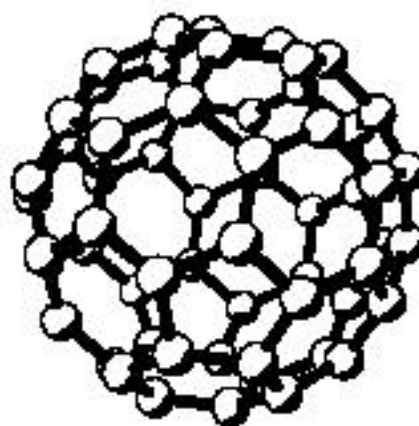New Traditions Curriculum Project
Topic Oriented Approach
Development

Buckyballs, Diamond and Graphite

Chemistry taught through real world topics.

Authors: Clark Landis, Tom Cleveland, Mary Cloninger, David Pollock

The most current version of these materials can be seen on the WWW at
http://fozzie.chem.wisc.edu/curriculum_development/CurrRef/TOAHome/TOAHome.html

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Buckyballs, Diamond, and Graphite

1.0 Introduction

1.1 Why are old materials catching current attention?

The cutting edge of new materials technology is represented by surprisingly mundane and old forms of matter. Consider diamond (the gem) and graphite (the main component of pencil leads). Although both have been known for many years, recent newspaper and magazine headlines (see Figure 1.1) demonstrate tremendous current interest in these materials. For example, diamond was named "molecule of the year" by Science magazine in 1990. Also, a material closely related to graphite, carbon fiber, recently has entered our everyday lives in the form of reinforcing material in bicycle frames, tennis racquets, and even the B-2 Stealth bomber.

Figure 1.1 Headlines from magazines and newspapers

Buckyball' Molecule May Block AIDS Step

Buckyballs Give Researchers Big Bounce

Tossing Plastic Into an Oven,
Scientists Cook Up Diamond

By MALCOLM W. BROWNE

Diamond: Glittering Prize for
Materials Science

Buckyball' Molecule May Block AIDS Step
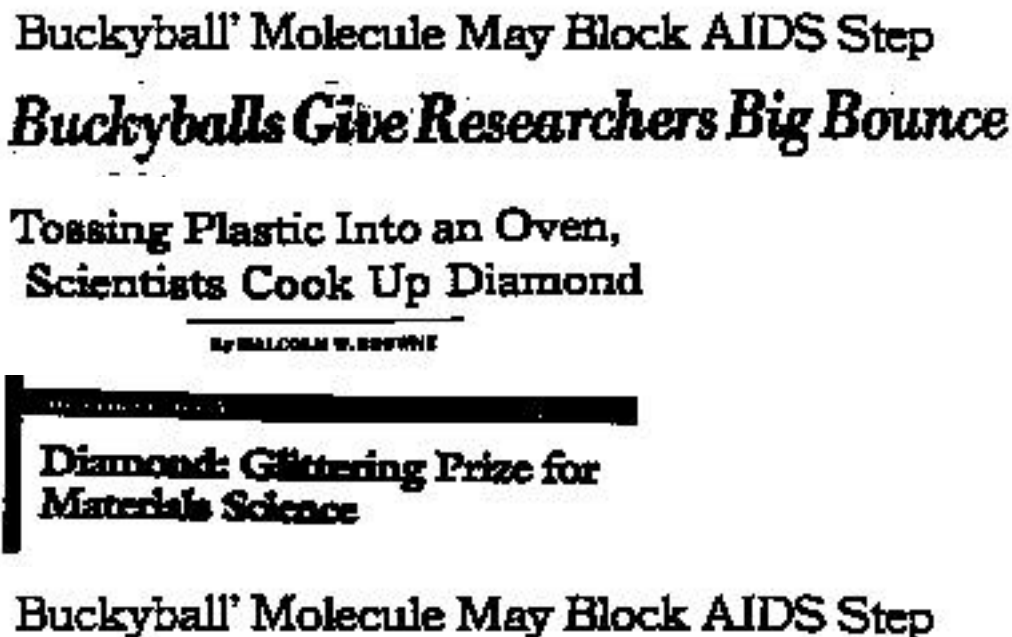
Since 1985, a new compound called buckyball has received much publicity in both the scientific and popular press. Buckyball, which has the full name buckminsterfullerene in honor of the architect of the geodesic dome, Buckminster Fuller, was added to the group of fascinating materials that included diamond and carbon fiber. Following the footsteps of diamond, buckminsterfullerene was named "molecule of the year" by Science magazine in 1991.

1.2 What's the connection?

The properties of these new materials are so different that it seems illogical to group them together. Diamond is the hardest known substance (however, this designation is under challenge by yet another new material, carbon nitride). In contrast, graphite is flaky and so

slippery that it is often used as a lubricant. Pure diamonds are clear and colorless (some diamonds are colored, but this is due to impurities). Graphite, on the other hand, is a black, lustrous solid that is completely opaque. Buckyball, too, is deeply colored, so much so that the solid looks black. However, solid buckyball dissolves readily in organic solvents such as gasoline whereas diamond and graphite do not dissolve in common solvents. In solution buckyball's deep red color is revealed. Although practical uses for buckyball have not yet been discovered, researchers believe that it may find applications in medicine, new types of polymers, and other areas. Figure 1.2 shows real diamond, graphite, and buckyball samples.

Figure 1.2 Samples of Buckyball, diamond and graphite

Why do chemists group together materials with such different properties? What's the connection? Carbon! Despite their widely varying appearances, diamond, buckyball, and graphite are closely related because each is a form of carbon. In the language of chemistry, carbon is an element. Formally, this means it is a substance that cannot be decomposed into simpler substances by ordinary chemical or physical means. Another useful definition of an element is to say that all of the atoms of an element are the same (soon we will discover that atoms of the same element do have variants called isotopes). The chemistry viewpoint emphasizes the role of the atom as the building block of matter, even though it recognizes that atoms themselves are made of smaller particles.

Is this confusing? Consider an analogy with language. A word in a sentence is comparable to an atom. Each word contributes charactersic meaning, meter, and sound to the sentence. However, a word can be isolated from a sentence, yet retain its characteristics. Analogously, a carbon atom can be removed from a substance and isolated, but still retains recognizable characteristics. A word can be further broken down into letters, but this action causes the characteristic meaning, meter, and sound to be lost. Similarly, an atom can be broken into its component subatomic particles but its unique character is lost in the process. At the risk of over-extending our analogy, we can say that an element in language would be a sentence in which all of the words were the same. The atoms for diamond, buckyball, and graphite are all the same (they are all carbon), but the way these building blocks are assembled is not the same. Different forms of matter made of a single type of atom are called allotropes. Diamonds, buckyballs, and graphite are allotropes of carbon. It is the difference in the assembly of carbon atoms that gives the three different compounds such different properties.

1.3 Atoms--What are they?

If an element could be cut up into tiny pieces, then the atom is the smallest piece that would still have the essential properties of that element. Regardless of whether you started with a diamond, a buckyball, or graphite, when you finished cutting you would have carbon atoms only. Chemists organize all the different elements using the periodic table (Figure 1.3). The periodic table gives many different levels of information about the elements. The columns on the periodic table organize elements according to similar properties. Thus, because bromine (Br) and chlorine (Cl) are in the same column, it is easy to remember that they have many properties in common. Each box on the periodic table contains a wealth of information about the element it is describing. The symbol in the center of the box ("C" for carbon) is the accepted symbol for the element. The integer found above the symbol describes the number of a particular subatomic particle contained within each atom of that element.

Figure 1.3 A periodic table

An atom, even though it is the smallest piece that makes up every element, is made up of even smaller (i.e., subatomic) particles. Think of an atom as a large indoor football stadium. In the middle of the stadium, there is a small but very heavy marble. This marble is the nucleus of the atom and contains protons and neutrons. Protons have a positive charge while neutrons are electrically neutral, but protons and neutrons have almost exactly the same mass. In fact, protons and neutrons each weigh one atomic mass unit(amu). These particles are very light; an atomic mass unit equals just 1.66×10^{-24} grams. This number is written in scientific notation and is equivalent to

$$\frac{1.66}{1,000,000,000,000,000,000,000,000}$$ grams. The rest of the stadium is where an atom's electrons are found. Each electron has a mass equal to only about $1/2000^{th}$ the mass of a proton or neutron, but the electron has a negative charge equal in magnitude to the positive charge of the proton (Table 1.1).

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Table 1.1 Subatomic particles

	relative charge	relative mass
proton	**+1**	**1**
neutron	**0**	**1**
electron	**-1**	**1/1838**

1.4 What makes a carbon atom uniquely carbon?

But what makes the carbon atom different from all other atoms? The number of protons in the nucleus. In the box on the periodic table, the number above the element's symbol is the number of protons in an atom of that element. Each element has a unique number of protons, or atomic number. For carbon, this number is 6, so there are 6 protons in one atom of carbon. Most carbon atoms have 6 neutrons as well. In order to neutralize the charge of the 6 protons there must be 6 electrons. Therefore, the most common carbon atom has 6 protons, 6 neutrons, and 6 electrons. However, variants of carbon atoms exist. These are called isotopes. Different isotopes of the carbon atom have different numbers of neutrons. Three different isotopes of the carbon atom are found commonly (Table 2). Carbon-12 is the most abundant isotope and is represented as ^{12}C (12 is the sum of the protons and neutrons); the mass of one atom of ^{12}C is approximately 12 amu. Carbon-13 (or ^{13}C) has 7 neutrons and 6 protons; approximately 1.1% of all carbon atoms are made of this isotope which has an approximate mass of 13 amu. Carbon-14 (^{14}C) has 8 neutrons and 6 protons, hence, a mass of around 14 amu; less than of all carbon atoms found on earth are the radioactive ^{14}C isotope.

Table 2. Carbon Isotopes

isotope	abundance	protons	neutrons	mass (a.m.u.)
^{12}C	98.9%	6	6	12
^{13}C	1.1%	6	7	13
^{14}C	0.0000000001%	6	8	14

The number below the element's symbol is the average mass of the atom; this number is called the atomic mass. Notice that this number is an average. Because there are three different isotopes of carbon, not all carbon atoms have the same mass. A similar situation exists for many coins. Dimes that were minted in 1940 do not have the same mass as today's dime. We cannot give a single, definitive mass for either atoms or for coins because each has a distribution of defined masses. However, we can talk about average masses. About 98.9% of all carbon atoms are ^{12}C atoms with a mass of about 12 amu. The remaining 1.1% of carbon atoms are essentially all ^{13}C isotopes. If you were to randomly pick out 1000 atoms from a pile of carbon, on average 989 of the atoms would be of the ^{12}C isotope and 11 would be of the ^{12}C isotope. You can guess that the mass of the average carbon atom will be very close to 12 amu but let's calculate the result more exactly.

$$\text{Atomic Mass} = \frac{\left(989 \ ^{12}\text{C atoms} \ \times \ 12 \ \text{amu per} \ ^{12}\text{C atom}\right) + \left(11 \ ^{13}\text{C atoms} \ \times \ 13 \ \text{amu per} \ ^{13}\text{C atom}\right)}{1000 \ \text{C atoms}}$$

$$= \frac{11868 \ \text{amu} \ + \ 143 \ \text{amu}}{1000 \ \text{C atoms}}$$

$$= 12.01 \ \text{amu per C atom}$$

Many elements have one dominant isotope, like carbon. Because electrons weigh so little compared to protons and neutrons, for these elements the number of neutrons can be estimated from the atomic mass. Thus for carbon, 12.01 - 6 = 6.01, and we estimate the number of neutrons to be 6.

To make a neutral carbon atom, 6 electrons must be present to neutralize the 6 protons in the nucleus. The way in which the electrons are arranged in an atom is called the electronic structure of the atom. Figure 1.4 depicts the electronic structure of a carbon atom. Notice that the electrons are arranged in shells around the nucleus. The shells correspond to rows of the periodic table. For example, H and He (hydrogen and helium) have electrons only in the first shell. Carbon, in the second row in the periodic table, has 2 shells of electrons around its nucleus. The first shell contains 2 electrons and the second shell, or valence shell, contains 4 electrons. The valence shell is the outermost occupied shell of an atom. Let's focus now on the number of electrons in each valence shell. Carbon has 4 valence electrons in its valence shell as does Silicon (Si). Elements in the same column of the periodic table not only have similar properties, they have the same number of valence electrons (with the exception of H and He). Note that the valence shell of He is filled. Atoms with filled valence shells are particularly reluctant to undergo chemical reactions. Other examples of filled valence shells occur for Ne and Ar. The elements in the last column of the periodic table frequently are called the inert or noble gases due to their low chemical reactivity.

Lewis dot representations of the atoms of the first three periods are shown in Figure 1.5. A Lewis dot structure depicts the valence electrons. The first four dots are arranged singly on the four sides of the elemental symbol; if there are more than four electrons the remaining dots are arranged pairwise with those that are already present. We will see later that a simple examination of the Lewis dot structure reveals much about the ways in which an element arranges itself with other atoms.

Figure 1.4 Shell structures of H, He, C, Ne, and Si
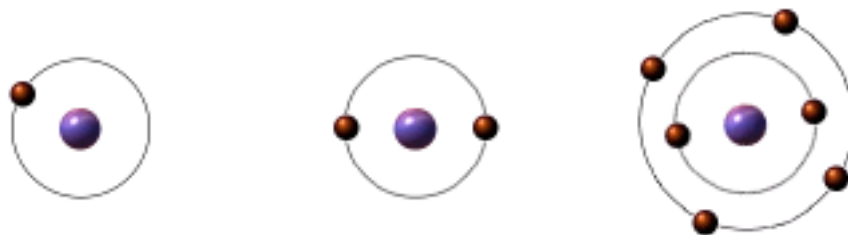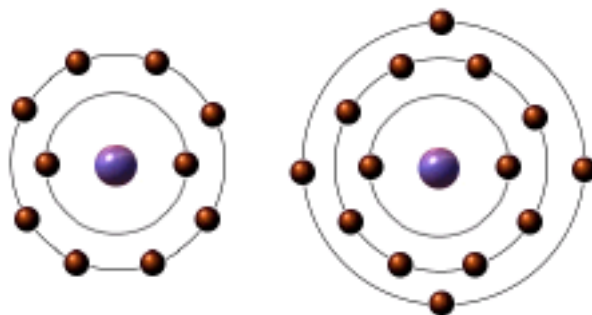
Figure 1.5 Lewis dot structures of first three periods
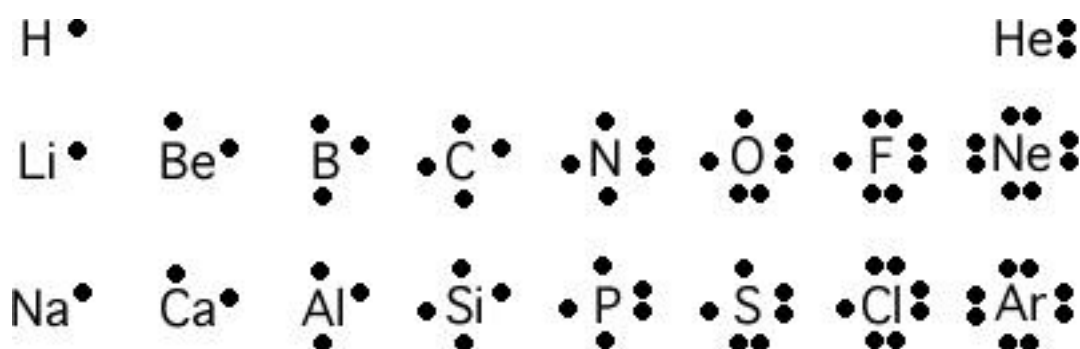
1.5 So how are the carbon building blocks assembled?

Recall the samples of carbon in various forms shown in Figure 1.3. Now examine Figure 1.6. In this figure, buckyball, diamond, and graphite are all shown using a frequently used representation called the ball-and-bond model. In these models each "ball" represents a Carbon atom. Each stick represents a chemical bond, i.e., a strong force that holds two atoms close in space. Before we delve into the details of what is meant by a chemical bond, let's see what we can understand about differences between diamond, graphite and buckyball based only on the ways in which the atoms are arranged.

Figure 1.6. Buckyballs, diamond, and graphite in a ball-and-bond representation.
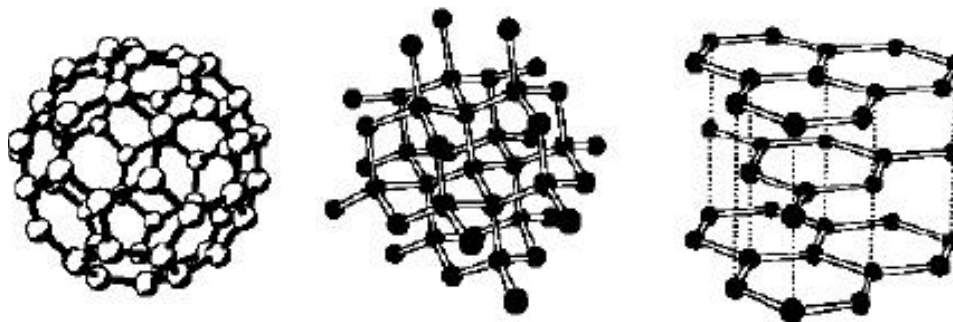
Understanding how carbon is oriented in each of the three types of material allows for a better understanding of why these compounds have different properties. Notice that graphite, for example, has large sheets of hexagonal rings. The sheets do interact, but they are so far apart that the interactions are weak and broken easily. Because the layers of carbon rings can rub over each other, graphite is a good lubricant. Diamond, however, has each carbon bonded to four other carbons in a tetrahedral arrangement. Diamond can be cleaved along its planes, but it cannot flake apart into layers because of this tetrahedral arrangement of carbons. Buckyball has a structure very different from the structure of either diamond or graphite. Buckyball is shaped like a soccer ball, and a soccer ball is another symbol that is often used to represent a buckyball.

Perhaps the biggest difference in the structure of buckyball compared to diamond and graphite is that every buckyball has an exact number of carbon atoms (60) but diamond and graphite do not. Buckyball is a discrete structure or a molecule; diamond and graphite are extended lattices. Just as the soccer ball is an object used to represent buckyball, C_{60} symbolically represents buckyball. Because diamond and graphite are not composed of a discrete number of atoms (they are not molecules, the number of atoms in a piece of diamond depend on the size of the piece), their symbols are $C_{diamond}$ and $C_{graphite}$.

1.6 More on bonding

The carbon atoms in buckyball, diamond, and graphite are held together by bonds. As we have seen it is the arrangement of atoms and bonds that differentiate these forms of elemental carbon. Every carbon atom in these materials has four bonds or connections between itself and neighboring atoms. However the connections between pairs of carbon atoms are not all identical. Whereas diamond only has single bonds (represented by one stick) between atoms, both buckyball and graphite have two bonds (represented by two sticks) to one neighboring carbon and two single bonds to two other neighboring carbons. The two bonds that span a pair of carbon atoms commonly is called a double bond. Refer to Figure 1.6, where the picture of both buckyball and graphite shows the network of single and double bonds that are present in these compounds. Note how each carbon atom atom has two single bonds and one double bond.

Why are all the bonds in diamond represented as single bonds whereas graphite and buckyball have mixtures of single and double bonds? Although you will later learn theoretical models for rationalizing these bonding patterns, ultimately the answer derives from experiment. The lengths of the carbon-carbon bonds in diamond, graphite, and buckyball have been measured by a technique called x-ray diffraction. In diamond the bond lengths are 1.54 Å (1.54 x 10-10 m, the Å unit represents 1 x 10-10m). Although these absolute distances between adjacent carbon atoms are very small, just [Image] meters long, the distances in buckyball and graphite are even shorter. Bond distances in buckyballs and graphite are about 1.4 Å. We can rationalize the shorter bond lengths as arising from greater forces of attraction between atoms sharing bonds. Thus we expect that double bonds should be stronger and shorter than single bonds. In other words the shorter bonds observed in buckyballs and graphite relative to diamond are consistent with the presence of more than a single bond between the carbon atoms.

The number of bonds formed by atoms of various elements is correlated with the position of the atoms in the periodic table. For example, we have seen that carbon atoms generally make four bonds. Similarly, the elements in the same column of the periodic table as carbon (Si, Ge, Sn, Pb) all are observed to make stable forms of matter in which each atom has a total of four bonds to other atoms. This column of periodic table is called Group 14.

As one proceeds to the right of carbon on the periodic table, the number of bonds commonly formed by the element decreases by one for each column moved. Thus the elements in the nitrogen column (or Group 15) form three bonds, elements in the same column as oxygen (Group 16) form two bonds, and the elements from the same column as fluorine (Group 17) usually form one bond. Neon and the other elements in the last row of the periodic table (helium, argon, krypton, xenon, and radon, Group 18) resist the formation of bonds unless special conditions are used. Hydrogen is a special case. Hydrogen tends to form just one bond. This feature makes it similar to Group 17 elements. However, many of the other properties of hydrogen are not like those of fluorine, chlorine, and bromine so that H usually is not placed in the column adjacent to He. Figure 1.7 shows several examples of molecules that illustrate these bonding patterns.

Figure 1.7 Simple molecules and bonding patterns
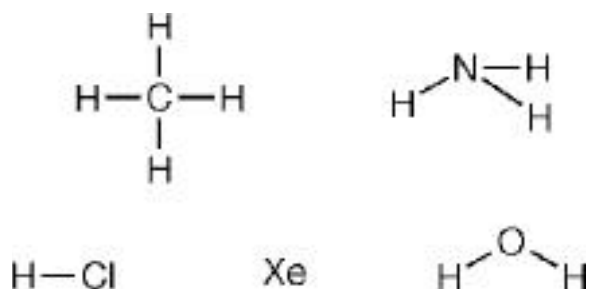
How can we make sense of these bonding patterns? Early in this century, Gilbert N. Lewis at the University of California, Berkeley proposed that atoms form bonds such that each atom in the molecule experiences a complete valence shell. For example, the formation of methane (CH_4) involves four bonds between carbon and hydrogen. Each of these bonds involves sharing a pair of electrons between C and H. The Lewis dot structure of CH_4 is shown in Figure 1.8.

Figure 1.8 Lewis Dot Structures of CH_4, C_2H_4, and C_2H_2.
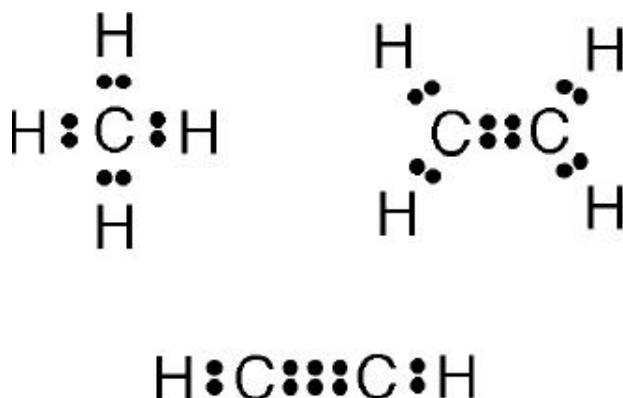
The driving force behind the sharing of electrons between atoms is that it enables negatively charged electrons to feel the positive charges of two nuclei rather than one. Although sharing of electrons also creates repulsions between the electrons that are shared, overall the formation of bonds is usually favorable. As suggested by the Lewis dot structure, each H

of CH_4 now senses two electrons (one electron originated from H and one from C), or a filled valence shell. Similarly, the C sees a total of eight electrons (four from H and four from C) which is a filled shell for C. A very useful rule is that atoms form bonds so as to complete the valence shell of all of the atoms involved. For most elements this rule means that each atom should have eight electrons in the valence shell (H and many of transition metals such as iron (Fe), cobalt (Co), nickel (Ni) are the exceptions). Therefore, this rule is frequently called the octet rule.

For the molecule ethylene (C_2H_4) one can make four C-H bonds, two per C atom. However, this does not fulfill the bonding requirements of the carbon atoms. Only formation of two C-C bonds, which is called a double bond, allows the octet rule to be satisfied for carbon. In forming a double bond, four electrons are shared between the two carbons. A triple bond is observed in C_2H_2, with a total of six electrons shared between the two carbons. Add to this the two electrons in each of the two C-H single bonds and one arrives at an octet for each carbon atom.

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Buckyball, Diamond, and Graphite

2.0 Buckminsterfullerene

2.1 How was buckyball discovered?

As with many important scientific discoveries, buckyball was discovered by accident. In 1985, the American chemist R. E. Smalley at Rice University, the British chemist H. F. Kroto at Sussex, and graduate students working under their direction were studying the nature of interstellar matter. They wanted to know what forms of carbon-containing materials can be found between the stars. The overall strategy of the research was to compare spectroscopic readings from unidentified matter in interstellar space with those obtained from well-characterized materials in the laboratory. If a match is found, then one can infer the nature of the interstellar matter. This strategy reveals a fundamental principle of the rules describing matter: they apply equally throughout the universe. The intrinsic properties (such as color, mass, etc.) exhibited by diamond or graphite or buckyball in space are identical to those on earth.

When buckyball was discovered, Kroto and his coworkers already knew that long chains of carbons were present in space. This knowledge was based on the readings obtained from a radio telescope. Every molecule exhibits a characteristic reading on this telescope that is like a fingerprint. This fingerprint can be compared to the fingerprint given by known molecules on earth, hence, the molecules in interstellar space are characterized. The nature of spectroscopic analyses used to characterize interstellar matter is a topic that is too involved for further discussion at this point. Instead, we turn our attention to the methods used to discover buckyball.

Smalley's apparatus (Figure 2.1) was designed to generate long chain carbon molecules so that their spectroscopic fingerprints could be measured. In the Smalley apparatus a laser is aimed at a rotating graphite disk in a helium-filled vacuum chamber. This apparatus uses the ability of lasers to deliver short, high energy bursts of energy in the form of light. The rapid, intense heating of the graphite surface by the laser enables many of the C-C bonds in the graphite to rupture. As a result, carbon atoms and small clusters of carbon atoms sputter from the graphite surface. Thus, the energy of the light produced in the laser is used to break the bonds between atoms in graphite, a process that involves the conversion of light energy to chemical energy. The high energy C atoms and small clusters of carbon atoms cool and collide in the He atmosphere yielding new bonding arrangements of C atoms. These new materials can be characterized by different instruments. The two instruments that played a key role in the discovery of buckyball are mass spectrometers and nuclear magnetic resonance spectrometers.

Figure 2.1 Smalley's apparatus for generating and detecting buckyball.
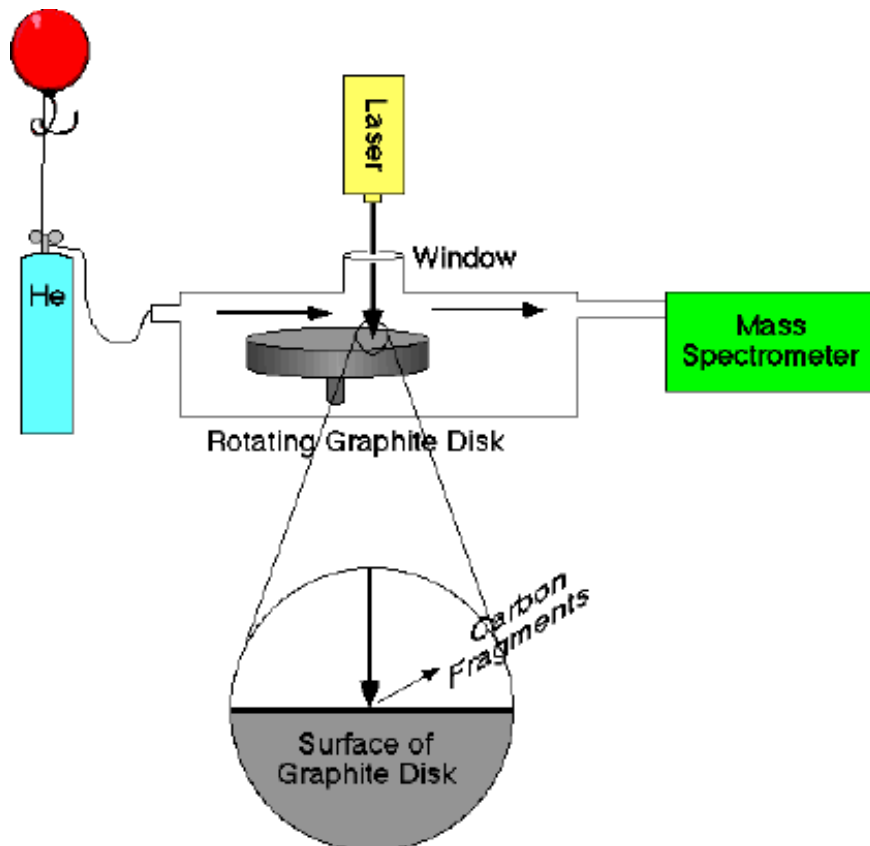
2.2 How does mass spectrometry work?

A mass spectrometer measures the mass of molecules and atoms. First a source of atoms or molecules is volatilized, or converted into a gas. In the Smalley apparatus, carbon atoms and clusters of carbon atoms are volatilized by the rapid heating of the rotating graphite block by the laser. The flow of He gas carries the volatilized matter into the mass spectrometer. At the entrance to the mass spectrometer, the atoms and clusters of carbon are ionized by bombardment with high energy electrons. Consider what might happen to a carbon atom that enters the mass spectrometer. Prior to ionization the carbon atom will have 6 protons in the nucleus and 6 electrons that occupy most of the volume of the atom. Thus the carbon atom is neutral (no charge). Upon collision with a high energy electron the carbon atom expels one of its electrons, leaving a carbon atom with 6 protons and just 5 electrons. The resulting ion has a net +1 charge. Ions with a net positive charge are called cations.

Mass spectrometers separate ions according to their mass-to-charge ratio. Because most of the ions have a charge of +1, we can consider the mass spectrometer to separate ions with different masses. A schematic of a mass spectrometer is shown in Figure 2.2. A simple way to understand how a mass spectrometer works is by analogy to a car on racecar track. The ion is analogous to the cars. First the ions are accelerated to high speed by electrical plates; the positively charged cations are attracted to the negative charge of the plates. Heavy ions will move more slowly than light ions just as heavy cars will move slower than light cars when they are pushed by the same amount of force. One might expect that the

ions would simply crash into the plates. However, the plates have many large holes in them so that many of the ions are accelerated and then pass through the holes. Next, the ions enter a region in which a magnetic field is present. The trajectory of ions moving through a magnetic field is bent. This is analogous to a set of racecars entering a banked curve. As the racecars travel around a curve at high speed, the cars that are too slow (heavy) will slide down the bank toward the inside wall, and the cars that are too fast(light) will hit the outside wall. The racecars with just the right mass will continue along the track without crashing into either wall. Similarly, ions moving at high speeds through the mass spectrometer will travel along different trajectories from which their masses can be determined. The detector of the mass spectrometer measures how many ions travel through the curved trajectory without colliding into the walls of the instrument.

Figure 2.2 Schematic of a mass spectrometer
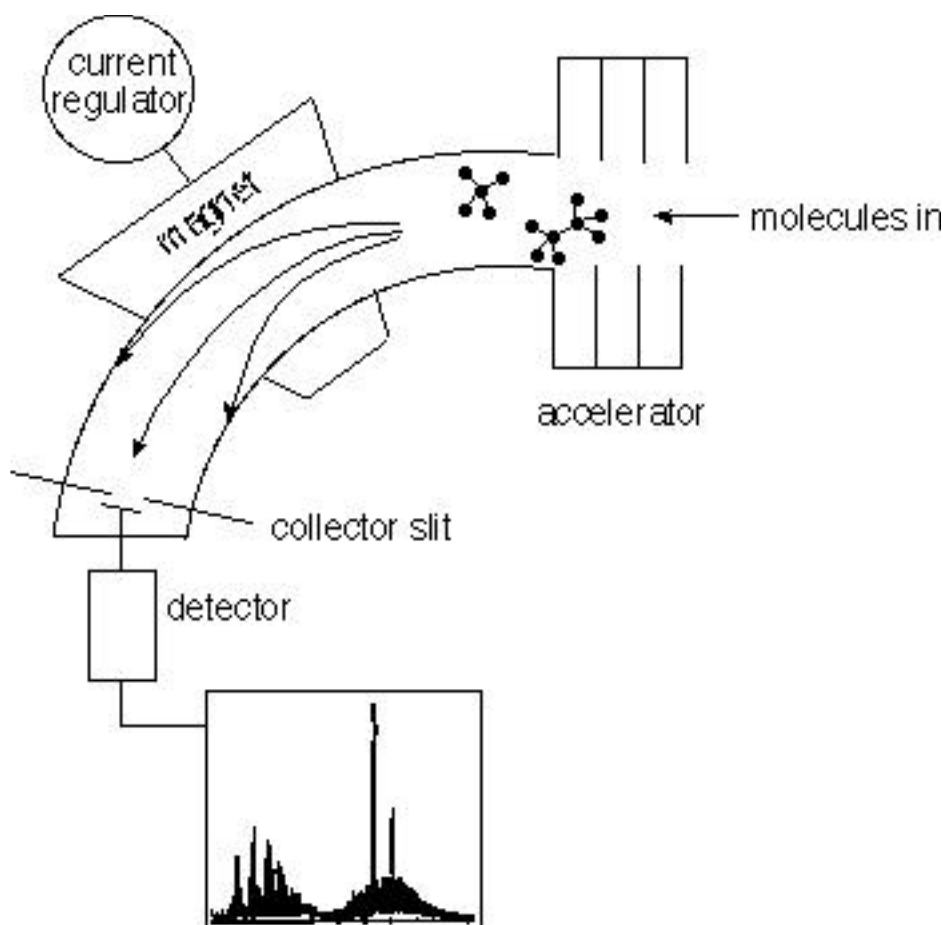
Consider what the mass spectrometer would measure if 1000 atoms of C in a graphite sample were subjected to such a high energy pulse of laser light that all of the bonds were broken. The matter moving toward the spectrometer entrance would consist of 1000 separated C atoms. Although each atom would be a carbon atom, not all atoms would have the same mass. On average 11 of the atoms would have mass 13 amu (due the 1.1% abundance of the ^{13}C isotope) and 989 would have mass 12 amu (due to the 98.9% abundance of ^{12}C. These atoms would be ionized at the entrance of the mass spectrometer to yield carbon cations, written as C+. If we set the strength of the magnetic field first so that masses of 12 amu were measured (or kept on track) and then switched the magnetic

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field such that masses of 13 amu were detected, the resulting mass spectrum would exhibit two peaks (Figure 2.3). The peak corresponding to 12 amu would be larger than the peak at 13 amu by approximately $\dfrac{989}{11} \equiv \dfrac{99}{1}$ times. In fact the peak at 13 amu would be so small that it would be easy to miss.

Figure 2.3 Mass spectrum of carbon atoms
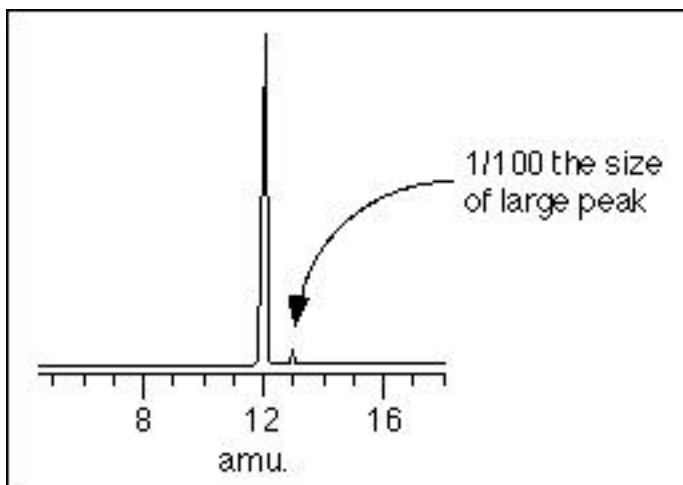
Smalley, Kroto, and coworkers found surprising results when the intensity of the laser was decreased. At high laser energies they observed large peaks at many different masses, suggesting that high energy atoms and clusters of carbon were volatilized from the graphite surface (Figure 2.4). However, decreasing the laser power led to the predominance of a single peak in the mass spectrum with a mass of 720 amu. Because the starting material, graphite, has only carbon atoms the matter with mass of 720 amu must consist of carbon, only. Chemical reaction cannot change the nature of the individual atom; only their arrangements are changed. Because most carbon atoms are 12C isotopes, this matter must correspond to $\dfrac{720}{12} = 60$ carbon atoms that are bonded together. Apparently, the formation of molecules with exactly 60 carbon atoms must be very favorable.

Figure 2.4 Smalley mass spectra at high(a) and low(b) laser power

a)

b)

Number of atoms of mass 12.00
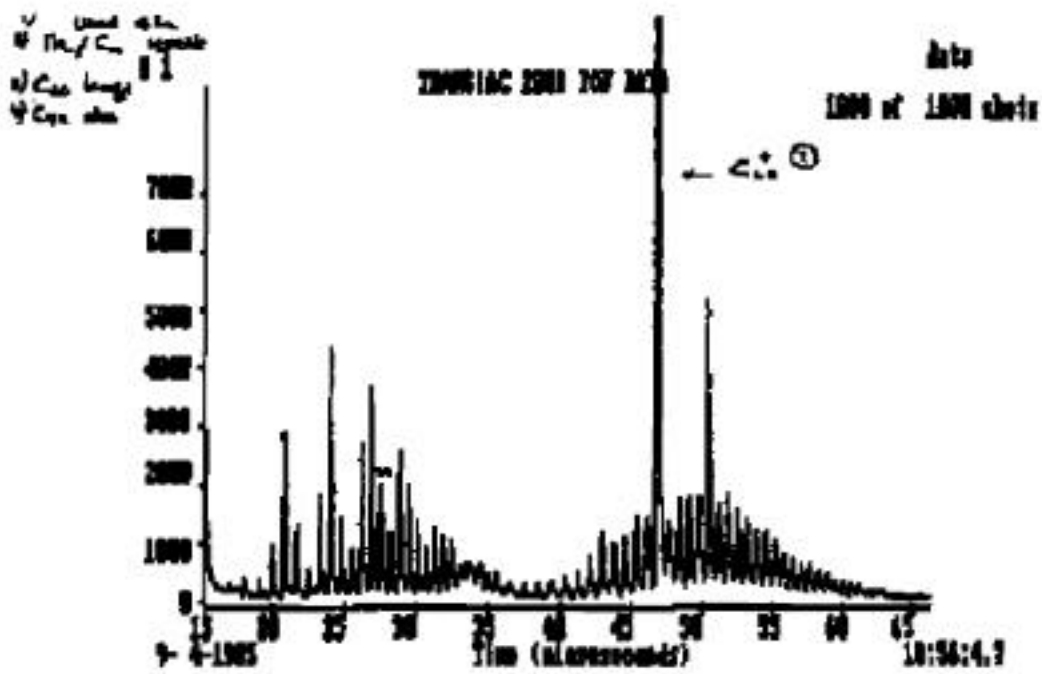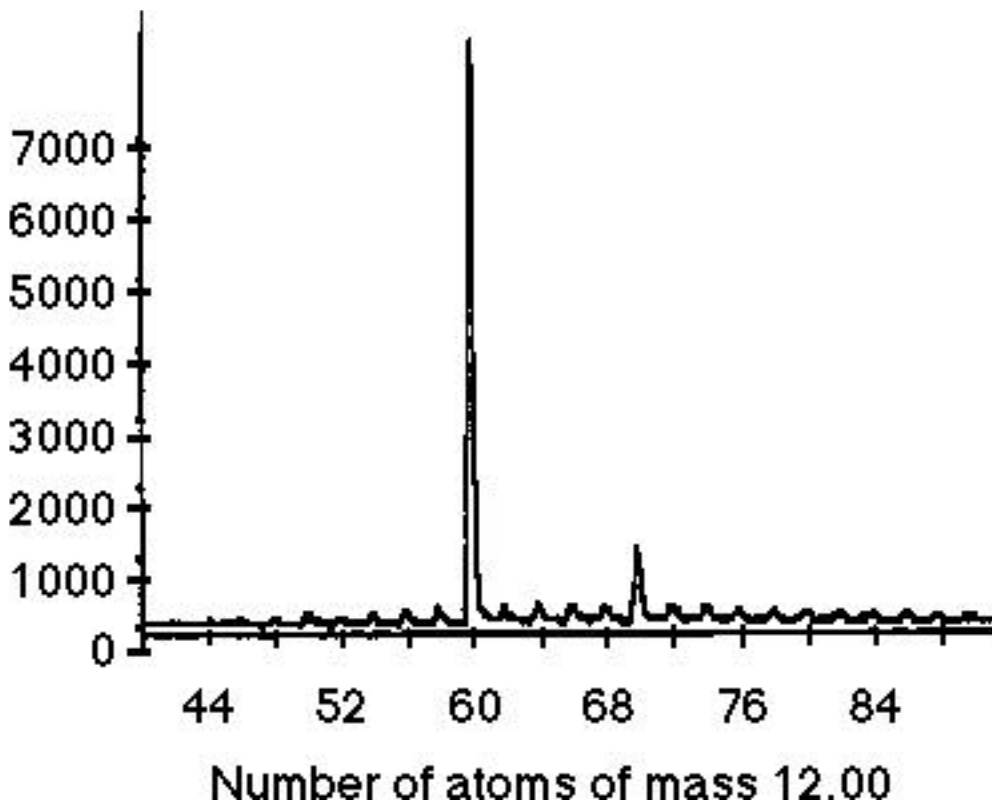
2.3 The structure of Buckminsterfullerene: the Kroto-Smalley proposal.

On the basis of the information provided by mass spectrometry, Kroto, Smalley, and coworkers were faced with the problem of rationalizing the unusual stability of 60 carbon atoms bound together to make a molecule of buckyball. The fundamental issue concerned how to construct a molecular structure that satisfied normal bonding (four bonds per carbon atom) and comprised exactly 60 atoms of C. With a great leap of both insight and faith, as well as considerable influence from the geodesic dome structures designed by Buckminster Fuller, these collaborators proposed that C_{60} adopts an arrangement of carbon atoms that is similar to the stitching on a soccer ball (Figure 2.5).

Figure 2.5. Soccer Ball and Buckyball (ball-and-bond)

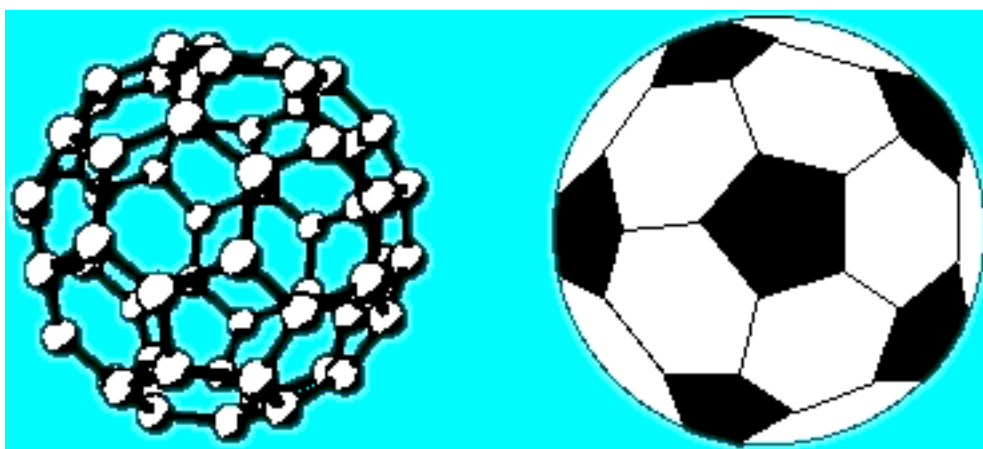Why a soccer ball? If one traces the stitching on a soccer ball, one finds exactly 60 vertices, or points where three lines of stitching intersect. A soccer ball has both 6-membered (hexagonal) and 5-membered (pentagonal) patches. These are sewn together to make a round ball. Taken in by the beautiful symmetry of such structures, Kroto and Smalley conjectured that if 5-membered and 6-membered rings of carbon were placed together in the same pattern then a round molecule containing 60 carbon atoms would result. This structure can be reconciled with the tendency of carbon to form four bonds if one assumes that each C engaged in one double bond and two single bonds with the neighboring carbon atoms. Overall, this results in a structure that has patterns of alternating single and double bonds as one traces the C-C bonding framework. Each carbon lies at the vertex of fused 5- and 6-membered rings.

But why should C_{60} be so stable? The alternation of single and double bonds in a molecule has been found to correlate with unexpected stablility in molecules closely related to C_{60}. By stability we mean that the forces, or bonds, holding the carbon atoms close together are stronger than one might have expected from comparison with simpler, related materials. Consider the example of C_6H_6. Various experimental measurements indicate that benzene (C_6H_6) contains six carbon atoms arranged at the vertices of a hexagon. Attached to each carbon atom by a single bond is a hydrogen atom (Figure 2.6). One can satisfy the bonding rules for carbon and hydrogen by (1) joining each hydrogen to a carbon atom with a single bond and (2) arranging bonds between the carbon atoms in an alternating single-double-single pattern as shown in the figure. Two arrangements of C-C double bonds in

benzene are possible; the two structures differ only in the positioning of the double and single bonds.

Figure 2.6 Benzene and resonance structures
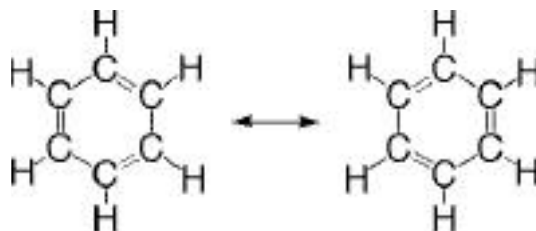
Which of the two structures for benzene is correct? Neither! Although each of the two structures implies alternation of C-C bond distances, experimentally it is found that all of the C-C distances are equal. Furthermore, benzene is found to be more stable than is expected for a molecules that has C-C single bonds and C=C double bonds. The American chemist, Linus Pauling, suggested a way to resolve this dilemma: benzene is best considered to be both structures simultaneously. In the language originated by Pauling, modern chemists state that the best description of benzene is a superposition of the two resonance structures shown above. By resonance we mean that benzene is at all times a mixture of the two limiting structures. This is subtly, but importantly, different from saying that benzene is one structure half of the time and the other structure the rest of the time. The best description of benzene is that is always half of each structure. Molecules that can engage in this type of bonding resonance are found to have more stablity than molecules that do not. Thus, we say that the effect of resonance is to (1) even out the alternation of bond lengths and (2) add stability to the molecule. A general postulate of Pauling's resonance theory is that the greater the number of resonance forms, the greater the stability of the material.

The special stablilization of C-C bonds associated with resonance in benzene is manifested in the C-C bond lengths. An average C-C single bond is 1.54 Å in length, whereas an average C-C double bond length is 1.34 Å. Based on the two resonance strucutures for benzene one might approximate each bond to be equivalent to 3/2 of a bond (the average of 1 and 2). This would lead to a predicted bond length of about 1.44 Å. The experimental C-C bond length is observed to be 1.39 Å, illustrating that the forces of attraction between carbon atoms in benzene are unexpectedly strong.

We can extend the concept of resonance to understand the unusual stability of C_{60}. Just as different patterns of alternating single and double bonds can be drawn for benzene, different resonance structures can be drawn for C_{60}. Thus, by arranging the carbon atoms in hexagonal and pentagonal rings, we find that a nearly spherical molecule with substantial resonance stablilization can be formed from 60 carbon atoms. These features are consistent with the properties observed for buckyball. For example, by analogy to benzene we would expect the average C-C bond distances in buckyball that is less than 1.44 Å the average C-C bond lengths of buckyball are found to be ??.

2.4 Does the Kroto-Smalley experiment prove the structure of buckminsterfullerene?

No. Although the soccer-ball shape of C_{60} is consistent with the observation of a peak at 720 amu and the unusual stability associated with resonance structures, the mass spectrum alone does not reveal the spatial arrangements of atoms in buckyball. The mass spectrum reveals the mass only, not the bonding arrangement. The critical piece of evidence that effectively "proved" the structure of buckyball awaited the isolation of sufficiently large amounts of material to perform a different type of spectroscopic measurement called nuclear magnetic resonance spectroscopy.

2.5 How does nuclear magnetic resonance spectroscopy work?

Magnetic Resonance Imaging (MRI) (MRI) is an increasingly common source of physiological information. For example, MRI can be used to probe the brain for irregularities. The information obtained from MRI is complementary to X-Ray photographs and CAT scans. Whereas X-Rays produce images of body regions with contrasting density (such as the dense bones vs. low density soft tissue), MRI yields images of regions with contrasting water content (such as different areas of the brain). A MRI image of a human head is shown in Figure 2.7. It may come as a surprise to you that MRI is actually a form of a more general spectroscopic technique with the ominous sounding name of Nuclear Magnetic Resonance (NMR) spectroscopy. NMR is a very powerful spectroscopic method that reveals direct information about the environment of atoms in different materials.

Figure 2.7 MRI of a human head

Just as the name implies, NMR (as well as MRI) involves observation of nuclei in the presence of a magnetic field. Atoms that have odd numbers of protons (^{2}H, ^{14}N, etc.) or odd numbered sums of protons and neutrons (^{1}H, ^{15}N, ^{31}P, ^{13}C, ^{19}F, ^{17}O, etc) have nuclei that behave like tiny, spinning bar magnets. These nuclei can be detected in nuclear magnetic resonance spectrometers; such nuclei are called NMR active nuclei. It is common to refer to these spinning bar magnets as nuclear spins or, more simply, just spins. If these tiny magnets, or spins, are placed in a strong magnetic field such as that in an NMR or MRI spectrometer, they align so that they are either parallel (in the same direction of the large magnetic field) or antiparallel (opposite in direction to the large magnetic field) to the field of the spectrometer's large magnet. The parallel alignment is more stable than the

antiparallel alignment, so that slightly more spins are aligned with the external magnetic field than with it.

You may wonder why all of the spins are not in the more stable, parallel arrangement. They would be at temperatures approaching absolute zero. However, at room temperature the spins have thermal energy. Thermal energy is the amount of kinetic energy characteristic of that temperature. At room temperature the thermal energy available exceeds the difference in energy between the parallel and antiparallel spin orientations in a magnetic field. We say that the spins are constantly excited into the less stable spin orientation by thermal energy. On average, just a slight excess of spins have the more stable orientation than the less stable orientation.

The energy difference between the parallel and antiparallel orientations depends on the size of the applied magnetic field (Figure 2.8). Larger magnetic fields yield greater energy differences. A spin in the lower energy orientation can be induced to change its orientation by the action of electromagnetic radiation. This process is called a spin flip. Spin flips require that the energy of the electromagnetic radiation, or light, match exactly the energy difference between the parallel and antiparallel spin orientations. Nuclear magnetic resonance spectrometers measure the energy of the radiation required to induce spin flips. Soon we will see that such measurements yield detailed information about the structure of molecules with NMR active nuclei. But first, let's explore what is meant by electromagnetic radiation.

Figure 2.8 Behavior of nuclear spins in the presence and absence of magnetic fields.
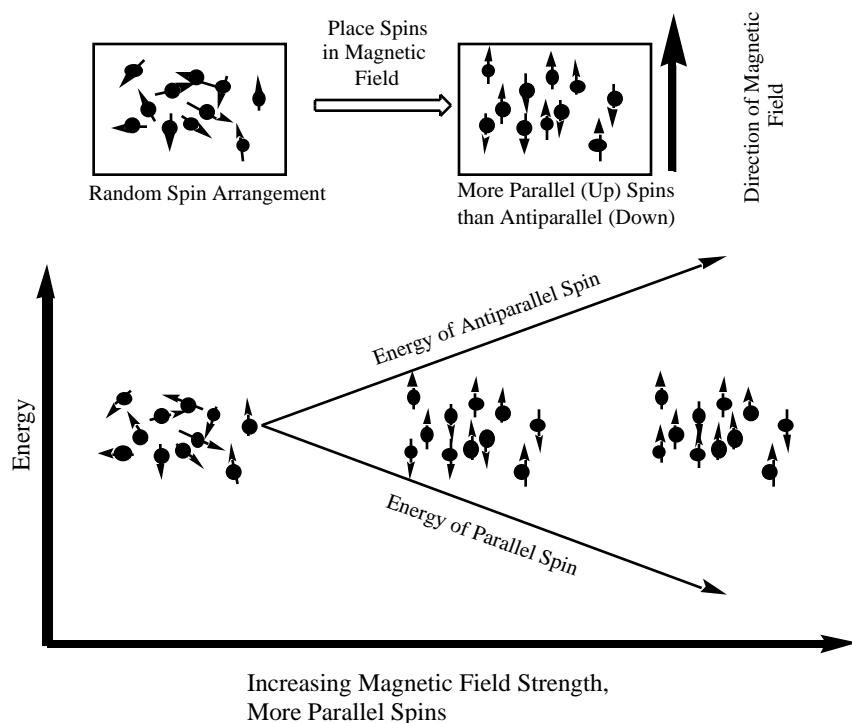
2.6 Electromagnetic Radiation

We normally think of light in the context of what we can see: blue light, green light, red light, etc. However you probably have heard of other forms of light without realizing that

they are closely related to the light that we see. For example, concerns about ultraviolet radiation are frequently associated with discussions of the "ozone hole", we use microwave ovens (which emit microwave radiation) to warm foods, and x-rays are used for medicinal purposes. Each of these is an example of electromagnetic radiation. All electromagnetic radiation consists of oscillating electric and magnetic fields that move at the speed of light (186,000 miles per second in vacuum). The oscillatory behavior of the electric and magnetic fields of light can be described as waves. What distinguishes one form of light from another is the wavelength and frequency of the electromagnetic radiation (Figure 2.9). For example, radio waves have long wavelengths (1-100 meters) and low frequencies (106 or one million cycles/second). X-rays have short wavelengths (1/10,000,000,000th of a meter) and very high frequencies (1018 cycles/second).

Figure 2.9 Electromagnetic Spectrum and Wave Illustration
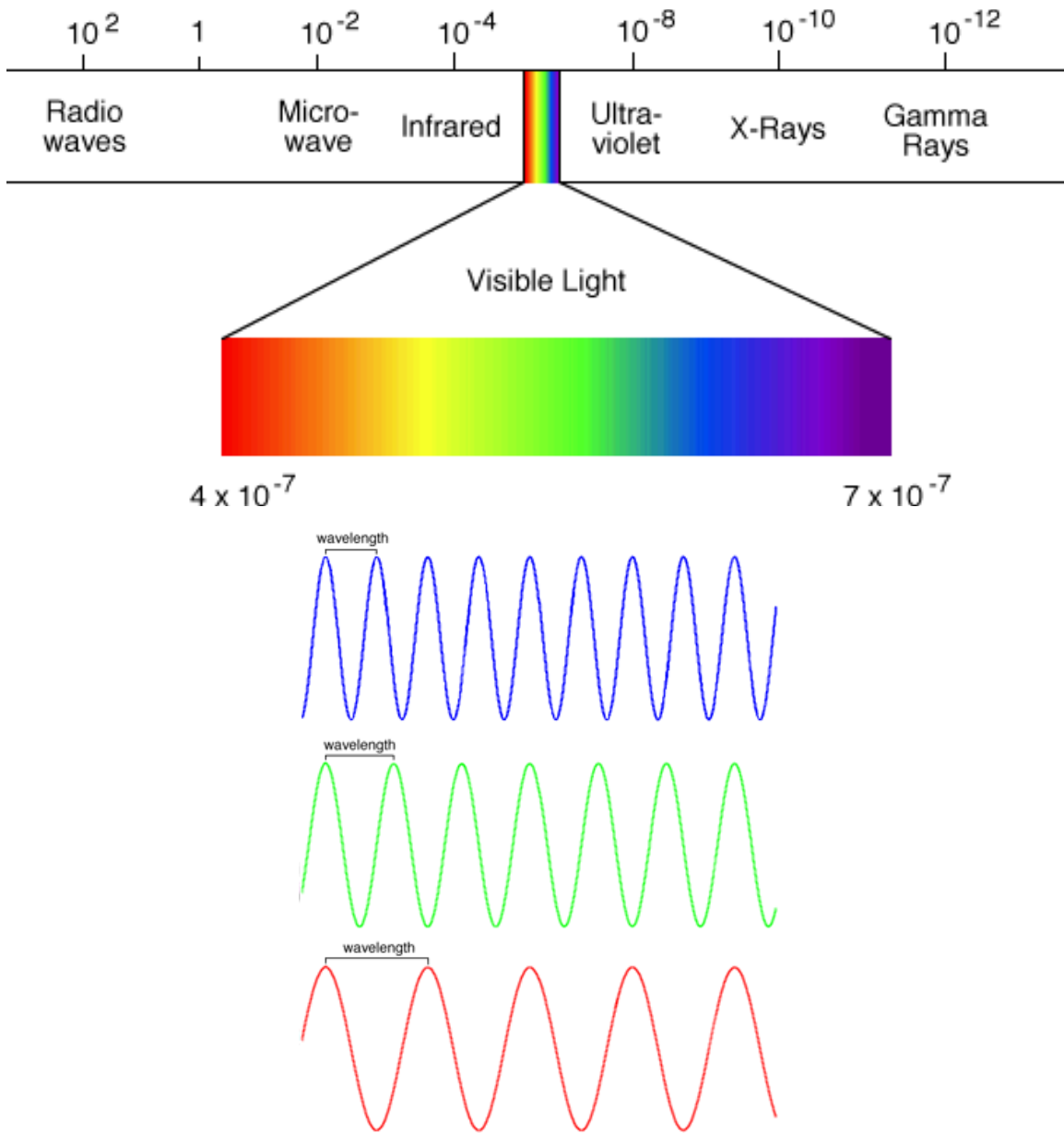
The energy of electromagnetic radiation varies with the frequency. High energy radiation such as x-rays, gamma-rays, and ultraviolet light have high frequencies and short wavelengths. These forms of light are particularly hazardous because of their high energy and penetrating power. In particular, exposure to x-rays and gamma-rays must be monitored carefully. Lower energy forms of radiation such as microwaves and radiowaves pose less of a hazard than high energy radiation. Radio stations, television stations, and NMR instruments all use long wavelength, low energy radiation.

2.7 NMR measurements and radiofrequency radiation

When a sample that contains NMR active nuclei is placed in the magnetic field of an NMR instrument, it is possible to induce a "spin-flip" by the absorption of electromagnetic radiation. That is, by absorbing light energy the nuclear spins may be stimulated to change from the lower energy, parallel orientation of the spin to the higher energy, antiparallel orientation. When this spin-flip occurs the nuclei are said to be in resonance, hence the name nuclear magnetic resonance. Resonance is not brought about by just any form of electromagnetic radiation, the energy of radiation precisely must match the difference in energy between the parallel and antiparallel orientations.

To get a better feel for the resonance phenomenon consider an analogy with musical instruments. Imagine that you removed all but one string from a guitar and tuned that string to concert A. When plucked this string will vibrate at the frequency characteristic of concert A. An NMR sample that is analogous to the one-string guitar would be a sample that had just one NMR active nucleus. When a trumpet is pointed at the one-string guitar and a scale is played, the guitar string will exhibit little vibration until concert A is played on the trumpet. At that point, the natural frequency of the guitar string and the frequency emitted by the trumpet are in resonance. The frequencies match and some of the energy of the trumpet's sound waves will be absorbed by the guitar string. As a result the guitar will play the note although the string was not plucked. Note that this type of resonance, which is very different from the kind of resonance that we have used to describe bonding in certain molecules, occurs only when the frequencies of the sound waves and the guitar string match. Similarly, when the radio-frequency transmitter of an NMR instrument is pointed at the NMR sample containing one NMR active nucleus, no energy is absorbed until the frequency of the radio waves match the natural frequency of the nuclear spin. That frequency corresponds to the radiation energy that equals the energy difference between the different spin alignments. At resonance, the radio-frequency light is absorbed and the nuclear spin flips its orientation. In considering this analogy it is important that you realize that sound and light are different, although they share wave-like properties. Sound waves are due to the movement of air or other matter, and are not forms of electromagnetic radiation. As a result sound does not move at the speed of light; instead, sound waves propagate at a far slower rate.

2.8 NMR measurements and the atomic environment

The power of NMR spectroscopy arises from the ability of the measurements to distinguish not only the natural frequencies of different nuclei (e.g. C and H have very different resonance frequencies) but also similar nuclei in different chemical environments. The bonding environment around a nucleus influences its resonance frequency. Consider two molecules that we have seen before, benzene and methane. NMR spectrometers could be used to measure the resonance frequencies of either the 1H or the ^{13}C nuclei in these molecules since both elements have NMR-active nuclei. Let's look at the ^{13}C NMR spectra first. The methane molecule has just one carbon atom so that there can be just one bonding

environment for the carbon nuclei. Therefore the ^{13}C NMR spectrum of methane has just one peak (Figure 2.10). Now consider benzene. Unlike methane in which the carbon atom has four single bonds to hydrogen atoms, each benzene carbon atom has two single bonds (one to carbon and one to hydrogen) and one double bond (to another carbon atom). Clearly the bonding environment of a carbon atom in benzene is different from that of a carbon atom in the methane molecule. As a result the NMR resonance frequency for benzene is different from that of methane as shown in Figure 2.10. As a general rule, atoms in benzene rings have resonance frequencies that are lower than those of methane (assuming of course that the magnetic field strength of the NMR instrument is the same).

Figure 2.10 NMR Spectra of methane, benzene, and hexane.
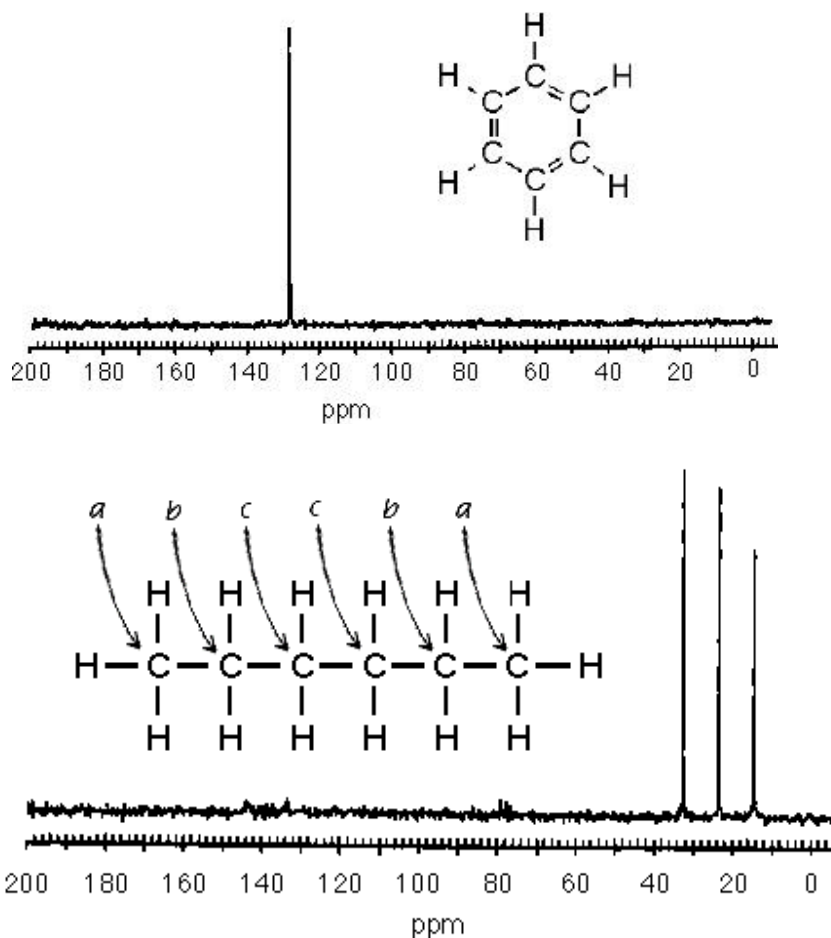
Note that the ^{13}C NMR spectrum of benzene has just one peak! Although there are six carbon atoms in a benzene ring, the bonding environment of each C is identical. We can understand this in two different ways. First, trace the bonding topology (or connectivity) of benzene and you find that each carbon is identical. Each carbon has the equivalent of one and one-half bonds to adjacent carbon atoms and a single bond to hydrogen. A second approach utilizes symmetry considerations. The flat, hexagonal structure of benzene is highly symmetric. This is particularly clear if we use the simple hexagonal representation of benzene in Figure 2.6. This kind of representation is very common for carbon-containing molecules. None of the atoms are drawn explicitly, rather the vertices of the

polygon represent carbon atoms and the hydrogen atoms are implied. Visually one can see that there is no distinction between the vertices of a hexagon. The hexagon can be rotated or flipped such that different vertices are interchanged without any apparent change in the hexagon. As a result of this symmetry, there can be no distinction between carbons. Hence, just one NMR signal is observed.

Now we consider a more complicated molecule, hexane. Hexane has a chain of six carbons, but the NMR spectrum exhibits just three peaks. This is because the carbons are in three different environments as shown by the a, b, and c notations in Figure 3.0. The carbons at the ends of the molecule (type a) have three bonds to hydrogens and one to another carbon. This bonding environment is clearly different from the four internal carbons which each have two bonds to hydrogens and two bonds to carbons. The distinction between carbon types b and c is more subtle. Look closely at the C-C bonds. Carbon type b is joined on one side to a carbon with three bonds to H and on the other side to a carbon with only two attached hydrogens. In contrast, carbon type c is joined on either side to a carbon that has two bonds to hydrogens. Although the difference is subtle, it is sufficient to create different NMR resonance frequencies for type b and c carbons. Thus, hexane has three carbon environments and three 13C NMR peaks.

2.9 NMR and the structure of buckyball

Finally returning to buckyball, note that the structure proposed by Kroto and Smalley (Figure 2.5) is highly symmetric. Each carbon atom is located at the intersection of two hexagons and one pentagon. The 60 vertices of the buckyball are identical. Therefore, all the carbon atoms in buckyball are in the same environment. One expects such a structure to exhibit just one ^{13}C NMR resonance despite the fact that there are 60 carbon atoms! By 1990, methods of obtaining the milligram quantities of buckyball required for NMR measurements had been developed. Consistent with the structure proposed by Kroto and Smalley, just one peak was observed in the spectrum of C_{60}! This observation severely limited the number of acceptable structures: there is no simpler way of arranging 60 carbon atoms in agreement with the bonding rules of carbon such that the bonding environment of each C atom is identical. For most chemists, the structure of buckyball was considered proven by the observation of a single resonance in the ^{13}C NMR spectrum.

2.10 What is happening in current research with Buckyball?

After scientists discovered how to make buckyball in large enough quantity for characterization and study, a whole new field of chemistry was opened to creative exploration. As many scientists began working with buckyball in their own research labs, a flood of information hit the scientific journals. So many papers on buckyball were submitted that, in 1993, a journal entitled "Fullerene Science and Technology" was born.

Two of the most interesting areas of current research with buckminsterfullerene deal with building onto the outside and catching smaller molecules in the inside of buckyball. In 1991, addition of an osmium-containing sidearm to buckyball to make a derivative of C_{60} allowed for absolute confirmation of the structure of buckyball using a process called x-ray diffraction. (A full explanation of x-ray diffraction is presented in the unit of graphite and carbon fibers.) The osmium derivative and another deriviative of C_{60} are both shown in Figure 2.11. Derivatives are analogs of an original compound which can be said to be derived from the original molecule. Analogs of buckyball that have extra atoms attached to the original 60 atom carbon framework are derivatives of buckyball.

Figure 2.11 Derivatives of C_{60}.
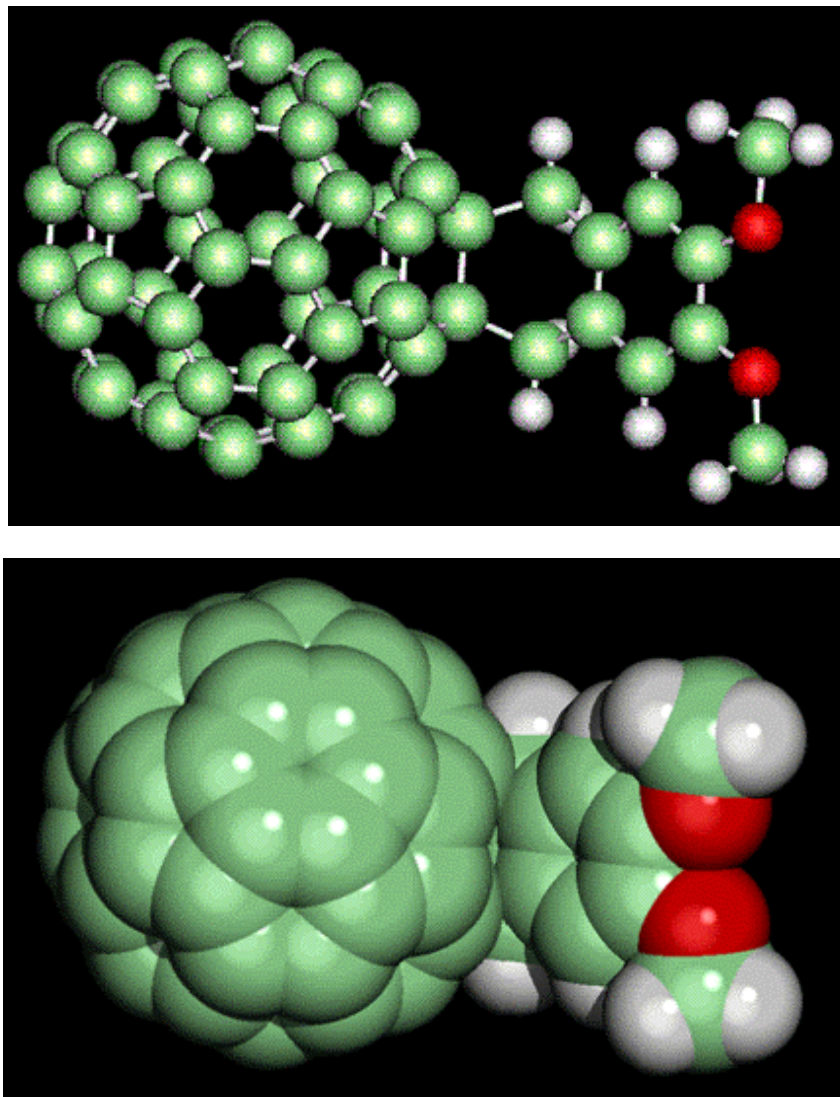
Trapping gases such as helium and neon in the interior of a buckyball appears to be quite easy. The common method of making buckyball involves the creation of an electronic arc between two graphite rods that are placed in a helium atmosphere. An arc welder supplies the power. A helium atmosphere is used because helium is an unreactive gas that is capable of transfering heat rapidly. Therefore the tremendous energy at the site of the arc is rapidly dissipated as the fragments of carbon cool and form buckyball. Because helium is abundant in the buckyball generator, helium is trapped inside some of the molecules of C_{60}. Indeed, molecules of buckyball prepared in helium have probably always generated some of the material with helium gas trapped in the interior cavity of buckyball. Only one out of every 880,000 molecules of buckyball are believed to have helium trapped inside them, though, and these special complexes remained undetected until very sophisticated mass spectroscopy techniques were applied to the problem in 1993. The interior of C_{60} is large enough to accommodate an atom of any element in the periodic table, and many metals including lanthanide, uranium, cesium, and scandium have been trapped by fullerenes

ranging in size from C_{28} to C_{82}. The hope of scientists working in this area is that fullerenes with metals trapped in their interiors will be superconductors.

2.11 What are the possible applications of Buckyball?

Although practical applications for buckyball have not yet been realized (Figure ??-- newspaper headline "Buckyballs apps slow to develop"), promising groundwork has been laid in two areas. In one area, materials called buckytubes have been made in much the same way as buckyball is made. Buckytubes typically consist of 2 to 50 concentric tubes, and each tube is an array of carbon atoms linked together in a curved sheet. The ends of each set of concentric tubes fit together like Russian nesting dolls and consist of hemispherical arrays of carbon atoms similar to the spherical arrays of atoms found in buckyball. Shaped like needles, each buckytube is about one micron long (one micron is about 1/70 of a human hair). If buckytubes can be lengthened into fibers, they will likely be far stronger than ordinary reinforcing fibers.

In another area of work with buckyball, a derivative of C_{60} was shown to inhibit HIV-1 and HIV-2, the human immunodeficiency viruses that cause AIDS. Researchers at the Univeristy of California, San Francisco, noticed that buckyball fit perfectly into the active site of HIV proteases. (The active site is where reactions occur.) A water-soluble derivative of C_{60} was made by Fred Wudl and co-workers at the University of California, Santa Barbara, and this compound was indeed shown to disarm the HIV virus and block HIV protease from cutting proteins. (Figure 2.12 shows the computer-generated model of C_{60} docked in the protease active site.) The infected cells themselves, however, were not damaged. At Emory University, inhibition of HIV's ability to infect cells was also shown using a water-soluble derivative of buckyball. Unfortunately, the potency of the buckyball analog is low when compared to AZT and other HIV enzyme-inhibiting drugs. To be useful, the buckyball compound must be at least 1000 times more potent than it is now.

Figure 2.12 Model of C_{60} docked in the binding site of HIV-1 protease
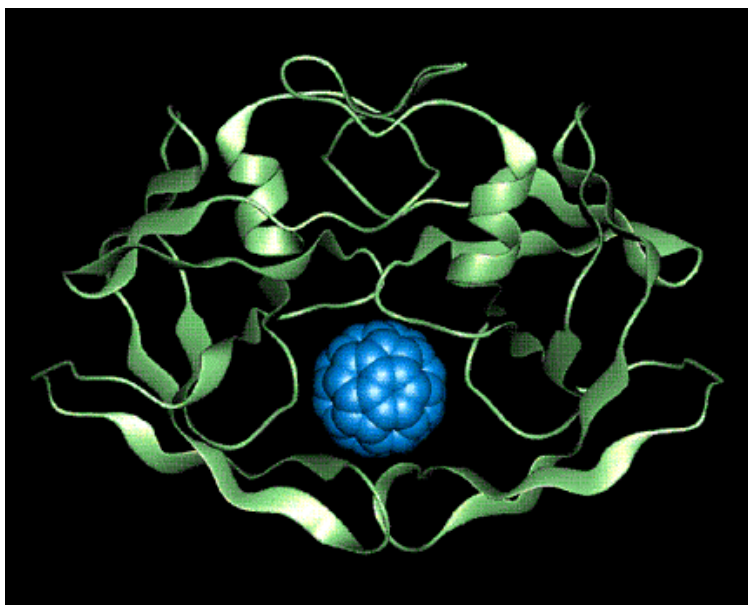
Currently, no actual applications of buckyball have been realized. Groundwork using buckyball in reinforcing materials and in drug design have both produced positive results,

and it is likely that more uses for buckyball will evolve as more and more scientists enter this new and challenging field.

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Buckyballs, Diamond, and Graphite

3.0 Graphite and Carbon Fibers

3.1 Introduction

When you go to a sports shop you are inundated with new "graphite" based materials for sports equipment: golf clubs, tennis rackets, bicycles (frames and wheel disks), ultralight airframes, and even America's Cup yachts feature these new lightweight materials. But, we are also familiar with graphite as being a very common and mundane substance. Graphite has long been a component of pencil lead, and is used as a basic lubricant. How is it that graphite is both a hi-tech and low-tech material? Could we take a bunch of pencil leads and epoxy them together into a cutting edge tennis racquet? Anyone who has used mechanical pencils knows that the leads break far too easily to provide a strong frame. It would seem as if there are two different kinds of graphite. In fact, this is true. When vendors market "graphite fiber" products they are usually selling a "carbon fiber" product. The correct name for the fibers used in all strengthening and reinforcing applications is carbon fibers. But, there is more to the story than just a general misconception over the term "graphite fibers." Surprisingly, if we look at a small section of graphite and carbon fibers on the atomic level they appear to be identical.

Figure 3.1 Headline from Chicago Tribune, May 23, 1993.

3.2 How are carbon fibers and graphite produced?

Carbon fibers are made from organic polymers such as poly(acrylonitrile). Although a full description of polymers is not really appropriate at this point, it should be noted that polymers are giant molecules comprised of repeating units. Poly(acrylonitrile) is a polymer with chains of carbons connected to one another. To make carbon fibers, the polymer is stretched into alignment parallel with what will eventually be the axis of the fiber. Then, an oxidation treatment in air between 200 and 300 °C transforms the polymer into a nonmeltable precursor fiber. This precursor fiber is then heated in a nitrogen environment. As the temperature is raised, volatile products are given off until the carbon fiber is composed of at least 92% carbon. The temperature used to treat the fibers varies between 1000 °C and 2500 °C depending on the desired properties of the carbon fiber. The process used to make carbon fibers is summarized in Figure 3.2. Each carbon fiber is very thin; the total diameter of a carbon fiber is 6-10um or about five times thinner than an average human hair (Figure 16). When carbon fibers are used in industry, they are woven into sheets, tubes, or other desired shapes (Figure 3.3). Epoxy resins or other binders are often added to the carbon fibers. The resulting composite of epoxy and carbon fibers is stronger than either component individually.

Figure 3.2 Schematic showing the process for making carbon fibers

poly(acrylonitrile)
organic polymer

stretched

oxidized at
200-300 ˚C

heated at
1000-2000 ˚C
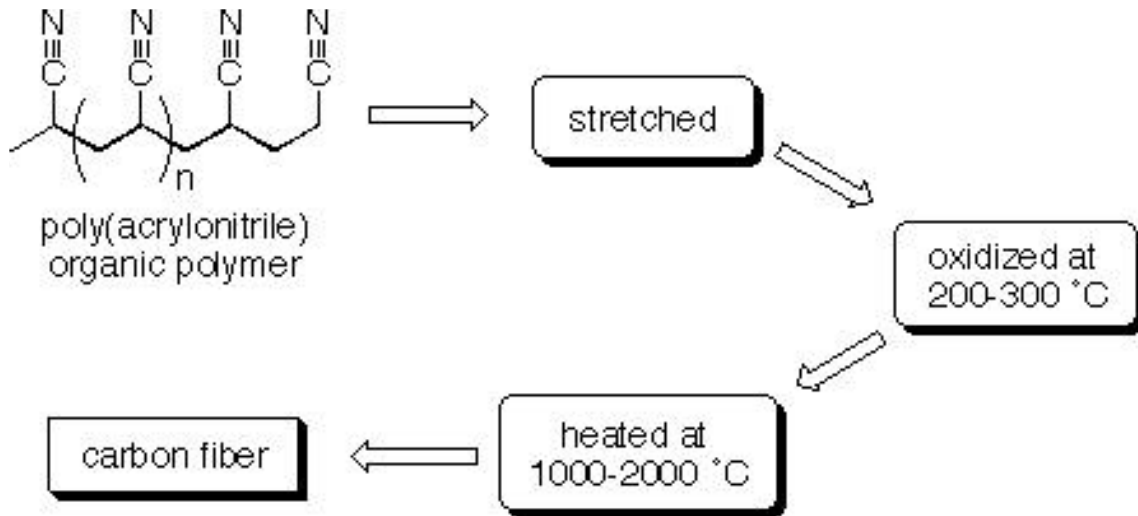
carbon fiber

Figure 3.3 Braiding of carbon fibers
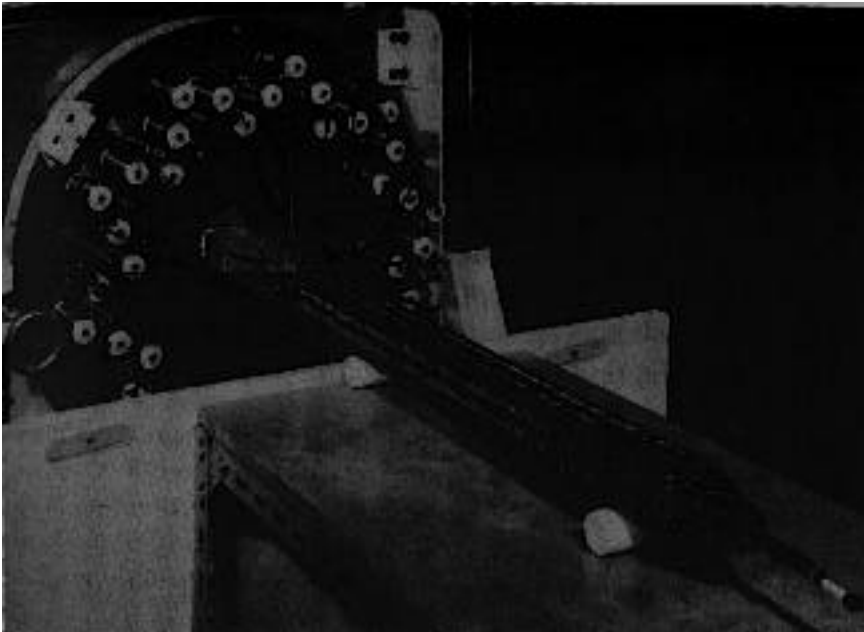
If during the treatment process the temperature is raised above 2500 °C, graphite will be formed instead of carbon fibers! We will return to why the higher temperature leads to graphite later. Graphite can also be found in nature as flakes mixed with clay and other impurities. While graphite can be mined or formed through the carbon fiber process, most of the graphite used in industry is manufactured by heating petroleum byproducts to about 2800 °C. The petroleum byproducts are similar to the polymers used in the carbon fiber process in that both contain chains of carbon atoms.

3.3 What are the properties of graphite and carbon fibers?

Both graphite and carbon fibers are rigid materials that are resistant to stretching and compression. They are also chemically inert or unreactive materials. This is critical because it means that carbon fibers don't react with the outer part of a bicycle frame or a tennis racket and graphite pencil leads don't react with paper. The inertness of carbon fibers makes them suitable for medical applications such as hip and knee ligament replacements. Graphite, a black, lustrous solid, is shown in Figure 3.5. Carbon fibers, tiny black strands, are shown in Figure 3.6.

Figure 3.5 A sample of graphite

Figure 3.6 A spool of carbon fibers

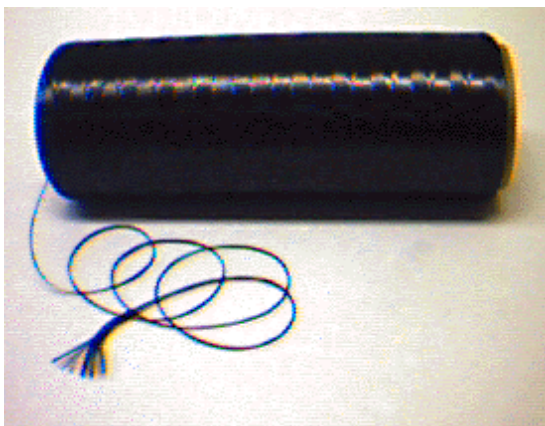The biggest difference between carbon fibers and graphite is that graphite is flaky and breaks apart very easily while carbon fibers are strong materials that do not break until much more force is applied. Figures 3.7 and 3.8 show carbon fibers after tensile failure and flexural failure respectively. Tensile failure occurs when the fibers are stretched along their axis; flexural failure occurs when the fibers are compressed along their axis. Chemists are usually interested in examining structures on an atomic level which is far smaller than the microscopic views in Figures 3.7 and 3.8. If the regions around break points have definable atomic structural features, stronger carbon fibers can be produced by excluding these characteristics. Chemists have learned that the straight lines around the fracture in Figure 3.8 are regions where the carbon fiber was the most graphite-like. But, how do chemists get such detailed information about atomic structures which are almost inconceivably small? There are a wide variety of tools available to explore substances on the atomic level. One of the most powerful methods for structural determination is called x-ray diffraction.

Chemists often favor this method because the results of a successful analysis is a clear picture of the atomic arrangements - perhaps one of the closest things to an "atomic photograph." The drawback to the technique is that it can only be used on crystalline solids. The difference between crystalline and amorphous materials is an important distinction to make before discussing the details of the x-ray diffraction experiment.

Figure 3.7 Microscopic view of tensile failure in carbon fibers
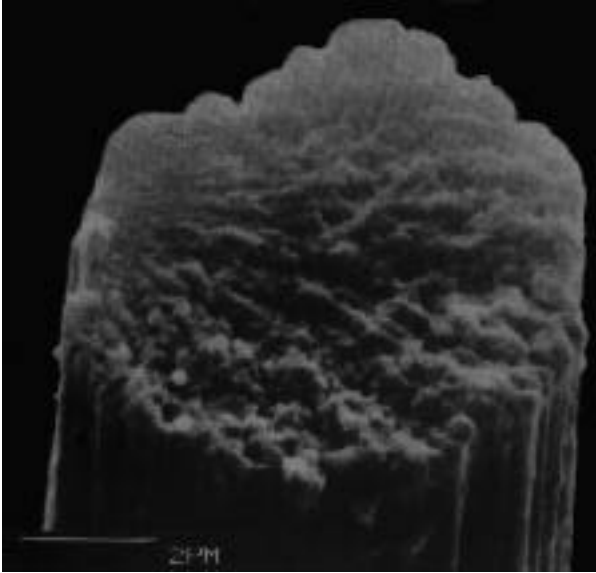
Figure 3.8 Microscopic view of flexural failure in carbon fibers
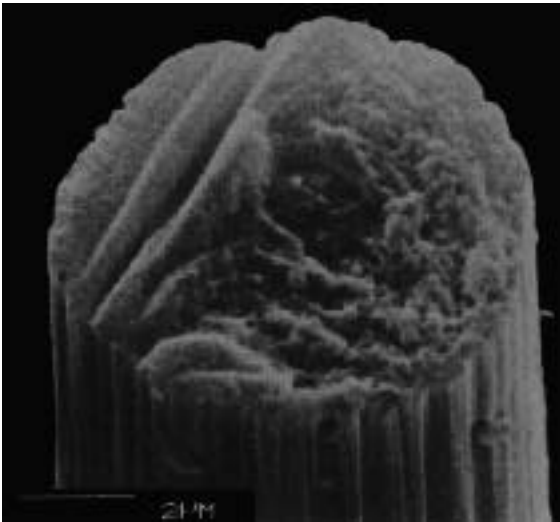
3.4 What is the difference between crystalline and amorphous solids?

Although the heart of the difference between crystalline and amorphous solids occurs on the atomic level, there are several physical characteristics which can often indicate one type or the other. Crystalline substances have regular shapes, and form flat faces when they are cleaved or broken. When they are heated, crystalline solids melt at a definite temperature (unless they decompose before melting). The regularity of crystalline solids is due to the arrangement of structural units into an orderly array or lattice. A unit cell is the smallest

repeating unit of a crystal and the smallest portion from which the structure of the crystal can be understood. Stacking unit cells together forms the crystal much as stacking bricks together forms a wall. The unit cells of graphite and diamond are shown in Figure 3.9.

Figure 3.9 Unit Cells
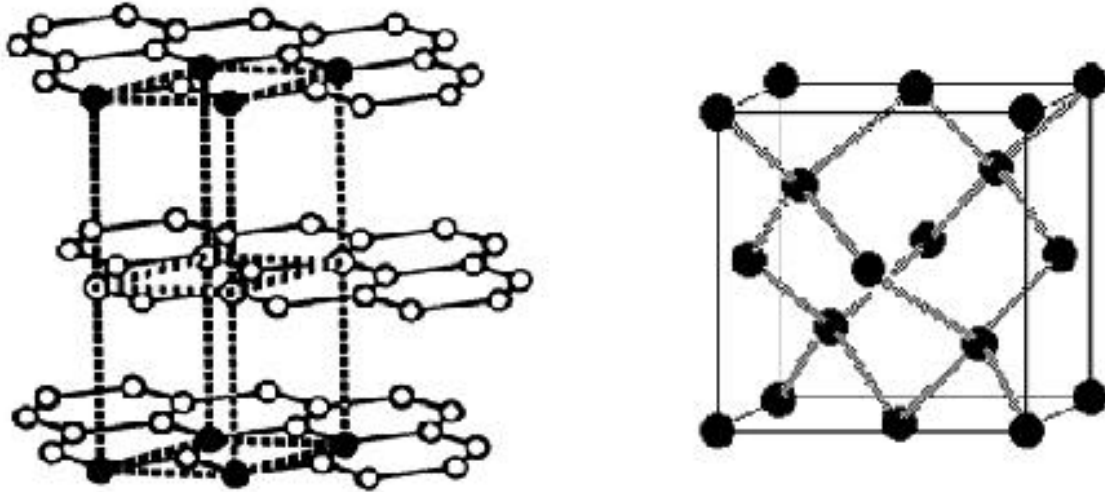
Most solids you encounter regularly --wood, papers, and plastics--are amorphous rather than crystalline solids. When amorphous solids are broken, curved and irregular faces are formed. An amorphous solid does not have a melting point. Instead, it softens over a broad temperature range. The change from solid to liquid is slow. A summary of the properties of amorphous and crystalline solids is given in Table 3.1.

Table 3.1 Comparison of amorphous and crystalline materials

Type of solid	Characteristics	Examples
Crystalline	Consist of individual crystals, each with well-defined shape. Cleave to well-defined faces. Melt at definite temperatures.	Sodium chloride, sucrose, metals
Amorphous	Have no well defined shape. Break to give curved or irregular faces. Soften and then melt over a temperature range.	Asphalt, paraffin, window glass, obsidian, glassy form of glycerol

There are three important subdivisions of crystalline solids.(Figure3.10) The first two are covalent and ionic networks. Network solids have an undefined size and all atoms are indirectly connected to one another. That is, you can start at any atom and trace a path to any other atom through bonds in the structure. Networks are classified by the kind of bonds that are formed between the atoms in the structure. The bonds in covalent networks are formed by the equal sharing of electrons between two atoms (called covalent bonds). When atoms of different elements form bonds, they don't share the electrons equally. Some elements have a strong pull for electrons when they form bonds resulting in an uneven distribution of electrons around the two atoms. In an extreme case, atoms can sometimes remove electrons from their neighbors. When atoms gain or lose electrons, they become

charged atoms called ions. The attractions between oppositely charged ions are called ionic bonds.

The final classification of crystalline solids which will be discussed is molecular extended lattices. The repeating unit for this class are molecules which are packed next to each other. It is important to note that there are no covalent or ionic bonds between the individual molecules -- they are held together by weaker attractions called intermolecular forces.

Figure 3.10 Classification scheme for pure solids
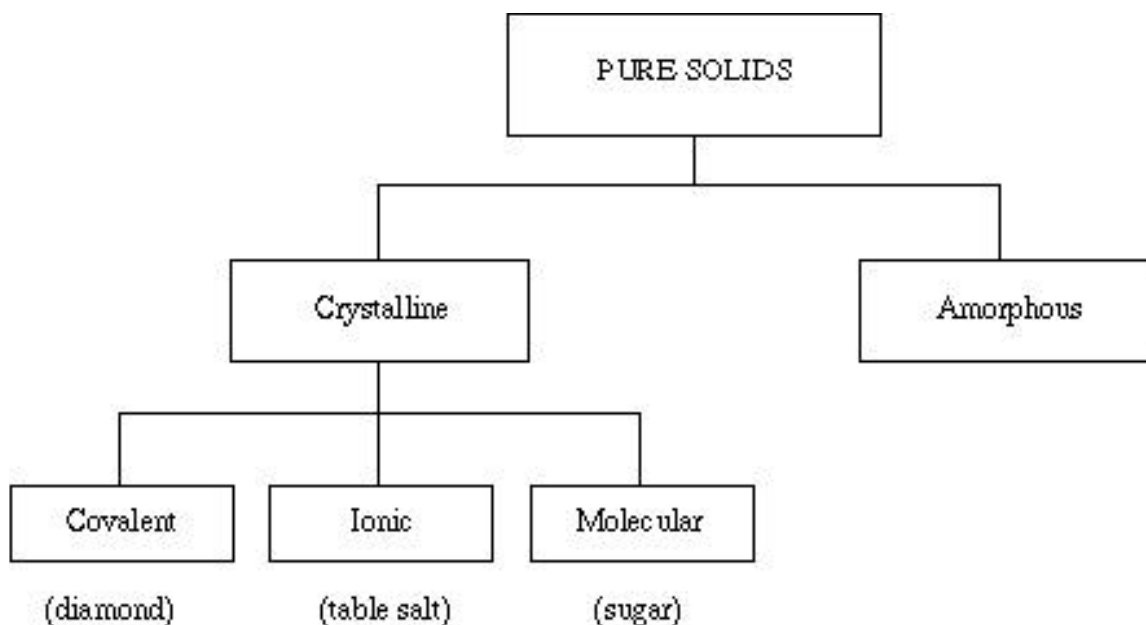
3.5 How does x-ray diffraction work?

X-ray diffraction is an analytical technique which uses a beam of x-rays to probe repeating planes of atoms. The reflection of x-rays off of repeating planes of atoms creates a series of spots called a diffraction pattern. The orientation of the x-ray and the crystal is of utmost importance. As the angle between the x-ray beam and the crystal face is varied, the diffraction pattern will change as well. By collecting data from a series of orientation angles, the three dimensional atomic structure can be calculated. You can think of this in simpler terms. Say you wanted to document a sculpture for a museum. A single photograph of the sculpture would record only a fraction of its overall form. Instead, you could take a series of photographs from several angles to flush out the entire sculpture. From your collection of photographs someone who had never seen the actual sculpture could build a replica.

The sample used in x-ray diffraction must not only be crystalline, but it must also be a single crystal. We have defined crystalline solids as being arranged into an orderly array or lattice. But, in reality, there can be small defects within the lattice, and crystals often fuse together. Both of these situations imply that repeating planes of atoms are interupted. To get good x-ray diffraction data, chemists use only single crystals with minimum defects.

The diffraction patterns of graphite and diamond are shown in Figure 3.11. Diffraction patterns from early experiments were recorded on photographic film, and the analysis of

data was performed by hand calculations. Modern methods, which employ automated diffractometers and high speed computers, have made diffraction studies a very powerful technique for determining the structure of crystalline solids.

Figure 3.11 X-ray diffraction patterns of graphite and diamond.

A schematic of an x-ray diffractometer is shown in Figure 3.12. The main components are an x-ray source, a goniometer (or crystal orienter), a detection system, and a computer control system. The x-ray source is a high-vacuum tube, and the x-ray beam passes out of the tube through a thin window. A single crystal is generally mounted on the end of a glass fiber. This fiber is then attached to a metal pin which is secured to the goniometer head. The goniometer precisely orients the sample in the x-ray beam. As the x-rays pass through the crystal, the detector collects information to generate a diffraction pattern. Finally, the computer control system processes the information from the detector, and the structure of the crystal is solved.

Figure 3.12 Schematic of X-Ray Diffractometer.
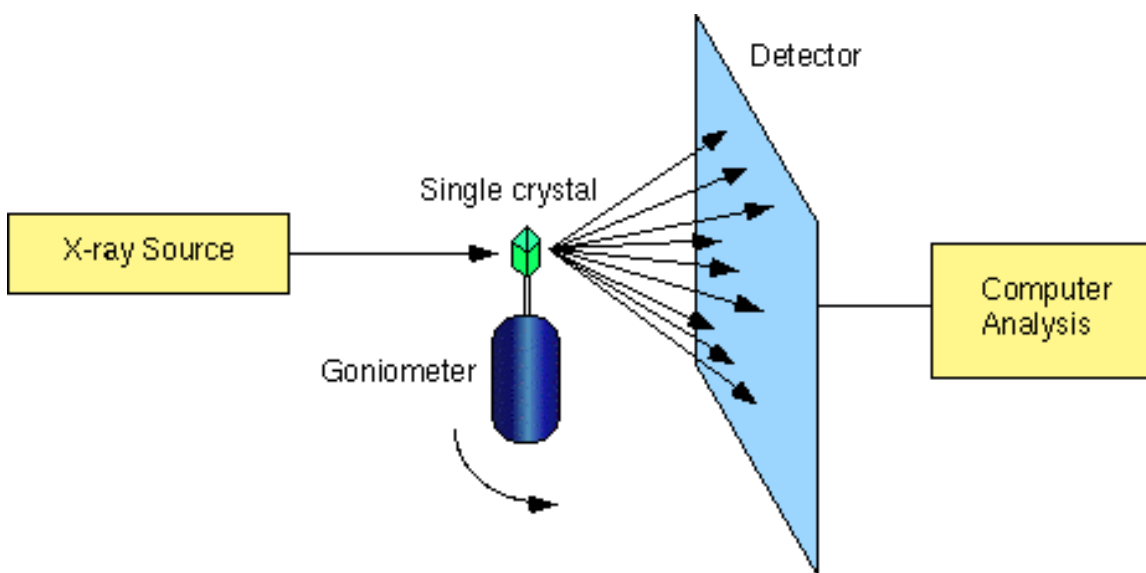
To understand how a diffraction pattern occurs, consider the diffraction patterns of two waves. Two waves of the same wavelength can come together either in phase or out of phase. If the two waves come together in phase, this means that the maxima and minima on both waves are at the same points. In other words, the hills and the valleys from both waves are lined up together. The waves reinforce or cause constructive interference, and the intensity of the resultant wave is increased. Conversely, two waves coming together out of phase have each minimum from one wave combining with a maximum of the other wave. The hills from the first wave line up with the valleys from the second wave while the valleys from the first wave line up with the hills from the second wave. This is called destructive interference and destroys the wave. Figure 3.13 shows constructive and destructive interference.

Figure 3.13 Constructive and Destructive interference.
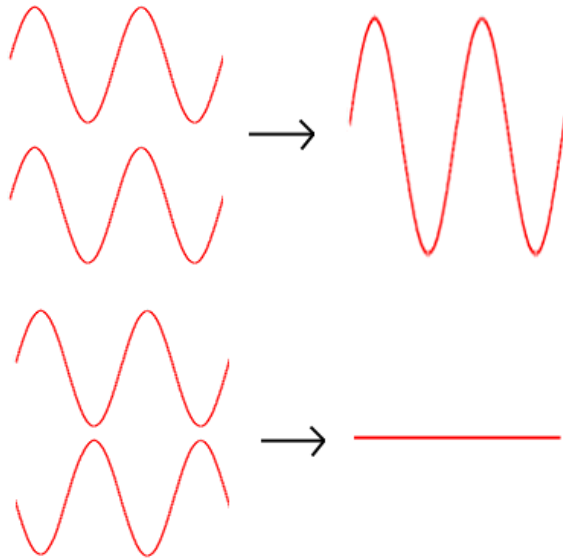
In a crystal, x-rays are reflected from the different planes of atoms that are present. If two x rays travel to two different planes, then one x-ray must travel further than the other. The x-rays may end up out of phase after they are reflected. Only at certain angles of reflection do the two rays remain in phase (Figure 3.14). In the diffraction pattern, dark areas are caused by constructive interference while lighter areas are caused by destructive interference. Thus, the diffraction pattern can be related to the structure of the crystal, and the position of each atom in a molecule as well as the type and size of a unit cell can be determined by using x-ray diffraction.

Figure 3.14 Constructive(a) and destructive(b) interference.
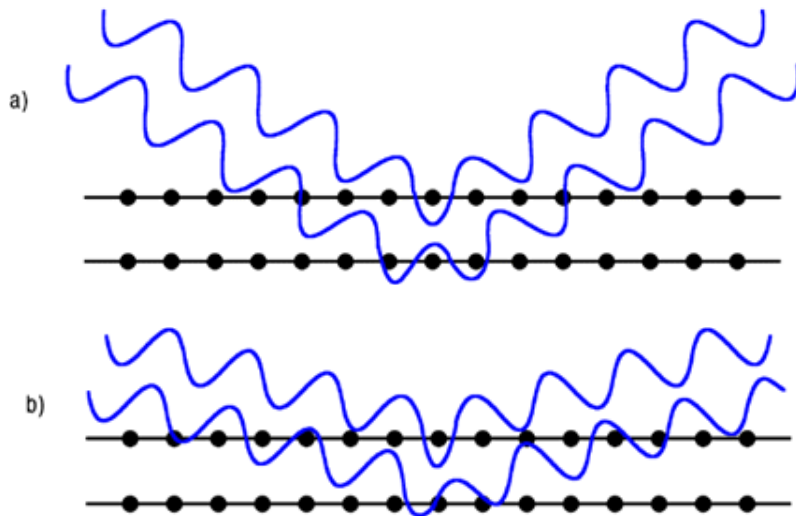
To see how different patterns of atoms result in different diffraction patterns, we can use a series of optical transform experiments. Optical transform experiments use the same physics of x-ray diffraction, but, the scale is much larger. Instead of a series of repeating atoms, the experiment uses a plastic slide with printed patterns. Instead of x-rays, the optical transform experiment uses visible light. You may wonder why x-rays are used for experiments on the atomic level and the visible light is used for the optical transform experiment. The diffraction phenomena depends on using a wavelengths which are of the

same order as the distance between the pattern components (atoms or dots). The much shorter wavelengths of x-rays are needed for the tiny distances between atoms, while the longer wavelengths of visible lights are suitable for the printed dots in the optical transform experiments. Of course, visible light is also convenient because we can see the diffraction patterns with the naked eye! You should note that the optical transform slides are one dimensional, and the light source is always perpendicular to the slide. This is a simplification of the x-ray diffraction experiments where a three dimensional structure is probed by varying the angle between the crystal face and the x-ray beam. The schematics of the two experiments are presented below (Figure 3.15).

Figure 3.15 X-ray and optical transform experiment schematics.
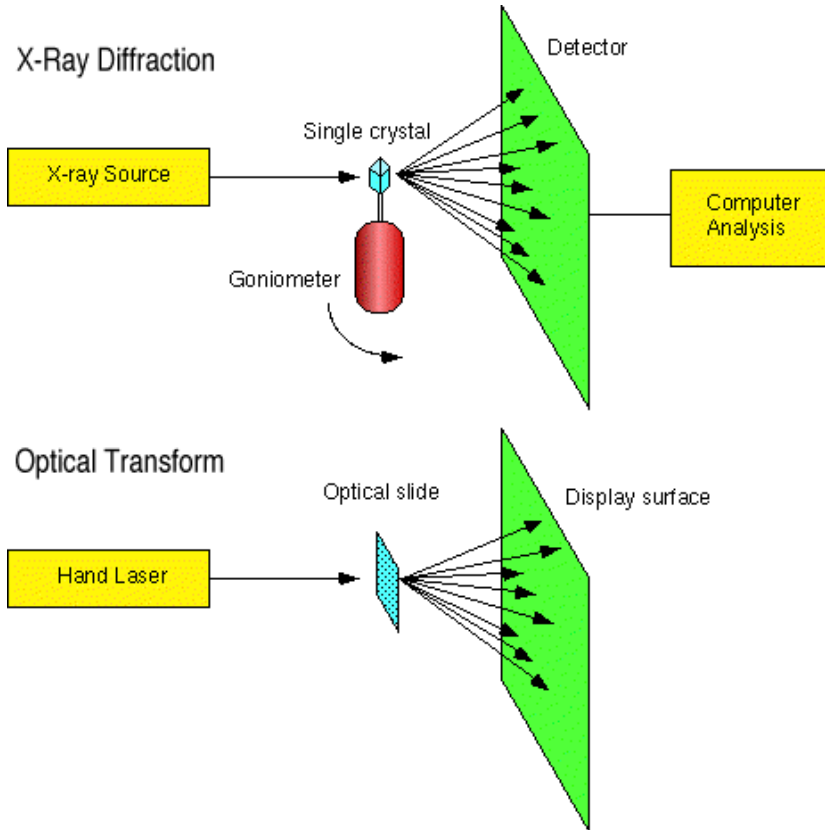
In the following series of diagrams, two optical transform slide patterns are presented side by side, with their diffraction patterns placed directly beneath them.

Figures 3.16 Optical slide patterns with differing distances between repeating units and their resulting diffraction patterns.
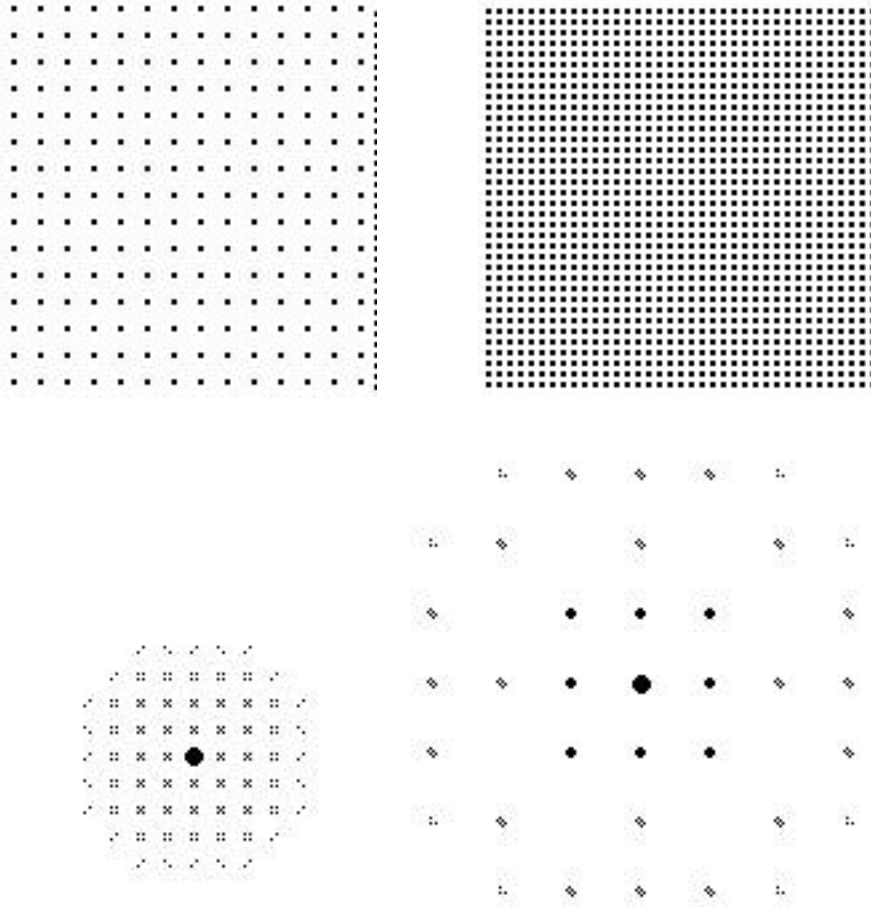
Notice that the only difference between the two patterns on the slides is that the second has a closer spacing between the printed squares. The resulting diffraction patterns have the exact same arrangement of dots, except the case where the dots were closer produced the more spread out diffraction pattern. Now consider two cases where the printed shapes have different symmetries.

Figures 3.17 Optical slide patterns with differing repeating unit shapes and their resulting diffraction patterns.
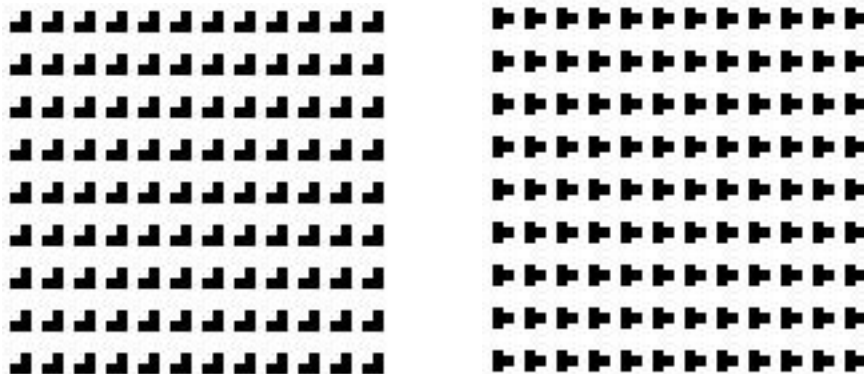
Now the arrangements of dots on the diffraction pattern itself changes. These examples show how slight differences in printed patterns lead to distinct changes in their diffraction patterns in the optical transform experiment. The same kind of information is obtained in the x-ray diffraction experiment which can ultimately lead to atomic structure determination.

3.6 What are the structures of graphite and carbon fibers, and what can they tell us?

The atomic structure of graphite has been determined by x-ray diffraction and other analytical techniques and is shown in Figure 3.18. Parallel sheets of hexagonal rings are spaced 3.35 Å apart. Bonds within the chickenwire-like sheets are very strong, but interactions between the sheets are weaker and can be broken easily. Given this atomic arrangement, we can begin to explain some of the properties of graphite. When the interactions between sheets break, the planes slide over one another. It is this sliding that makes graphite such a good lubricant, and also explains why it is a soft brittle substance.

Figure 3.18 Structure of graphite
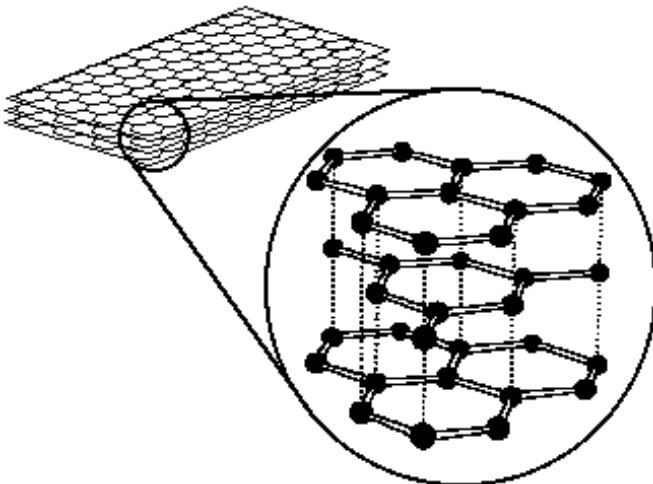
The great stability of graphite can be explained in terms of its bonding. From the interlocking hexagonal rings we see that each carbon is bonded to three other carbon atoms. We know that the bonding rules for carbon call for a total of four bonds. This suggests that there are two single and one double bond from each carbon. It is observed from the x-ray

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structure that all of the carbon bond lengths are equivalent. We encountered a similar situation with benzene. As with benzene, we can explain why the bond lengths do not alternate between single and double bond lengths by saying the bonds are in resonance. That is, the bonds are all a blending of single and double bonds. Having the double bond character spread evenly throughout the entire structure makes the sheets of atoms in graphite very stable.

So, what does the structure of carbon fiber look like? The truth is that it is very difficult to get an accurate description of the atomic structure of carbon fibers because these materials are amorphous. Chemists have used similar techniques to x-ray crystallography and can provide a qualitative description of the structure of carbon fibers. A very tiny piece of a carbon fiber would look like graphite, but carbon fibers have less long-range ordering. Instead of the planar layers of carbon atoms which are found in graphite, carbon fibers consist of ribbons of carbon atoms aligned parallel to the axis of the fibers. Although the ribbons are essentially parallel on the surfaces of a carbon fiber, the fiber's inner layers fold in a "hairpin" fashion as seen in Figure 3.19. This is a stark contrast to graphite in which the carbon sheets remain parallel on a long range scale. The layer planes along the axis of the carbon fiber are interlinked in a complex way (Figure 3.20). It is believed that the great strength of carbon fibers is due to the interlocking and folding of ribbons (the sheets of carbon atoms can not slide past each other as they did in graphite).

Figure 3.19 Model of how sheets are arranged in carbon fiber. Inset shows hexagonal array of carbon atoms.
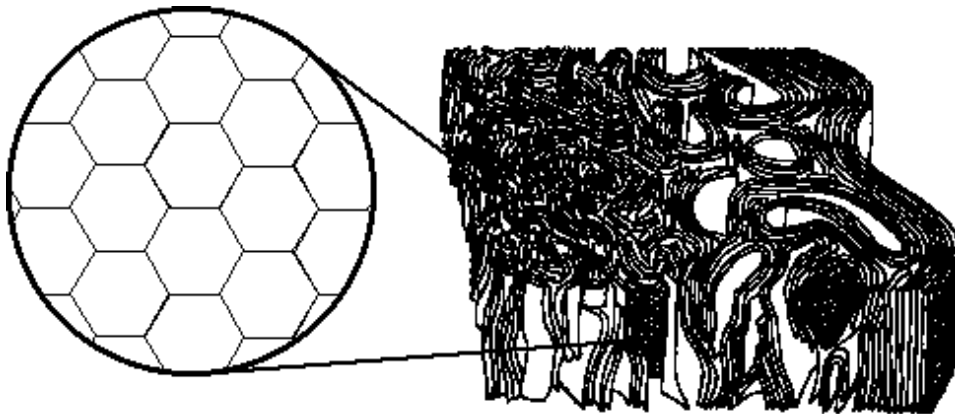
Figure 3.20 Interlinking nature of sheets of carbon atoms

3.7 So, why does carbon fiber convert to graphite at high temperatures?

Recall that graphite is an extremely stable form of carbon, due to the extensive resonance of single and double bonds. Carbon fibers are also stabilized by resonance, but because the structure is irregular, the effect is not as extensive. Ultimately, graphite is more stable than carbon fibers. The figure below shows a depiction of the reordering from carbon fibers to graphite as temperature is increased.

Figure 3.21 The transition from amorphous carbon to graphite
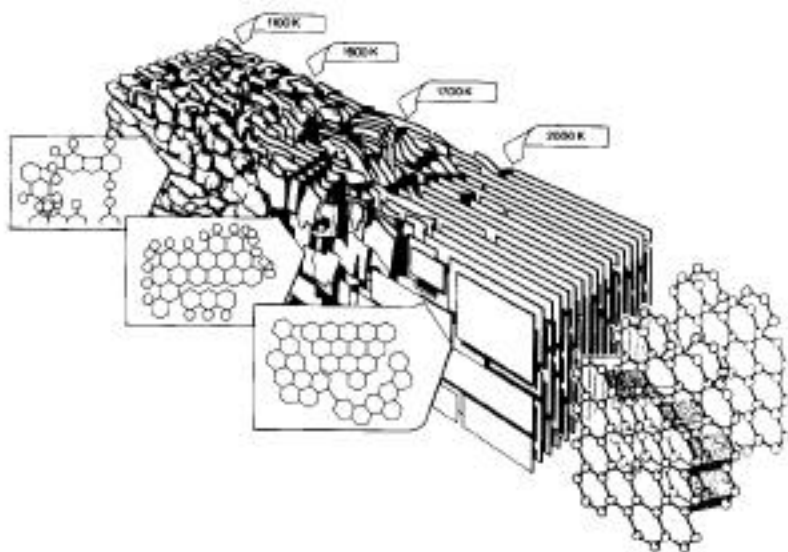
Why is temperature related to the reordering process? You may not have given much thought to what temperature physically represents. In a formal sense, temperature is a measure of the average kinetic energy in a system. So, when higher temperatures are applied to the carbon fibers, eventually enough energy is present to break the bonds in the carbon fibers, allowing them to reorganize to the more stable graphite form. We will return to a more detailed account of energetics in the next section concerning diamonds.

3.8 What are the other amorphous forms of carbon?

Although the crystalline forms of carbon (diamond, buckyball, and graphite) are often in the limelight, amorphous carbon materials cannot be overlooked. Along with carbon fibers, carbon black and activated carbon are also amorphous materials composed completely of carbon.

Carbon black is used as a pigment, in printer's ink, and as a filler for rubber goods. It is made by combustion of materials with a high carbon-content under oxygen-free conditions. Small parts of carbon black are like graphite, and the overall structure of carbon black is believed to consist of a folded version of the graphite network.

Activated carbon, prepared from the controlled pyrolysis of organic material, is useful because of its very high surface area. It is an efficient absorbent and finds applications as filters for fish tanks, drinking water, and air pollution. Chemists use activated carbon to remove impurities from reaction mixtures. Parts of the surfaces are believed to be covered with oxidation products which may account for some of the surface activity.

Graphite and Carbon Fibers References

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Buckyballs, Diamond, and Graphite

4.0 Diamond and Diamond Films

4.1 Why all the excitement?

Diamond is not an average substance. We are all familiar with the characteristics of jewelry-grade diamonds that make them among the most coveted gems: their extreme hardness (diamonds are the hardest substance known), resistance to tarnishing, exquisite clarity, clean facetting, and lack of color (unless they contain small amounts of metal impurities which can impart slight tints and may increase their value even more). Diamonds demonstrate distinctive properties of which you may not be aware: e.g., diamonds are excellent conductors of heat but poor conductors of electricity. The heat conductivity of diamond is so extraordinary that modern tests to determine whether a gem is a genuine diamond or a fake is based on measurement of the gem's heat conductivity.

Diamonds play another role in modern society: an industrial workhorse. The unusual properties of diamond makes it technologically very important. Because of its extreme hardness diamonds are excellent for surgical cutting tools and coatings on cutting tools for drilling, mining, and industrial productions. A rapidly emerging technology centers on thin films of diamond. Diamond films have been marketed on tweeters in stereo speakers and as scratch-proof coatings on watches. Diamond-coated windows for infrared-scanning systems and light-filtering masks are also on the market. Diamonds offer promise for new electronics materials. Diamonds containing small amounts of other elements (generally called dopants) dramatically change the electrical properties of the diamonds. Doped diamonds are semiconductors, much like the electronics based on silicon and compounds such as GaAs, in contrast to undoped diamonds which are non-conducting insulators. Diamond-based chips are desireable because they can operate at 1000 °C, handle very high power, and operate in highly radioactive environments. Figure 4.1 shows headlines from some of these current areas of interest in diamond films. Despite the tremendous promises of diamond film technology, applications of diamond films are not widespread yet.

Figure 4.1 Newspaper headlines

4.2 Why the holdup?

Why aren't all eyeglasses coated with diamond films to keep them from being scratched? Why aren't diamond-based electronics chips used to regulate the engines in all automobiles? Even Paul Simon's suggestion of "Diamonds on the Soles of Her Shoes" suggests a possible wear-limiting application. Put simply, large-area, high quality diamond films are very hard but hard to make. In 1990, diamond was named "molecule of the year" by Science magazine in recognition of the progress that has been made toward practical

synthesis of diamond films. Although diamond is not a molecule and the synthesis is still not ideal, the world market for synthetic diamonds was already between five hundred million and one billion dollars in 1990. As diamond film methodology improves, scientists predict that the value of the market for diamond films will be four to five billion dollars by the year 2000.

4.3 What is a diamond and how do we know?

On the basis of their macroscopic properties, it seems impropable that diamonds and graphite are made of exactly the same atoms. This begs the question, how do we know that diamonds are indeed carbon? Surprisingly, this has been known for over 200 years. In 1772 (before the signing of the Declaration of Independence) a talented French chemist, Antoine Lavoisier, burned diamond (ca. 150 milligrams) in a sealed container. Diamonds do not burn readily, so Lavoisier used the high heat provided by a large lens placed in the sunlight. By a simple analysis of the gases produced by burning, Lavoisier determined that the gas we now know as CO_2 was produced. Furthermore, the same amount of this gas was produced when 150 milligrams of amorphous carbon in the form of charcoal was burned. Thus, Lavoisier concluded that charcoal and diamond are the same. However Lavoisier was reluctant to publicize such a radical and counterintuitive result. It took more than 20 years before Lavoisier's conclusions were confirmed by Tenant, an English chemist. Let us examine Lavoisier's conclusion in the context of the times. Lavoisier's discovery predated Dalton's formulation that all matter is made of elements by 29 years and Mendeleev's formulation of the periodic table by almost 100 years. Our modern understanding of chemistry allows us to formulate Lavoisier's experiments in a compact way, the chemical equation.

$$C_{diamond} + O_2 \longrightarrow CO_2 + heat$$

$$C_{charcoal} + O_2 \longrightarrow CO_2 + heat$$

These equations indicate that burning either diamond or graphite causes the bonds of the reactants (the carbon material and dioxygen) to be rearranged to form the product (CO_2) and energy in the form of heat. In general, a chemical reaction involves changes in the bonding between atoms in going from reactants to products. Let's contrast these combustion equations with the analogous equation for burning buckyballs.

$$C_{60} + 60 O_2 \longrightarrow 60 CO_2 + heat$$

Note how the buckyball equation has a subscript of 60 on the carbon, indicating that this form of carbon is molecular. As a result, 60 dioxygen molecules are required to convert the sixty atoms of carbon in each buckyball into 60 molecules of CO_2. In a proper, balanced chemical equation the number and types of atoms on the reactant (left) side of the equation equal those on the product (right) side. Because heat is released in this chemical reaction, heat is written as a product. Reactions that generate heat are called exothermic.

## 4.4 How do stability and energy affect diamond formation?

Ever since the late eighteenth century experimenters have tried to synthesize diamond. Most of the earliest efforts (and indeed most of the industrial processes today) focused on converting graphite into diamond at high pressure. Under normal conditions, graphite is the most stable form of carbon because the bonds in graphite are stonger. In part this stability

can be attributed to resonance. Having the double bond character spread evenly throughout the entire structure adds extra stability to graphite. When several different forms of matter with the same composition exist, the most stable structure is called the thermodynamically favored form. Under the usual conditions of atmospheric pressure and room temperature, the more stable or thermodynamically favored form of carbon is graphite. However, at high pressure, diamond becomes more stable than graphite. We can understand why the preferred arrangement of atoms may change with pressure. On average the carbon atoms in diamond are closer together than the carbon atoms in graphite. As a result diamonds are more dense (that is, more mass in a given volume) than graphite. When a piece of graphite is subjected to high pressure, the external forces compress the graphite or push the carbon atoms closer together. Under these conditions it is more favorable for the carbon atoms to rearrange themselves into the diamond structure. If graphite is squished (very high pressure is applied) then the graphite will be transformed into diamond.

One common way of depicting the relative stability of different materials is by using an energy diagram. It is generally true that more stable materials have lower potential energies. Figure 4.2 shows an energy diagram for the conversion between diamond and graphite. Compounds that are more stable are placed lower on the diagram (i.e., at lower potential energy) while the less stable compounds (higher potential energy compounds) are higher on the diagram. The x-axis in the energy diagram is the reaction coordinate and indicates the progress of the reaction. Thus, moving from left to right in Figure 4.2 shows the conversion of graphite to diamond. Because the density changes in coverting from graphite to diamond, one could quantitate the reaction coordinate for this transformation with the density.

Figure 4.2 Energy diagram for conversion of graphite to diamond and diamond burning
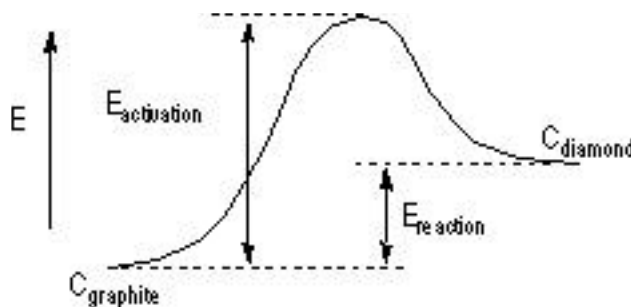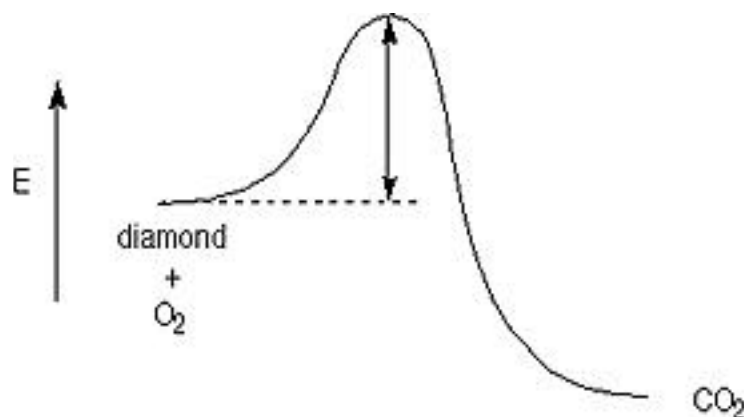
Because graphite is lower in energy than diamond, the conversion requires addition of energy to the system. Such reactions are called endothermic reactions. Contrast this situation with the burning of carbon allotropes; combustion reactions are exothermic. To a good approximation, we can rationalize the endothermicity of the graphite to diamond conversion by comparing the relative bond strengths. On average the C-C bonds of graphite are stronger than the bonds of diamond. If we were to turn our perspective around and look at the conversion of diamond to graphite, we would say the reaction is exothermic. That is, it is energetically more favorable for diamonds to simply turn into graphite.

4.5 Why don't diamond gems turn into graphite (or burst into flames)?

If carbon atoms would rather be arranged as the graphite structure rather than diamond, why don't these priceless gems discolor and crumble into low value graphite powder? Examine Figure 4.2. In order to trace from diamond and graphite one moves from right to left on the diagram. Notice that a high energy barrier (like a hill) must be passed over. The top of this barrier is called the transition state. The transition state represents the highest energy structure involved in a reaction. It is intrinsically unstable and can't be isolated. What might the transition state for the diamond to graphite conversion look like? We might imagine that it is a structure in which the some of the C-C bonds are stretched and the carbon atoms are beginning to arrange into the planes of graphite. At the transition state these planes will be buckled due to stretched bonds between the ultimately non-bonded planes of carbon atoms of graphite. As a result the stabilization afforded by four single C-C bonds at each C atom has begun to be lost, but the the resonance stabilization of graphite has not been fully realized. As a result the C-C bonds in the transition state on average are weaker than the bonds of either diamond or graphite. Therefore, the potential energy of the transition state is greater than that of reactant and product. The energy difference between the starting material (graphite) and the transition state is the activation energy, denoted by the symbol Eact. Note that the value of the activation energy depends on the direction of the reaction; the activation energy for the diamond to graphite transformation is lower than that for the graphite to diamond transformation. If the activation energy for a reaction is high, the reaction will occur slowly. The rate of reaction is determined by how frequently the atoms collect enough energy to "climb" over the hill. Therefore we expect that the higher the barrier the slower the reaction. Also we expect that increasing the temperature, or kinetic

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energy of the atoms, will increase the reaction rate because the atoms will collect the energy needed to "climb" the barrier more frequently.

Note that the rate of reaction is not determined by the reaction thermodynamics. An exothermic reaction can be very slow if the activation energy is high and an endothermic reaction can be fast if the activation energy is low. Because the activation energy in the reaction converting diamond to grapthite is high, much energy in the form of high temperature is needed to convert the starting materials (diamond) to the transition state so that the product (graphite) can be formed. The potential energy change of the reaction as a whole is the difference in energy between the starting material (diamond) and the product (graphite). The potential energy change of this reaction is -2,900 Joules for every 12.01 g of carbon. A Joule is a unit of energy that corresponds to the energy needed to lift 2 kg of mass by 10 cm in the presence of the earth's gravitational field. By convention, the plus sign indicates that the reaction is endothermic (or uphill) and a negative sign for the potential energy change indicates that the reaction is exothermic. Although diamonds convert to graphite exothermically, the reaction is slow due to the high activation energy; diamonds stored at ambient temperatures do not crumble into black graphite.

4.6 How do diamonds form in nature?

Diamonds are formed deep inside the earth's interior where crushing pressure and blistering heat work together to create the diamond lattice. Although scientists have long puzzled about how diamonds are transported to the earth's surface, a recent discovery of diamonds in Canada may have shed some light on this issue (Figure 4.3). Scientists now believe that narrow volcanic pipes running down into the earth's interior allowed diamonds to be transported via violent eruptions to the earth's surface. The eruptions were so fast and so violent that the diamonds were coughed straight to the surface. Although the pressure release as the diamonds rose to the surface conceivably could have allowed for transformation to graphite, the explosions were believed to be so fast that the diamonds reached cool temperatures at the surface quickly. Due to the rapid cooling, the back-transformation of the diamonds to more stable graphite was too slow to occuren route . Slow kinetics for the diamond-to-graphite transformation allowed the less stable allotrope of carbon to make it to the earth's surface.

Figure 4.3 Newspaper article

Clues Emerge to Rich Lodes of Diamonds

4.7 How are synthetic diamond stones made?

Synthetic diamonds can be formed in much the same way as natural diamonds; graphite is heated to temperatures exceeding 1500 C at about 60,000 atmospheres of pressure (that is a pressure that is 60,000 times greater than the pressure exerted by our atmosphere). Even at these temperatures and pressures, diamond formation is not easy. Addition of small amounts of the metallic elements, iron or nickel, speeds up the reaction. Why are metals added? The role of the metallic additives is to reduce the amount of energy needed to form diamond from graphite. Figure 4.4 shows an energy diagram for the conversion of graphite to diamond with and without metals. The metal in the reaction with the lower activation energy acts as a catalyst in the reaction. A catalyst is a substance that affects the rate of a reaction without being consumed by the overall reaction process. Chemists say that catalysts do not affect the thermodynamics of the reaction, rather they affect the kinetics. In

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diamond formation, the metal catalysts are trapped in the diamond lattice as it forms. This is why many synthetic diamonds are colored while naturally occuring diamonds which lack impurities are colorless.

Figure 4.4 Catalyst Energy Diagram
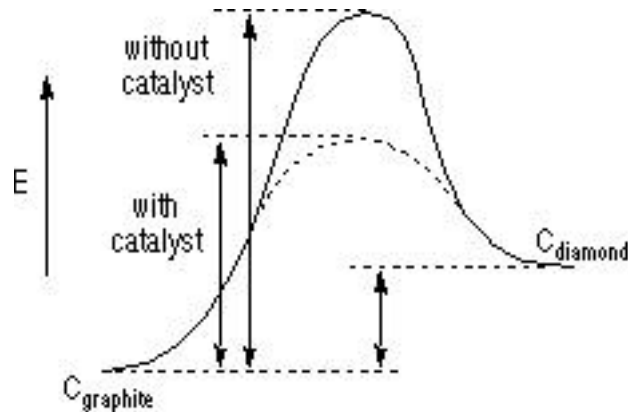
It has recently been shown that, if buckminsterfullerene is used instead of graphite, lower pressure (20+5 Gpa or about 20,000 atmospheres) and ambient temperature is enough to cause the transformation to diamond. This synthesis is mild enough that catalyts are not necessary. The synthesis of diamonds from buckyballs differs their synthesis from graphite in two important ways. First, the buckyball conversion to diamond (and to graphite) is exothermic. The C-C bonds of buckyball are weaker than those of either diamond or graphite. Second, the activation energy for the buckyball conversion is much lower than that for graphite. Both features combine to allow a low temperature pathway.

4.8 Why do diamond stones cleave when struck by a Jeweler's chisel?

The extensive network of carbon atoms makes diamond a very hard material. The only material that can cut diamond is diamond. Despite its hardness, if diamond is hit at just the right angle with a chisel, it will cleave to form two stones with perfectly flat faces. Until better tools were available, jewelers relied upon this ability to break diamonds with the sharp raps of a hammered chisel to make diamonds of desired sizes and shapes.

Why do diamonds break when force is applied at certain angles? If enough pressure is added to one plane of carbon atoms in a diamond, then that plane of atoms will begin to move (Figure 4.5). Essentially, the mechanical force will cause some of the C-C bonds made by atoms in this plane to stretch and some to compress from their normal values. As the atoms are further displaced the interactions eventually become so undesireable that the diamond splits apart along the planes where the bond stretching and compression is most undesirable. The key to obtaining a clean break is to orient the chisel such that force is applied along the direction of a plane of carbon atoms.

Figure 4.5 Diamond Cleavage.
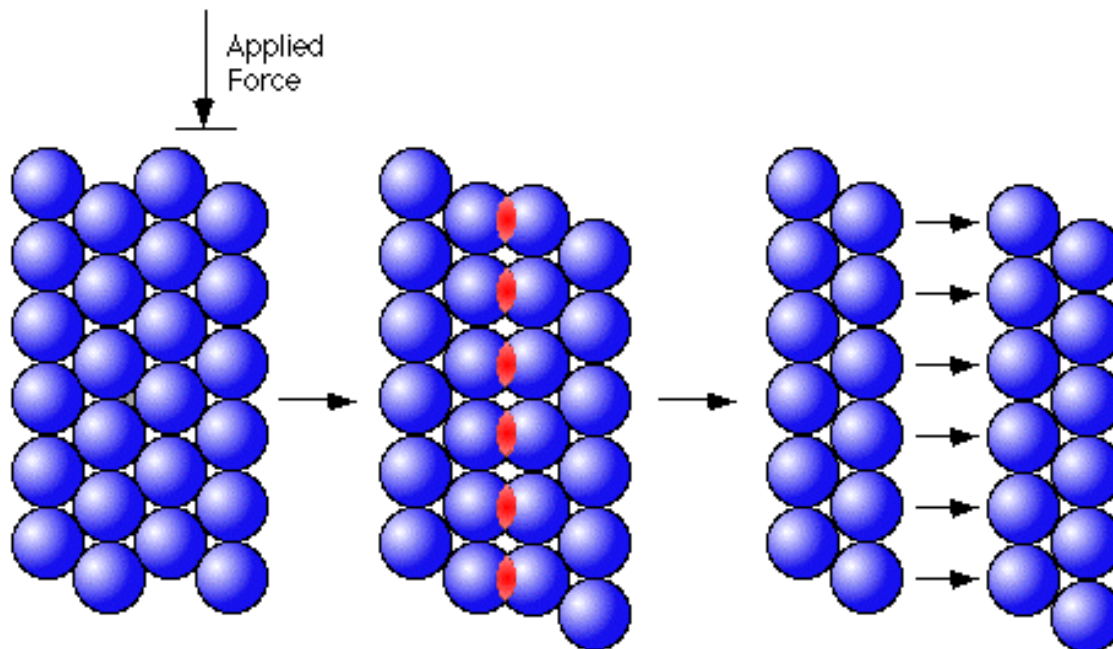
4.9 New diamond thin film technology

For many years, only high pressure synthesis of diamond from graphite was considered possible. However, it has recently been discovered that diamond films can be made at low pressures if one adopts a different strategy. Rather than starting with graphite, the reactant is methane (CH_4), a simple molecule containing carbon and hydrogen atoms. Note that methane satisfies the bonding rules of carbon by having four bonds to carbon and one to each hydrogen. In this reaction, methane is decomposed into diamond rather than graphite even though graphite is more stable. How can this occur? In a reaction, formation of the thermodynamically favored product (graphite) can be slower than formation of a less stable product. When more than one product can be formed, the product that forms faster is called the kinetic product. Such a situation occurs for the methane decomposition because the activation energy for forming diamond films from methane is lower than the activation energy for making graphite. Such a situation is not uncommon. Indeed, when an ordinary candle burns, an amorphous, sooty carbon form is synthesized. This soot is higher in energy than graphite, but once formed it is very slow to convert further to graphite. The decomposition of methane to give diamond films is similar. Figure 4.6 depicts the reaction energy profiles for a situation in which the kinetic product is not the thermodynamic product.

Figure 4.6 Energy diagram displaying kinetic vs thermodynamic control.
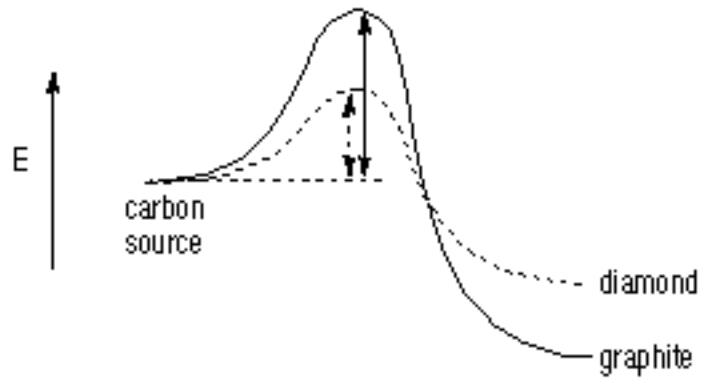
Synthesis of diamond films at low temperature must be controlled so that graphite formation does not compete with diamond formation. Although the reasons are not fully understood, the most successful way to keep graphite from forming is to form the diamond under a constant stream of hydrogen. CVD, or chemical vapor deposition, is the most common low temperature method for synthesizing diamond films. Figure 4.7 shows a picture of the deposition vacuum chamber for CVD growth of diamond films. Inside the chamber is a tungsten filament source of intense heat. This heat decomposes a carbon source such as methane as it is carried through the chamber on a stream of hydrogen. Carbon fragments are deposited on target surfaces at 600 to 900 °C that are also in the chamber. It appears that the role of hydrogen atoms may be to etch away any graphite that is formed so that only diamond crystals can grow. A diamond film made of countless tiny diamond crystals builds up slowly. The target surface can be silicon, graphite, diamond or tiny diamond chips, or even C_{70}. Microwave discharges and oxyacetylene torches have been used in place of the tungsten filament heat source, and the methane gas carbon source has recently been replaced by buckyballs to give high quality diamond films.

Figure 4.7 Deposition Chamber and Schematic Diagram

precursor gases
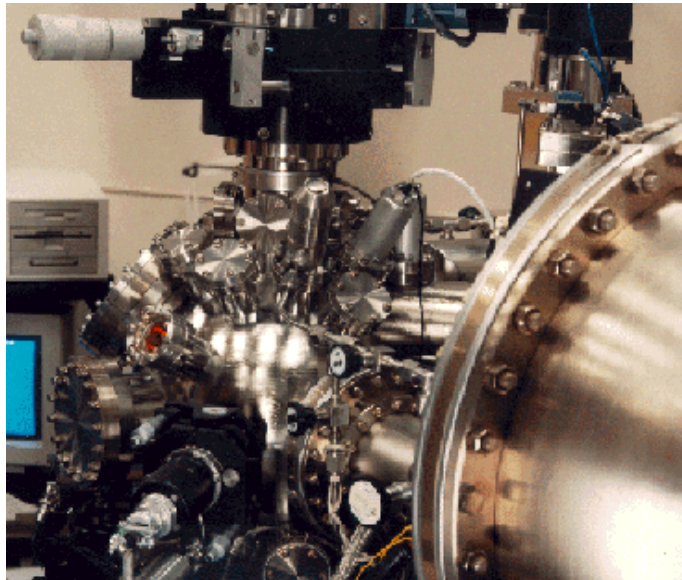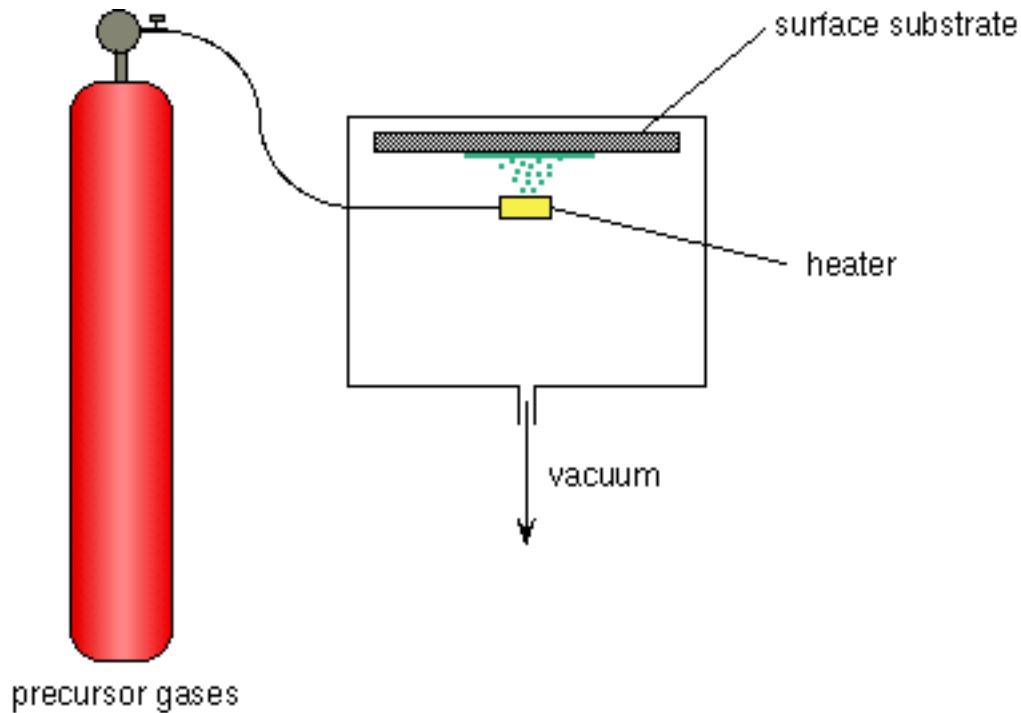
Due to limitations of the CVD method, scientists are searching for lower temperature and pressure methods for the synthesis of flawless diamond films. The CVD process requires high temperatures and pressures and produces a diamond-like film where many small diamond crystals are aligned together rather than one large single crystal of diamond. As a result many materials cannot be coated with diamond films because they will melt or decompose in the coating process. A potential alternate process involves passing carbon soot slowly through a laser beam. This process has been shown to make diamond films. An intriguing new process takes a polymeric carbon source called poly(phenylcarbyne) and heats it in a furnace to produce a diamond-like film (Figure 4.8).

Figure 4.8 Newspaper article.

Tossing Plastic Into an Oven, Scientists Cook Up Diamond

By MALCOLM W. BROWNE

By cooking plastic in an ordinary oven scientists at Pennsylvania State

much more efficiently than silicon.
Diamond is also the hardest of all

The first single crystal film was grown in 1991 by using an accelerator to ram carbon ions into a copper surface at a density of about one billion ions per square centimeter. Then the carbon-laden copper was blasted with a series of powerful laser bursts which rapidly liquified the topmost copper layer. Once the laser pulses stopped, the copper solidified and the carbon atoms aligned on its surface to make a diamond film. The film was too small for any electronic applications, but at 100 square microns in area it was a big advance.

4.10 What exactly are diamond films?

Diamond films are manmade replicas of the diamonds made by nature. Like natural diamonds, they have an extensive lattice or orderly array of carbon atoms bonded together in a tetrahedral arrangement. Each carbon has four bonds to neighboring carbons. (Figure 4.9) Diamond films, however, are not as ordered as natural diamonds. If they are made at high pressure, they include metal impurities that create slight imperfections in the crystal lattice. If diamond films are made by CVD, they are actually many tiny crystals of diamond that have grown against each other. These diamond films can be grown to be at least twelve inches long, and their thickness can vary from just a few nanometers to many microns or even larger. Which technique is used to grow the diamond film affects the size of the diamond more than anything else. Figure 4.10 shows several examples of diamond films.
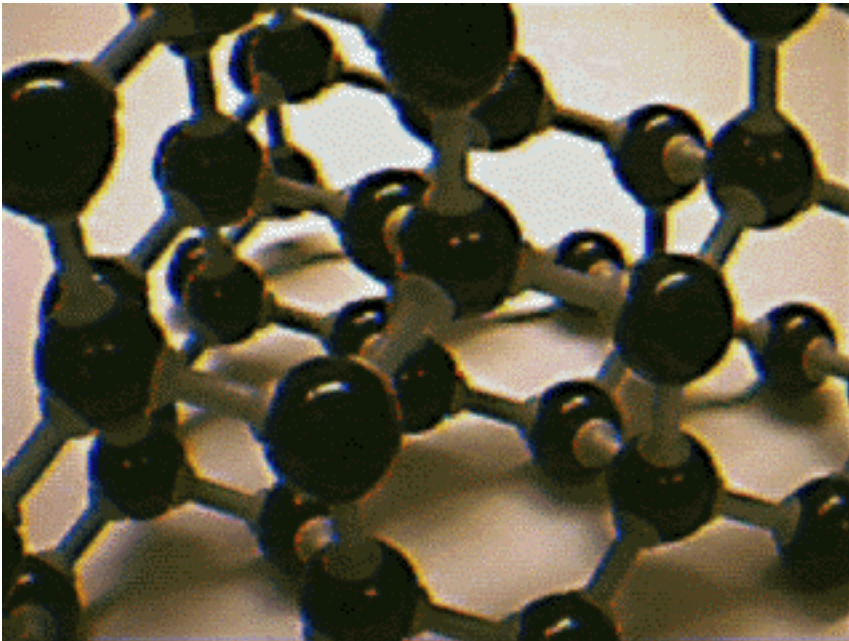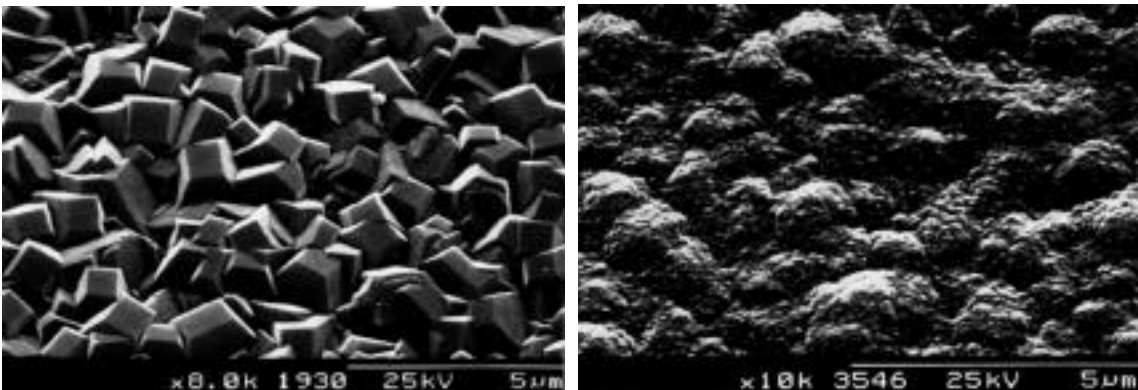
Figure 4.9 Diamond lattice

Figure 4.10 Diamond films

Even though diamond films are not as ordered as natural diamonds, they mostly retain the diamond lattice of natural diamonds. It is not surprising, then, that they also retain the

properties of natural diamonds. As in natural diamonds, the extensive network of bonded tetrahedral carbon atoms make diamond films very strong and difficult to break or compress. Also, the diamond lattice of diamond films spaces atoms at an ideal distance to serve as connections in electrical circuitry if metal impurities have been included during diamond growth.

4.11 Will materials harder than diamonds soon be available?

Although many big advances have been made, several problems still keep diamond films from being useful as electrical chips and other devices. One major obstacle is expense. CVD diamonds cost well over a hundred dollars a carat to produce. (High pressure diamonds sell for slightly over one dollar a carat, but they contain too many flaws for electronic circuitry and many other applications.) Before CVD diamond films find wide practical use, better adhesion to the substrate must be achieved and lower temperature processes must be developed.

Recent work with diamond films has led to synthesis of similar compounds composed of carbon and nitrogen atoms. In 1989, computer calculations suggested that a compound composed of carbon and nitrogen with the formula C_3N_4 in a diamond-like structure (Figure 4.11) would be even harder than diamond if it could be made. It wasn't until 1993 that the synthesis of this compound was achieved, and still only very small amounts of C_3N_4 have been made. Because only small quantities of this material, commonly called carbon nitride, are available, it remains to be proven that the substance is indeed harder than diamond.

Figure 4.11 The structure of Carbon Nitride (Chem and Eng. News)
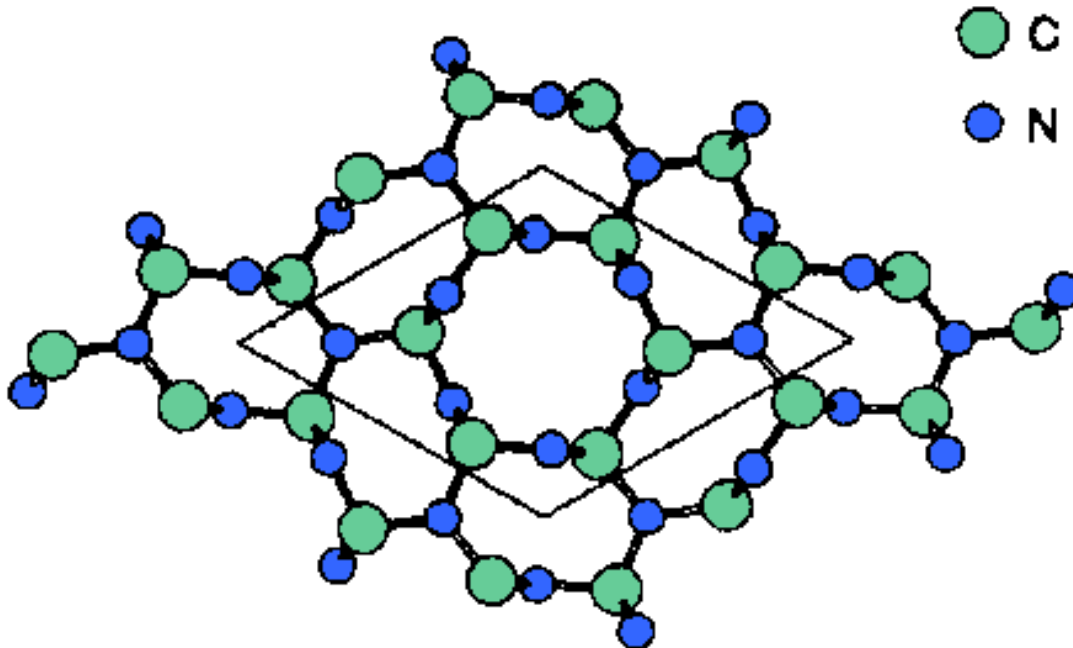
In order to make a compound harder than diamond, the compound should have a denser packing of tightly bound atoms than diamond. This suggests that the material must have bonds that shorter and stronger than those in diamond. The idea that a carbon-nitrogen

mixture might allow for very short bonds and very hard materials springs from the fact that silicon-nitrogen mixtures of the same type are known to be very strong and very hard. They actually rival diamond in hardness. Recall that elements in the same row of the periodic table have similar properties; because silicon is in the same row on the periodic table as carbon, the properties of these elements are similar. Because silicon is lower in the periodic table than carbon, it is larger. The larger atoms of silicon cannot fit together as closely as carbon atoms can, so their bonds must be longer. Carbon atoms bonded to nitrogen can have shorter bonds than silicon atoms bonded to nitrogen simply because they are smaller. The shorter the bond, the more energy is required to break the bond and the harder the material.

If materials such as C_3N_4 truly are harder than diamond, then the future of diamond films will also include films of this material. Whether diamond films or related films will be most applicable remains to be seen. In any event, diamond films are an exciting new area with potential that has only begun to be realized, and use of diamond films is expected to skyrocket in the future.

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Glossary

Activation energy
The activation energy is the amount of energy that must be placed into a system to enable the reactants to turn into products. On an energy diagram, this is the difference in energy between the reactants and the transition state. The activation energy is the energy barrier that must be overcome for the reaction to proceed.

Active site
Catalysts can be complicated molecules or surfaces with many different kinds of atoms and sites. Often the catalytic event is associated with just one of these sites; such sites are called active sites. For example, enzymes are biological molecules that usually have well-defined regions of the molecule that interact with the reactants during the catalytic reaction. Many poisons prevent normal enzyme function because they have the right structure to bind to particular enzymes in place of the normal reactants. Some drugs are designed to do this to stop unwanted reactions from occurring. When some molecule other than the starting material is bound into the active site, then the reaction cannot occur.

Allotrope
Atoms can be connected differently, even if they are all atoms of the same element. These different bonding arrangements allow for different forms of matter to be made from a single type of atom. Different forms of matter made in this way are called allotropes. For example, ozone (O_3) and dioxygen (O_2) are allotropes of the element oxygen. Also, diamond, buckyball, and graphite are allotropes of carbon.

Amorphous
Amorphous substances have no definite repeating pattern in their atomic structures. There may be small regions of order, but, overall there is considerable disorder. Most substances we contact on a day to day basis are amorphous.

Atom
All matter is comprised of tiny particles called atoms. An atom is the smallest piece of an element that still retains all the properties of the element. Atoms themselves are made up of smaller particles called protons, electrons, and neutrons. The protons and neutrons reside in the nucleus of the atom and make up most of the mass of an atom. The electrons that surround the nucleus contribute only a small amount to the mass of the atom, but comprise most of the volume.

Atomic mass
The atomic mass represents the average mass of an atom and is found on the periodic table below the symbol of the element in each box. For elements with only one isotope, this mass is the same as the mass of each atom. However, for elements with more than one isotope, not all atoms will have the same mass. Then, the atomic mass is the average mass for all the isotopes of the element.

Atomic mass unit (amu)
Protons and neutrons each weigh about one atomic mass unit. The atomic mass unit is defined as exactly 1/12th the mass of a carbon-12 atom, or 1.66057×10^{-24} g. Atomic mass units allow for determination of relative atomic masses of atoms for different elements.

Atomic number

The atomic number is the total number of protons in an atom. Each element has a unique atomic number, which is written on the periodic table above the symbol of each element.

Ball-and-stick model
One way to represent molecules is the ball-and-stick representation. Each atom is represented by a ball, and each bond between atoms is represented by a stick. Hydrogen atoms are not shown. Although the atoms are proportionally too small compared to the bondlengths shown in this model, the bonding pattern is clearly visible.

Bond dissociation energy
The bond dissociation energy is the amount of energy required to break a bond between two atoms. Higher bond dissociation energies correspond to stronger bonds.

Catalyst
Chemicals that are not consumed in a reaction, but, that speed up the reaction rate are called catalysts. Catalysts aid to form a transition state that is lower in energy than the transition state without the catalyst. Since the barrier to the reaction is lower, the reaction rate increases in the presence of catalysts.

Cation
An atom that loses an electron becomes a positively charged ion called a cation.

Chemical bond
A chemical bond is a strong attractive force between two atoms. This force holds the two atoms close together in space.

Chemical equation
A chemical equation is a method of expressing chemical reactions in a succinct way. The reactants involved are placed on the left, and the products are placed on the right. Usually an arrow seperates the reactants and products. Oftentimes, specific reaction conditions (temperature, pressure, catalyst, etc.) are placed above or below the arrow symbol.

Chemical vapor deposition
Chemical vapor deposition (CVD) is a method for growing solids in which a gaseous precursor (containing fragments of the desired solid) is decomposed and deposited onto a desired surface. CVD is one of the most powerful synthetic methods in material science due to its remarkable flexibility. A variety of surfaces can be coated, and very thin layers can be applied if necessary.

Combustion
Combustion reactions involve elements or compounds burning in the presence of dioxygen. The burning of the octane in gasoline is an example of combustion.

Constructive interference
Constructive interference occurs when two waves overlap such that they are in phase (the troughs and peaks of the two waves coincide). Note, for this to occur down the entire wave, the two waves must have the same wavelength. When constructive interference occurs, the amplitude of the resulting wave is the sum of the two waves. So, if the original two waves had the same amplitude, the resulting wave would have twice their amplitude.

Covalent network solid
Covalent network solids are structures in which the atoms are held together by the sharing of electrons between atoms (called covalent bonds). Network solids have an undefined number of atoms in their structure, and often extend into huge macromolecules.

Crystalline solid
Crystalline solids have the same repeating unit throughout their entire structure. Crystalline solids can be composed of individual molecules, or an extending network of atoms.

Derivative
A derivative of a compound resembles the original compound, except that some modifications in atomic structure are evident. Usually, derivatization of a molecule involves altering part of it slightly or adding a new part to the original compound.

Destructive interference
Destructive interference occurs when two waves overlap such that they are completely out of phase (the troughs and peaks of the two waves are opposed to each other). Note, for this to occur down the entire wave, the two waves must have the same wavelength. When destructive interference occurs, the two waves are subtracted from each other. If the two waves have equal amplitude before colliding they will completely cancel each other.

Diffraction pattern
When light is scattered by a regular array the resulting combinations of constructive and destructive wave interference leads to a diffraction pattern. In x-ray crystallography, an analysis of the diffraction patterns can lead to a determination of the exact positioning of atoms in the repeating unit of the given crystal.

Double bonds
Two pairs of electrons are shared between two atoms in a double bond. In many molecular representations, double bonds are drawn as two lines between the bonded atoms. Double bonds are shorter and stronger than double bonds.

Electromagnetic radiation
Energy that travels through space is electromagnetic radiation. Electromagnetic radiation exhibits both wave and particulate properties (often called the dual nature of light). All electromagnetic radiation consists of oscillating electric and magnetic fields moving at the speed of light, but the wavelength of the radiation can vary widely. The wavelength is inversely proportional to its energy . Radio waves have long frequencies (and low energy) while x-rays have short frequencies (and high energy).

Electron
Electrons are subatomic particles. They are located outside the nucleus and comprise a vast majority of an atom's volume. Electrons are negatively charged, so they are opposite in sign to protons. The magnitude of the two charges, however, is the same. Electrons are the lightest subatomic particles and have a mass of about 1/2000th the mass of a proton or neutron.

Electronic structure
The electronic structure or configuration of an atom is a cataloging of the distribution of electrons about the nuclei. Electrons are located around the atom's nucleus, and the electronic structure describes where these electrons are most likely to be found.

Element
An element is matter that is made of only one type of building block or atom. Therefore, all of the atoms in an element have the same number of protons. An element cannot be decomposed into simpler substances by ordinary chemical means. Only a small number of elements exist; 110 different elements are known at this time. Examples of elements include carbon, iron, hydrogen, sodium, and uranium.

Endothermic
Reactions in which heat flows from the surroundings into the system are called endothermic. Since we observe the "surroundings," endothermic reactions are often detected by noting a decrease in temperature.

Energy diagram
An energy diagram is a convenient way of depicting the thermodynamics of reactions. Typically, the y-axis is given in units of energy, and the x-axis is defined as the reaction coordinate. The reaction coordinate quantifies the progress of the reaction. Usually, the reactants are drawn at a certain level on the left side of the reaction coordinate, and the products are given on the right. A curved line connects the reactants and the products and shows the energies of any intermediates and/or transition states present in the reaction.

Exothermic
Reactions in which heat flows from the system to the surroundings are called exothermic. We can often detect exothermic reactions by observing an increase in temperature.

Heat of reaction
The heat of reaction describes the 'enthalpy' that is given off or absorbed during a reaction. If the pressure of the reaction remains constant, you can think of enthalpy as simply being heat.

In phase
When the peaks and troughs of two waves directly match each other they are said to be in phase. When "in phase" waves of the same amplitude collide, the result is a new wave with twice the amplitude of the original two. This kind of behavior is often called constructive interference.

Inert gases
The last column of the periodic table lists the inert or noble gases. In these gases, the outer shell of electrons in each atom is completely filled. This makes these elements very unreactive. This is why these gases are called inert or noble gases.

Ion
An ion is an electrically charged atom or group of atoms. An atom that gains an electron becomes a negatively charged ion called an anion. An atom that loses an electron becomes a positively charged ion or a cation.

Ionize
An atom is ionized when one of its electrons is ejected. This can occur when the atom is bombarded with other small particles (even other electrons) and one electron is expelled from the atom. This leaves the atom as a charged particle called an ion.

Isotope
Isotopes are atoms of the same element that have different masses. This is because these atoms have different numbers of neutrons in their nuclei, although the atomic number (the number of protons in each atom) for isotopes remains the same.

Joule
A joule is the standard unit for energy. Another common energy unit is the calorie. When we think of dietary calories, we are really thinking of Calories with a capital "C" which contain 1000 calories. Each Calorie contains 4,184 joules.

Kinetic

The study of the rates of chemical reactions is termed kinetics. The product that is formed the quickest is referred to as the kinetic product. The kinetic product need not be the most thermodynamically stable product. When a kinetic product is not the thermodynamic product, it will eventually convert to the more stable form.

Lattice

The positioning of atoms in crystalline solids is referred to as the lattice. The smallest division of the lattice that can still be used to represent the entire structure is called the unit cell.

Lewis dot

Lewis dot structures of atoms use dots to represent valence electrons. The first four dots are arranged on the four sides of the elemental symbol, and any remaining dots are arranged pairwise with those already present. Lewis dot structures of molecules also use dots to represent valence electrons. With molecules, the dots between molecules represent bonds. All of the atoms in a molecule are arranged so that eight dots or electrons surround each atom (except for hydrogen which only needs two electrons and boron which only needs six electrons).

Macromolecules

Macromolecule is a general term to describe a "huge molecule." Although there is no set criteria for macromolecules, they are generally considered to be structures with over 1000 atoms. DNA and proteins are common examples of macromolecules.

Magnetic Resonance Imaging (MRI)

MRI gives physiological information by showing images of regions with contrasting water content, such as different areas of the brain. MRI is a form of Nuclear Magnetic Resonance spectroscopy and uses the same basic principles.

Mass spectrometer

A mass spectrometer measures the masses of molecules and atoms by volatilizing and then ionizing them. The ions are then separated according to their mass-to-charge ratio.

Mass-to-charge ratio

The mass-to-charge ratio, denoted m/e, is the unit used by mass spectrometers to separate ions. It is simply a ratio of the mass to the size of the electronic charge for any given molecular ion or fragment. Since the charge is usually +1, the mass and the mass-to-charge ratio are often the same.

Melting Point

The temperature at which a solid changes to a liquid is called the melting point. A completely pure crystalline substance would have an exact temperature at which it melts. Impure substances and amorphous substances will begin melting at one temperature and end at another. For these substances the term "melting range" is more appropriate.

Molecular

Molecular substances are composed of discrete molecules. An exact molecular formula can be written for such substances since each molecule must be composed of the same number and type of atoms (for example, water is H_2O). Network solids can not have an exact molecular formula since an undefined number of atoms are involved in each structure.

Molecular extended lattice

Many crystalline solids are composed of individual molecules that are packed together in a regular repeating fashion. There are no bonds between the molecules, instead they are held to each other by weaker intermolecular forces.

Molecule
A molecule is a collection of atoms held together by chemical bonds into a discrete, finite structure. One way molecules can be represented is by a chemical formula where symbols for the elements are used to indicate the types of atoms present and subscripts are used to indicate the relative numbers of atoms. For example, buckyball can be written as C_{60}.

Neutron
Like protons, neutrons weigh one atomic mass unit and are housed in the nucleus of an atom. Unlike both protons and electrons, neutrons are neutral (without charge) subatomic particles.

NMR active nuclei
Atoms that have odd numbers of protons (^2H, ^{14}N) or odd numbers of protons and neutrons (^1H, ^{15}N, ^{31}P, ^{13}C, ^{19}F, ^{17}O) have nuclei that behave like tiny, spinning bar magnets. These atoms have NMR active nuclei.

Noble gases
The last column of the periodic table lists the inert or noble gases. In these gases, the outer shell of electrons in each atom is completely filled, making them very unreactive. Because of their unreactive nature, these gases are often called inert, even "noble" gases.

Nuclear magnetic resonance spectrometer
A nuclear magnetic resonance (NMR) spectrometer measures the energy changes associated with changes of orientation of nuclear spins in a molecule. These changes depend on the electronic environment of the nuceli and are obtained as radio wave frequencies in NMR spectroscopy. NMR spectrometers are very useful in determining the structures of molecules.

Nuclear spins
Nuclei that are NMR active are often called nuclear spins, or spins for short.

Nucleus
The nucleus of an atom is comprised of protons and neutrons. Although the dimensions of the nucleus are very small, most of the mass of an atom comes from the nucleus. If we were to blow up the scale of an atom to an indoor sports arena, the nucleus would have a volume comparable to a marble in the center of the arena, but, its mass would be much greater than the rest of the arena combined!

Octet rule
When atoms form bonds, they do so in a manner that will complete their valence shells. For most elements, a completed valence shell consists of eight electrons. The octet rule is the tendency of atoms in molecules to have eight electrons in their valence shells. Some common elements that do not follow the octet rule are hydrogen (H) which needs only two electrons to complete its shell, and boron (B) which only needs six electrons.

Out of phase
When the peaks from one wave are exactly matched by the troughs of a second wave, the two waves are said to be out of phase. If these two waves collide and have the same amplitude, they will mutually cancel. That is, for every positive point along one wave, the second wave would have a negative counterpart of the same magnitude. When these points

are added together, they cancel leaving no net amplitude. This kind of phenomena is often called destructive interference.

Oxidation
Oxidation is a common type of chemical reaction in which electrons are formally transfered between atoms in the reactants and products. When iron rusts it is undergoing an oxidation reaction.

Periodic Table
The periodic table is an arrangement of all the elements. The elements are listed in order of increasing atomic number. Elements listed in the same column on the periodic table have the same number of valence electrons and have similar properties while elements in the same row on the periodic table (called periods) all have the same valence shell. Each box on the periodic table contains information including the elemental symbol, the atomic number, and the average mass in amus of one atom of the element.

Polymer
Molecules which are composed of linked repeating units (called monomers) are refered to as polymers. Polymers are the basis for many plastics and synthetic fibers such as teflon and polyester.

Proton
Protons and neutrons are the building blocks of atomic nuclei. Protons are positively charged particles that weigh one atomic mass unit (amu) or 1.66×10^{-24} g. The positive charge of the proton is equal in size but opposite in sign to the negative charge of an electron.

Resonance
When a molecule is best described as a superposition of various resonance structures, it is often said that the molecule is in resonance. It is important not to confuse this kind of resonance with the completely different usage in nuclear magnetic resonance (NMR).

Resonance structures
Sometimes a molecule cannot be depicted by any one Lewis structure. Instead, the molecule may be a superposition of two or more structures. In this case, the electron structure of a molecule is described by writing all possible electron-dot formulas. These are called resonance structures, and the actual structure is a combination of all the structures that can be drawn.

Shells
In an atom, shells are distances from the nucleus. The shells that are closest to the nucleus are filled first, and then the higher energy shells farther from the nucleus are filled. In the periodic table, elements in the same row all have the same number of shells of electrons. Hydrogen and helium (H and He) have only one shell of electrons, elements such as lithium in the second row have two shells of electrons, elements such as sodium in the third row have three shells and so forth.

Single bonds
In a single bond, a single pair of electrons is shared between two atoms. A single bond is often represented by a line between two atoms. Single bonds are longer and weaker than double bonds.

Spin flip

Nuclear spins positioned in the field of a large magnet align either with (parallel to) or against (antiparallel to) the external field. Orientation with the external field is slightly lower in energy than orientation against the field, so there are slightly more spins aligned with the field. When the oriented nuclei are irradiated with electromagnetic radiation of the proper frequency, energy absorption occurs, and the lower energy state "spin-flips" to the higher energy state.

Spins
Nuclei that are NMR active are often called nuclear spins, or spins for short.

Subatomic particle
Although an atom is the smallest complete piece of an element, the atom itself is made up of even smaller components known as subatomic particles. The three subatomic particles in atoms are protons, electrons, and neutrons. Elements are defined by the number of protons in their atoms.

Superconductor
A superconductor is a material that conducts electricity with no wasted heat energy. Normal metals such as copper conduct electricity with up to 20% of the total energy wasted in the transmission of a current because of resistance heating of the wires.

Superposition
A hybrid structure is one that is derived from two different parent structures. This structure is not exactly like either of the two structures is came from. Instead, it is a combination of both structures.

Thermodynamic
Thermodynamics is the study of energy and its interconversions. Energy diagrams are often used to describe the thermodynamics of a given chemical reaction.

Thermodynamically favored
When a substance is refered to as the thermodynamically favored product, this means that of the possible products for a reaction, it is energetically the most stable. Sometimes, the thermodynamically favored product is not observed because a less stable product is kinetically favored.

Transition state
On an energy diagram, the maximas (peaks) represent transitions states. A transition state represents the highest energy arrangement of atoms between two more stable forms.

Unit cell
A unit cell is the smallest repeating unit of a crystalline solid that can be used to describe the entire structure. Unit cells are like templates that can be copied to produce an entire crystal.

Valence shell
The valence shell is the outermost shell of electrons in an atom.

Volatile
Substances that have a tendency to enter the gas phase easily (by evaporation, addition of heat, etc.) are called volatile.

Volatilize
Volatilizing liquids converts them into gases. Volatilizing liquids usually involves heating them.

X-ray diffraction
X-ray diffraction is an analytical technique used to determine the structures of crystalline solids. A beam of x-rays is diffracted off of the repeating planes of atoms in crystalline samples to produce a diffraction pattern. Through analysis of the diffraction pattern, atomic structures can often be determined.