand for industrial diamonds.

The selected raw diamonds are cleaved along suitable crystal planes to obtain stones for jewel manufacture. These are processed in a way to bring out the brilliance and its particular refraction of color (Figure 1.17). For grinding and polishing, diamond powder is used as no other material is hard enough to cause abrasion on diamond. The markedly varied hardness of its crystal planes is employed for this process: the polishing powder contains irregularly shaped fragments that represent material of every required hardness to abrade each crystal plane. The main task in diamond cutting is to accentuate the stone's luster. As much of the raw material as possible shall be preserved in doing so while achieving attractive gems nevertheless. Hence a multitude of cuts has been developed over the centuries, culminating in the so-called brilliant *full cut* that possesses at least 32 facettes and a plate on the upper half, and at least 24 facets and an optional calette on the lower. The stone's perimeter is circular. By this treatment the greatest possible dispersion of light is achieved (Figure 1.17b).

The quality of gem diamonds is judged by the *4 C-method*, comprising *color*, *clarity* (purity; size and kind of inclusions), *cut* (the quality of it), and *carat* (weight). 1 carat equals 0.2g. The measure originates from antiquity—it is defined to be the mass of a seed from the carob tree. These tend to weigh exactly 0.2g with surprising reproducibility.

As already suggested by the criteria of quality assessment, there are also colored or *fancy diamonds*. They are generated by substitution of foreign atoms to single

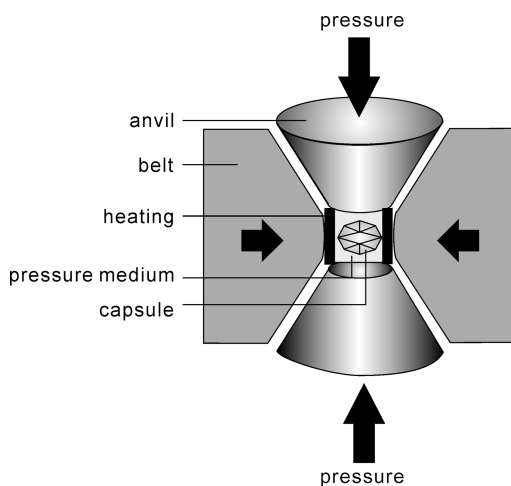


Figure 1.18 Press for the production of artificial diamond. The capsule in the heart of the press contains the carbon, a seed crystal and the catalyst.

lattice positions (Section 1.2.2). The black *carbonados* on the other hand are polycrystalline objects with inclusions of graphite, yet their natural color mostly is an unattractive brown that renders these stones only suitable to industrial purposes. Pure colors are rare, and the respective stones are very expensive.

Ways to produce artificial diamond had been sought for long. The first successful attempt in 1953 was largely ignored by the public, and to the present day it is not the Swedish scientists H. Liander and E. Lundblad of the ASEA company (Almänna Svenska Elektriska Aktiebolaget) being reputed for the diamond synthesis, but researchers from the General Electric company—even though they presented their effective procedure but in 1955. They employed the high pressure/high temperature transformation of graphite (*HPHT-synthesis*) in a hydraulic press generating several gigapascals (Figure 1.18) while the temperature was maintained at about 1500°C. The addition of a catalyst accelerates the process; molten metals from the subgroups of iron or chromium (groups VIB and VIIIA, mainly iron and nickel) are suitable. In parts, the catalytic effect presumably consists in forming unstable metal carbide intermediates. Furthermore, graphite is more soluble in the molten metal than diamond. The graphite is covered with a thin film of liquid metal in which it solves to saturation. As graphite is thermodynamically unstable under the given conditions, it changes into diamond. This now precipitates from the melt as the latter is already supersaturated regarding the less soluble product.

Today about 540 megacarat (108 t) of industry-grade diamond are synthesized per year. In terms of cost per amount, the production of artificial diamond can easily compete with the hauling of natural material and so the first clearly surpasses the latter in the annual output. Main suppliers in 2003 have been Russia (16 t), Ireland (12 t), South Africa (12 t), Japan (6.8 t), and Belarus (5 t) (according to US Geological Survey)(Table 1.2). Recently, China entered the market on a large scale as well.

Table 1.2 Annual production of natural diamond in 2003 (according to US Geological Survey).

| | Australia | Botswana | Congo | Russia | South Africa | Canada |
|---|-----------|----------|-------|--------|--------------|--------------------|
| Annual production of diamond in megacarats | 33.1 | 30.4 | 27.0 | 24 | 12.7 | 11.2 |
| of these: stones of gem quality in megacarats | 14.9 | 22.8 | 5.4 | 12 | 5.1 | n.a. ^{a)} |

a) n.a.: not available.

Industrial diamonds typically are colored gray to brown; they have numerous defects and a maximum size of 1 carat. It has been possible, however, to synthesize jewelry-grade diamonds as well. These may additionally be colored by deliberate doping. Still, for the time being, the considerable price for crystal-clear synthetic diamonds prevents a wide commercial use. The largest synthetic diamond to date, weighing 14.2 carat, was made in 1990. Synthesis starts with carbon strongly depleted of the isotope ^{13}C to distinguish artificial from natural stones.

Today there are several other ways of diamond synthesis besides the HPHT method. For example, it is possible to utilize the pressure of a shock-wave generated in an explosion. This process mostly yields powdery products with particle sizes in the range of micrometers (1 mm at max.) that may be employed for industrial purposes as well. Moreover, very small diamonds (5–20 nm) can be made by reacting explosives in confined containers. Diamond films are produced on various substrates by chemical vapor deposition (*CVD method*) using methane as a carbon source. Detonation synthesis and vapor deposition will be described in detail in Chapters 5 and 6.

1.4 Physical Properties

The variety of modifications is an outstanding characteristic of carbon. This becomes more than obvious from its phase diagram that has grown into the most complex figure considering ever new scientific results. Besides the long-known variants existent at normal pressure, there are also high-pressure phases. They are widely unexplored because their extreme conditions of existence render them almost impossible to study. Figure 1.19 exemplarily shows a simplified phase diagram.

Carbon is a typical main group element due to its properties. It is a nonmetal with the ground state electron configuration $[\text{He}]2s^22p^2$. The electronegativity of 2.55 on the Pauling scale is quite close to that of adjacent elements in the periodic table, for example, P (2.1), B (2.0), or S (2.5). The first energy of ionization is $1086.5\text{ kJ mol}^{-1}$ (refer to Table 1.3 for further values).

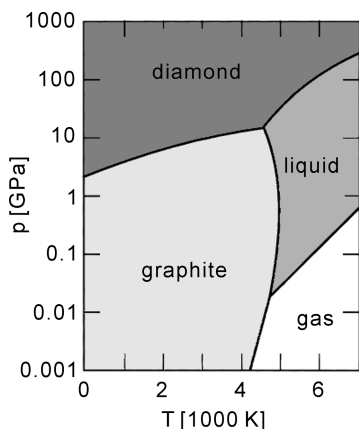


Figure 1.19 The phase diagram of carbon, not including fullerenes and carbon nanotubes (© Wiley-VCH 2000).

Table 1.3 Energies of ionization of carbon.

| Ionization energy | 1st | 2nd | 3rd | 4th |
|----------------------|--------|--------|--------|--------|
| kJ mol^{-1} | 1086.5 | 2351.9 | 4618.8 | 6221.0 |

Besides the most abundant isotope ^{12}C (98.89%) there are also the isotope ^{13}C (1.11%) and the radioactive ^{14}C (traces). The molar weight of carbon ($12.011 \text{ g mol}^{-1}$) results from this isotopic composition. ^{14}C is employed to determine the age of archeological objects (radiocarbon dating). The stable isotope ^{13}C is a valuable tool for molecular structure elucidation by NMR spectroscopy because its nuclear-spin quantum number is $I = \frac{1}{2}$.

In any further discussion of physical properties the considerable differences between modifications must be accounted for, so it is sensible not to describe the element's characteristics, but those of the respective allotropes.

1.4.1

Graphite and Related Materials

α -Graphite is the thermodynamically most stable form of carbon under normal conditions. Its standard enthalpy of formation is 0 kJ mol^{-1} , accordingly. The application of pressure and simultaneous heating convert it into diamond. β -Graphite can be obtained directly from milling α -graphite, whereas a straightforward transformation into further modifications like glassy carbon, fullerenes (Chapter 2), or nanotubes (Chapter 3) does not succeed. Table 1.4 compares some of the most important properties of graphite and diamond.

The density of graphite varies strongly depending on the material's origin and dispersity. It is 2.26 g cm^{-3} for ideal graphite, but it may be as low as 1.5 g cm^{-3} in

Table 1.4 Comparison of physical properties of graphite and diamond.

| Characteristic | Graphite | Diamond |
|---------------------------------------|--|--|
| Color | Black with metallic luster | Colorless |
| Refractive index $n_D(546\text{ nm})$ | 2.15 ; 1.81 \perp | 2.43 |
| Density | 2.266 (exp. 1.5–2.2) g cm^{-3} | 3.514 g cm^{-3} |
| Combustion enthalpy | 393.5 kJ mol^{-1} | 295.4 kJ mol^{-1} |
| Hardness (Mohs) | 1 ; 4.5 \perp | 10 |
| Band gap | 0 eV | 5.5 eV |
| Specific resistance | 0.4–0.5 $\times 10^{-4} \Omega \text{ cm}$; 0.2–1.0 $\Omega \text{ cm}$ \perp | 10 ¹⁴ –10 ¹⁶ $\Omega \text{ cm}$ |

||: parallel to graphene layer.

\perp : perpendicular to the planes (along z-axis).

poorly graphitized, powdery samples. Carbon black has a density of 1.8 g cm^{-3} that might be increased by thermal treatment—volatile hydrocarbons are expelled, and values of up to 2.1 g cm^{-3} may be achieved. The density of glassy carbon is about 1.5 g cm^{-3} .

The graphite's anisotropy regarding many characteristics is a noteworthy feature. It is caused by the layered structure and affects electrical and thermal conductivity as well as mechanical characteristics like modulus of elasticity or tensile strength. The first is $5.24 \times 10^5 \text{ N cm}^{-2}$ in parallel with the z-axis, but $18.77 \times 10^5 \text{ N cm}^{-2}$ in parallel with the xy-planes. The tensile strength perpendicular to the planes is two to five times higher than in parallel to them, and also the hardness according to Mohs is larger in the z-direction ($H_M = 4.5$) than parallel to the layers ($H_M = 1$).

In graphite possessing a more or less undisturbed lattice, the heat capacity at 25°C is $0.126 \text{ J mol}^{-1} \text{ K}^{-1}$, whereas in samples with a more defective lattice (soot, activated carbon, etc.) it is higher due to the imperfect stacking. Conduction of heat in graphite is mainly affected by lattice wave transmission along the graphene layers, which also reflects in the values of thermal conductivity. These pass a maximum of more than $4.19 \text{ W cm}^{-1} \text{ K}^{-1}$ at about room temperature. Once again the method of preparation substantially influences the exact value.

The electrical conductivity is caused by π -electrons that always belong to a specific graphene sheet and rarely ever change to another. Graphite thus is a good electric conductor in parallel to the lattice planes with a conductivity of 10^4 to $2 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ (specific resistance 5×10^{-5} to $10^{-4} \Omega \text{ cm}$). In the direction of the z-axis, on the other hand, the material behaves more like an insulator with a conductivity of 0.33 to $200 \Omega^{-1} \text{ cm}^{-1}$ (specific resistance 0.005 to $3 \Omega \text{ cm}$).

The most particular among the optical properties of graphite and related materials is the approximation to an ideal black body: microcrystalline forms of carbon have the highest absorptivity. Soot, for example, absorbs up to 99.5% of the incoming radiation. This value is much lower for other, better crystallized carbons, and very thin crystals of graphite are even transparent. The big absorptive capacity and black color of polycrystalline carbons is caused by their low particle size. Within

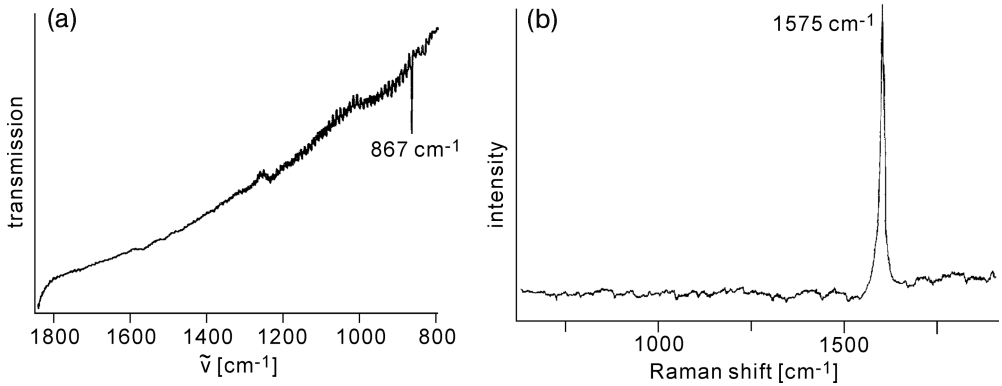


Figure 1.20 (a) IR spectrum of graphite (© APS 1985), (b) Raman spectrum of graphite (© AIP 1970).

the pores and in between particles the irradiated light is repeatedly reflected, leading to a stepwise absorption so it does not leave the surface again. The reflecting power of graphite is between 1 and 50%, depending on the wavelength. The UV spectrum exhibits a maximum at 260 nm related to the difference of energies between states of maximal density in valence and conduction bands (π -resonance). The IR and Raman spectra of graphite each show a solitary, characteristic signal (Figure 1.20) at 867 cm⁻¹ and 1575 cm⁻¹ respectively.

1.4.2

Diamond

Although the enthalpy of formation under standard conditions for diamond is 1.9 kJ mol⁻¹ higher than that for graphite, the first does not spontaneously transform into the latter, but rather represents a metastable modification under normal conditions. In contrast to graphite it is not at all anisotropic regarding any property.

The density of diamond is comparatively high, 3.514 g cm⁻³. Its hardness according to Mohs is 10, which is the highest value ever measured for a natural material. (Note that today there are several synthetic materials with a hardness higher than that of diamond; these include some of the polymeric fullerenes (Chapter 2) obtained under high pressure.) Still hardness is not equal for each crystal plane.

Furthermore, diamond exhibits the largest thermal conductivity among all naturally occurring materials. With 20 W cm⁻¹ K⁻¹, it is about five times higher than that of copper. At the same time it expands only to small extents, which reflects in a coefficient of thermal expansion of 1.06×10^{-6} K⁻¹(mK⁻¹). The specific heat capacity at 25 °C is 6.12 J mol⁻¹ K⁻¹.

Diamond without any defects is an electric insulator with a band gap of 5.5 eV. The specific conductivity of such isolating material is 8×10^{-14} Ω^{-1} cm⁻¹, whereas for semiconducting diamond of type IIb it is about 10^{-8} Ω^{-1} cm⁻¹.

The optical properties are the reason for diamond being used as a gem. Besides a high refractive index it features considerable dispersion: while the refractive index is 2.41 at a wavelength of 644 nm, it is already 2.54 at 300 nm and 2.70 in the UV at 230 nm. This gives rise to the so-called fire of the diamond—the varied refraction of different wavelengths and the associated ardent play of colors in cut stones. The good reflecting power ($R = 30\text{--}60$, depending on λ) is an additional contribution. Neat diamond is transparent both in the ultraviolet and the infrared range of the spectrum. Owing to their purity, type IIa diamonds are suited best to examine absorptive properties. The absorption edge at room temperature is situated at 230 nm and shifts toward higher wavelengths with increasing temperatures. Type I diamond shows two characteristic bands at $\lambda = 415$ nm and $\lambda = 503$ nm and the absorption edge lies at a markedly higher wavelength ($\lambda = 330$ nm) than in perfect diamond.

Samples of diamond sometimes also exhibit considerable fluorescence. Especially type I diamonds bearing impurities of nitrogen have a pronounced spectrum with two maxima already known from UV/Vis absorption. ($\lambda = 415$ nm: most likely from transitions without participation of foreign atoms or vacancies, but at defects generated from the breaking of C–C- σ -bonds; and $\lambda = 503$ nm: from transitions including foreign atoms on lattice positions.)

The Raman spectrum of diamond is very simple, with a single line at 1331 cm^{-1} resulting from the vibration of the two face-centered partial lattices moving against each other. In the infrared spectrum, on the other hand, there are several bands with in parts distinctive features of types I and II, respectively. In the range from 1500 to 5000 cm^{-1} , there are two signals for diamonds of type IIa (~ 2400 and $\sim 3600\text{ cm}^{-1}$) resulting from lattice vibrations. For type IIb, an additional band at 2800 cm^{-1} is perceptible. Nitrogen-containing diamonds of type I show yet another signal at about 1200 cm^{-1} caused by the nitrogen; this may be split into anything up to four maxima. In Chapters 5 and 6, the spectroscopic properties of diamond materials will be discussed in more detail.

1.5

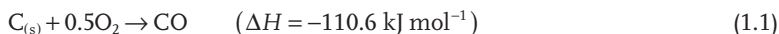
Chemical Properties

Carbon is a fairly inert element and most of its modifications may only be reacted under rather harsh conditions. Nevertheless the entire Organic Chemistry, known exclusively to deal with its compounds alone, is founded on the chemistry of carbon. This apparent contradiction is resolved by the simple compounds being hard to obtain from the elements, but any further reaction being quite easy to achieve. They succeed in impressive variety, mainly due to the manifold ways of carbon bonding with itself (chains, rings, single and multiple bonds, etc.).

Carbon's chemistry is governed by its position in the fourth main group. In contrast to the higher elements in this group it does not tend to exert only two out of its four valencies. The maximum connectivity, as present, for example, in diamond, is 4. The octet rule is strictly obeyed in covalently bound carbon, yet

there are several coordination compounds with up to eight bonding partners. On these occasions, carbon is engaged in three-center two-electron bonds (for example, $\text{Al}_2(\text{CH}_3)_2$). They are, however, only possible with more electropositive coordination partners. Due to its medium position in the periodic table, carbon reacts with oxygen as well as with hydrogen and may adopt any oxidation number from +4 to -4. Methane (CH_4) and carbon dioxide (CO_2) represent the extremes of this range.

Carbon monoxide and carbon dioxide, respectively, are obtained from reacting carbon with water or oxygen at a sufficiently high temperature. The latter determines the course of the reaction as well as the present amounts of oxygen or water vapor do. The different enthalpies of the oxidative steps may be explained by the destruction of the crystal lattice required in the reaction of solid carbon to give CO. No energy has to be applied for this process in the second step from CO to CO_2 , so more heat is released here.



Strong heating of carbon with gaseous sulfur yields carbon disulphide (CS_2) in an endothermal reaction. This may be further reacted with elemental chlorine to give carbon tetrachloride.

With metals and elements such as boron or silicon (in general, with less electronegative elements) carbon forms carbides. Consequently carbon is the electron acceptor in these compounds. There are three different types: salt-like, metallic and covalently bound carbides.

Salt-like carbides are obtained with the electropositive metals from main groups 1 to 3, and with certain lanthanides and actinides. The characteristic feature of this type is the presence of carbon anions. There are methanides (containing C^{4-}), acetylenides (C_2^{2-}) and allenides (C_3^{4-}). Methanides have been described for aluminum and beryllium; they yield methane upon hydrolysis. The acetylenides, that produce ethine when reacted with water, hold isolated $[\text{C}\equiv\text{C}]^{2-}$ -ions in their lattice. Elements from the first main group and subgroup form structures with a composition of $\text{M}_2(\text{C}_2)$, whereas it is MC_2 with those from the second main group and subgroup. With trivalent metals a stoichiometry of $\text{M}_2(\text{C}_2)_3$ is obtained ($\text{M} = \text{Al}, \text{La}, \text{Ce}, \text{Pr}, \text{Tb}$). The most important of acetylenides is calcium carbide. It is produced on a million-tons-scale to generate acetylene for welding or, by reacting it with atmospheric nitrogen, to give calcium cyanamide (CaCN_2), which is a valuable raw material for the fertilizer industry. As for the allenides, there are only Li_4C_3 and Mg_2C_3 known to date. These contain isolated $[\text{C}=\text{C}=\text{C}]^{4-}$ -ions and release propyne upon hydrolysis.

Elements from subgroups 4 to 6 form metallic carbides that feature a series of distinct metallic properties (conductivity, metallic luster). Where the atomic diameter of the metal is more than 2.7 \AA , the carbon atoms may sit in the octahedral gaps of the host lattice. If all of these sites are occupied, a compound with the composition MC ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Mo}, \text{W}$) is obtained regardless of

the metal's preferred valency. Usually they exhibit a cubic dense packing. Filling only 50% of the octahedral gaps yields carbides with a stoichiometry of M_2C ($M = V, Nb, Ta, Mo, W$), normally with a hexagonal dense packing. The different types of intercalary carbides show in parts remarkable properties: their melting points lie between 3000 and 4000 °C, chemically they are largely inert, and their hardness comes close to that of diamond. Especially tungsten carbide finds widespread application as material for heavy-duty tools. Furthermore there are metallic carbides of third period metals from the subgroups 6 to 8 whose atomic diameter is less than 2.7 Å. Their respective octahedral gaps are too small to harbor carbon atoms, and so the metal lattice is distorted on carbide formation. At the same time the carbon's coordination number increases, giving rise to a stoichiometry of M_3C (occasionally also M_3C_2, M_5C_2, M_7C_3 , etc.; $M = Cr, Mn, Fe, Co, Ni$). Herein the carbon atoms usually are trigonal-prismatically surrounded by metal atoms. *Cementite* (Fe_3C , an important structural constituent of steel) is an exponent of this class of carbides.

Elements with an electronegativity similar to that of carbon yield covalent carbides. They also feature great hardness. Most of all, silicon carbide has several applications for mechanically stressed objects (grinding and cutting tools) or as material for high-temperature transistors, light-emitting diodes, infrared radiators, etc. It is produced, for example, according to Acheson by the direct reaction of coke and quartz sand in an electric furnace. Boron as well forms several covalent carbides with stoichiometries of $B_{12}C_3, B_{13}C_2$, and $B_{24}C$, which are employed for steel borination, as neutron absorber in nuclear reactors, or for vehicle armoring.

Carbon forms a multitude of compounds with the halogens. Typical stoichiometries are CX_4, C_2X_6, C_2X_4 , and C_2X_2 . Commercially important examples for this class of compounds include carbon tetrachloride, FCCs (fluoro-chloro-carbons) and PTFE (polytetrafluoroethylene, teflon). The FCC's significance has decreased, though, because of their detrimental effect on the ozone layer and the resulting ban of their use.

With nitrogen, carbon forms a series of nitrides with a composition of $(CN)_n$ ($n = 1, 2, x$, where x can be any large number except ∞) among which the cyanogen ($n = 1$) is stable at high temperatures only. Paracyan $(CN)_x$ is obtained from dicyan by polymerization.

1.5.1

Graphite and Related Materials

Graphite may be the thermodynamically most stable modification of carbon. Still it is chemically attacked more easily than diamond due to its layered structure and the comparatively weak interaction between the graphene sheets. Altogether the graphite's reactivity toward many chemicals is rather low nevertheless. With chlorine, for example, it does not react at all under usual conditions, and even with fluorine reaction occurs only at more than $\sim 400^\circ\text{C}$. Suitable performance yields the transparent, colorless carbon monofluoride CF (up to $CF_{1.12}$ due to additional fluorine atoms at marginal positions and defects), a chemically very resistant

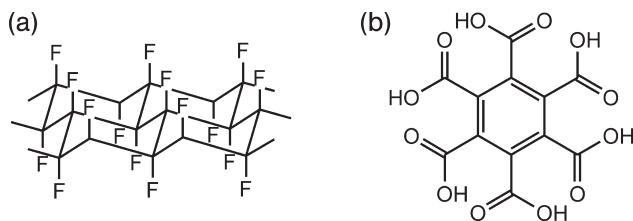


Figure 1.21 (a) Structure of the compound $(CF)_x$, resembles an undulated graphene sheet or the structure observed for *Lonsdaleite*, (b) mellitic acid.

insulator that is employed as dry lubricant. The individual layers of the graphitic lattice are conserved in $(CF)_x$ (Figure 1.21a), with the fluorine atoms alternatingly pointing upward and downward. This causes an interlayer distance of 6 \AA , compared to 3.35 \AA in graphite. On nonstoichiometrical fluorination ($CF_{0.8-0.9}$), the obtained graphite fluoride retains its electrical conductivity. Fluorination at temperatures $>700^\circ\text{C}$ converts graphite into CF_4 , whereas concentrated nitric acid turns it into mellitic acid $C_6(CO_2H)_6$ that contains planar C_{12} -units (Figure 1.21b). In the mixtures of HNO_3/H_2SO_4 , graphite reacts with potassium perchlorate to give the so-called graphitic acid, named such for the existence of weakly acidic OH-groups. This compound is obtained as greenish-yellow, lamellar crystals that explode on heating. Aqueous bases do not perceptibly attack graphite, and the reaction with hydrogen succeeds only at high temperatures, for example, in an arc, mainly to yield acetylene. Graphite is not soluble in any of the common solvents; only molten iron does solve significant amounts.

A particularity within the chemical behavior of graphite is the formation of the so-called intercalation compounds. These result from embedding atoms or molecules in between single graphene sheets (“sandwich” structure). Their weak interaction enables the formation of this kind of compounds. There is a rearrangement of charges upon intercalation so the carbon layers are polarized (or even ionized) either negatively or positively, depending on the kind of intercalate (embedded atom or molecule). The exchange of electrons between the intercalate and the graphite’s π -bands increases the number of charge carriers in the conduction or the valence band, respectively. Electron-withdrawing species cause holes in the valence band of the graphite, whereas electron donors partly fill the conduction band with electrons. Therefore graphite intercalation compounds exhibit an increased electrical conductivity.

The longest known among these compounds are the C_nK phases ($n = 8, 24, 36, 48$), with the first of them, C_8K , having been made in 1926 already. Depending on the stoichiometry, the potassium atoms are separated by one to four graphene layers (Figure 1.22) in these compounds, which are referred to as *steps*. The first of these steps deviates from the $C_{12n}K$ -rule ($n = 2, 3, 4$) that holds for higher homologs—it represents the compound with the highest possible number of potassium atoms incorporated. It is noteworthy that the distance between graphene layers increases only by 2.05 \AA , which after all is much less than could be

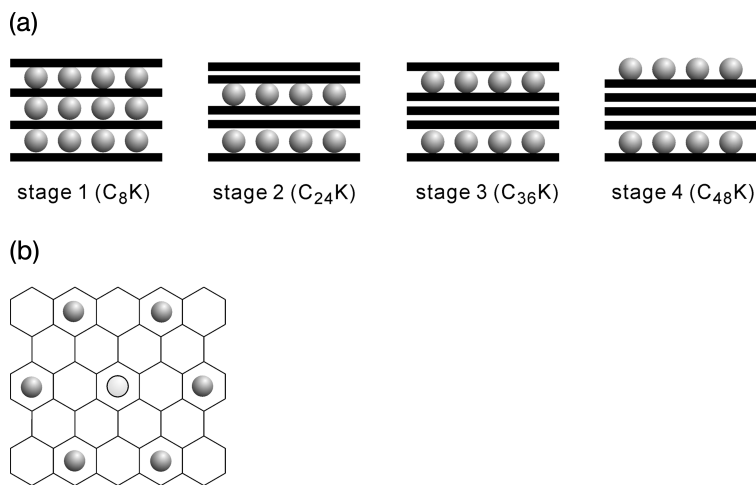


Figure 1.22 Intercalation compounds of potassium with different contents of metal are highly ordered structures. (a) Stacking of graphene layers and metal atoms (side view), (b) top view of the metal atoms arranged in

the graphene lattice. The dark circles indicate positions occupied in all cases, while the position marked by the light circle is only occupied in C_8K .

expected upon the intercalation of metal atoms measuring 3.04 \AA . This indicates an interaction of the potassium atoms with the clouds of π -electrons of the surrounding graphene sheets.

Actually, K^+ ions are formed—the released electron is transferred into the graphite's conduction band, causing the high electrical conductivity. C_8K is a versatile reducing agent in organic synthesis. Besides potassium, other alkaline or alkaline earth metals may form ionic intercalation compounds as well. Their composition is C_nM (e.g., $M = Rb, Cs, Ca$ with $n = 8, 24, 36, 48$ or $M = Li, Ca, Sr, Ba$ with $n = 6$) with the graphite being reduced. Sodium–graphite compounds, on the other hand, are hard to obtain. The golden-colored C_6Li is employed in efficient batteries.

As the valence and the conduction band exhibit similar energies, the graphite in intercalation compounds may also be oxidized when electron acceptors are embedded. The intercalation compounds with bromine or certain interhalides are important examples here: iodine and chlorine do not react with graphite, whereas with fluorine, the aforementioned carbon fluorides are obtained. In C_8Br , then, electrons from the valence band of graphite are transferred to the bromine. However, it is not present as isolated anions, but in the shape of polybromide ions. The $Br-Br$ distance of 254 pm correlates quite well with that between the centers of the hexagons in the graphite lattice (256 pm). For other polyhalogenide anions, on the other hand, the interatomic distance ($Cl-Cl$: 224 pm and $I-I$: 292 pm) is too low or too high, respectively, to perfectly fit in these voids, and consequently no interstitial compounds are formed. Iodine monochloride (expected $I-Cl$ distance: 255 pm) then again is incorporated. Halogen intercalation com-

pounds are also good electric conductors. However, the charge transport occurs via holes (defect electrons) instead of electrons, similar to the mechanism in p-doped semiconductors.

Apart from graphite halogenides, there are also intercalation compounds with sulfuric, nitric, phosphoric, perchloric, and trifluoroacetic acid. They all exhibit a considerably larger distance between their graphene layers, and the graphite donates electrons to the respective intercalate. With sulfuric acid, for example, graphite hydrogensulfate is obtained, and the reaction with nitric acid yields graphite nitrate. Also metal salts and oxides like FeCl_3 , AlCl_3 , SbF_5 , CrO_3 , CuS , etc. may be embedded between the graphene sheets. The chromium oxide compound CrO_3 -graphite is a selective oxidant to convert secondary and tertiary alcohols into the related keto-compounds (*Lalancette* reagent), whereas AlCl_3 -graphite is employed as a selective Friedel–Crafts catalyst.

1.5.2

Diamond

Diamond is extremely hard to subject to a chemical reaction. Due to its perfect crystal structure, it is only attacked at very high temperatures. It is true that diamond powder is inflammable, yet bigger lumps are only ignited in an oxygen blower at more than 800°C . The oxidation rate depends on the size and surface characteristics of the single particles; the temperature of combustion varies between 750 and 880°C . In a stream of oxygen at 900 to 1200°C , diamond reacts completely to carbon dioxide, whereas graphite yields a CO/CO_2 mixture.

No reaction takes place with acids or bases, appreciable attack only occurs with chromosulfuric acid, producing carbon dioxide. With fluorine at more than 700°C , diamond reacts to give carbon fluorides or to be surface-fluorinated. The hydrogenation of the diamond's surface succeeds in a stream of hydrogen at high temperatures, yet the entire sample is not converted. The action of iron at more than 1150°C yields an alloy. With nitrogen, no appreciable reaction is observed even at high temperatures, and with water vapor at about 1000°C , diamond weakly reacts forming carbon monoxide. Highly oxidating melts of KClO_3 or KNO_3 do not attack diamond (with the exception of black, polycrystalline material). Altogether, little is known about “diamond chemistry” in the true sense of the meaning, because this modification of carbon largely resists any chemical transformation.

1.6

Application and Perspectives

The main part of the carbon employed is consumed for fueling and in the steel industry. The combustion of fossil raw materials alone absorbs the largest fraction of the hauled carbon, but besides that there is a multitude of applications of its different modifications.

1.6.1

Graphite and Related Materials

The applications of graphite are as manifold as the existing variants of graphitic materials. Large amounts (natural or artificial) are used for electrodes in arc furnaces to run different electrolytic processes like production of certain metals or alloys (sodium, aluminum, steel, etc.), and chlorine or carborundum are likewise obtained by electrolysis on graphitic electrodes. Graphite further is needed for carbon brushes in electric engines. In addition, graphitic substances are employed in arc lamps, as materials for molds or to line ovens and apparatus. In chemical facilities, graphite rendered gas-tight by impregnation with plastics is utilized, and in nuclear reactors, rods of graphite are used as moderators due to their large neutron-capture crosssection. Provided the distinctly anisotropic thermal conductivity at highly parallel orientation of the crystal lattices, the respective material may be used in making heat shields for spacecrafts, brake blocks or the like. Graphite is also employed as a dry lubricant due to its low hardness. In particular for chemically aggressive environments, it usually is a better choice than, for example, hydrocarbon-based agents. The leads of modern pencils contain graphite as well, and finally, it is used as carrier for certain stationary phases in reversed-phase high performance liquid chromatography (RP-HPLC).

1.6.2

Diamond

While its brilliance and fervent iridescence make it one of the most coveted gems, diamond is also most profitably applied to a number of far less decorative purposes. This is due to its great hardness, chemical and mechanical resistance, large thermal conductivity, and good electrically insulating properties. A considerable part of the natural and artificial diamond produced is employed for grinding, cutting or drilling instruments. Their use pays off even at their high price because there are less down-times due to failure or change of tools. Furthermore so-called wire drawing stones are made by drilling a hole through diamond with the desired diameter. They are used to draw wires from hard metals. In apparatus construction, bearings for fast-rotating axles can be made from diamond. Finally, diamond windows are employed for special spectroscopic applications as they are transparent over a wide spectral range, in particular for the UV where many of the materials commonly used for spectroscopic windows let pass only little or no light at all.

1.6.3

Other Carbon Materials

Apart from being a popular filler for elastomeric materials, soot is an excellent black pigment. Several properties make it downright ideal for printing purposes: it is light-fast and insoluble in almost any common solvent as well as it exhibits low particle size and great color depth and strength. Yet more than 90% of the

carbon black produced is used as a filler—about two-third of it for tires, and the rest for other things made from rubber. An average tire for cars contains about one-third of soot that serves not only to increase the wear- and tear-resistance of the rubber (caoutchouk), but also to blacken it. Other plastics, lacquers and inks for writing or printing are likewise colored by the addition of carbon black.

Owing to their chemical, thermal, and mechanical resistance, carbon fibers are an ideal material for highly durable composites. Compared to steel, they are four times lighter at similar strength, which in addition is preserved up to temperatures of more than 2000 °C. Certain threads, ribbons, and fabrics are made from pure carbon fibers, as well as there are carbon-reinforced plastics which are employed to manufacture, for example, components of aircrafts or cars, sporting devices, implants, or filters for dusts and aerosols.

Activated carbon is a versatile adsorbent, for example, to decolorize sugar or to free spirit from fusel oil. Gases may be purified and toxic substances may be removed from breathing air (application in gas masks) same as flue gases are desulfurized using activated carbon.

Glassy carbon is chemically very inert even at elevated temperatures because there is virtually no porosity at all and its structure does not allow for intercalation. It is only attacked by oxygen and oxidizing melts at more than 600 °C. Accordingly, it is employed in ultratrace analysis (no memory effects in crucibles of glassy carbon) and in the semiconductor industry.

1.7

Summary

Under standard conditions, there are several modifications of carbon which may be all traced back to the basic graphite and diamond.

Box 1.1 Graphite.

- Most stable form of carbon under standard conditions ($\Delta H_0 = 0 \text{ kJ mol}^{-1}$).
- Two modifications: hexagonal α -graphite and rhombohedral β -graphite.
- The carbon atoms are sp^2 -hybridized, σ -bonds with three adjacent atoms within one layer (bond angle 120°). Additional delocalized π -bonds within these layers. Only weak van der Waals interaction between the graphene sheets.
- Considerable anisotropy of properties like electrical conductivity, modulus of elasticity, etc due to the layered structure.
- Despite chemical inertness several compounds are known, above all intercalation compounds with alkali metals or halogens.

Besides crystalline graphite, there are a number of related materials that are less crystallized and usually exhibit a finer particular subdivision. Their properties differ (in parts considerably) from those of the parent system, which is mainly due to the smaller particle size and the disordered lattice.

Box 1.2 Diamond.

- Metastable modification of carbon. Appears as cubic or as hexagonal diamond (*Lonsdaleite*).
- Each C-atom is tetrahedrally connected to four adjacent atoms by σ -bonds. The C-atoms are sp^3 -hybridized.
- Greatest hardness and highest thermal conductivity among all natural materials. Electrical insulator, yet semiconductance achievable by doping.
- Chemically extremely inert, is only attacked by aggressive reagents like chromosulfuric acid.

Proceeding from the facts presented in this chapter, we will now discuss the “new” carbon materials, starting with the fullerenes. These have first been discovered in 1985, many years after their theoretical prediction.