

Mr. Stone

CHEMICAL BONDING 2

The following topics will be covered in this set of notes:

Hydrogen and Metallic Bonding
Van der Waals Forces
Hybridization
Molecular Shapes-- VSEPR Models
Exceptions to the Octet Rule
Polar Molecules
Molecular Substances
Network Solids
Ionic Crystals
Bond Energy / Bond Strength

Hydrogen Bonding

When the molecules of a compound contain hydrogen bonded to a very electronegative atom, an attraction occurs between the slightly positive hydrogen atom of one molecule and the highly electronegative atom of another molecule. This type of intermolecular bonding is known as **hydrogen bonding**.

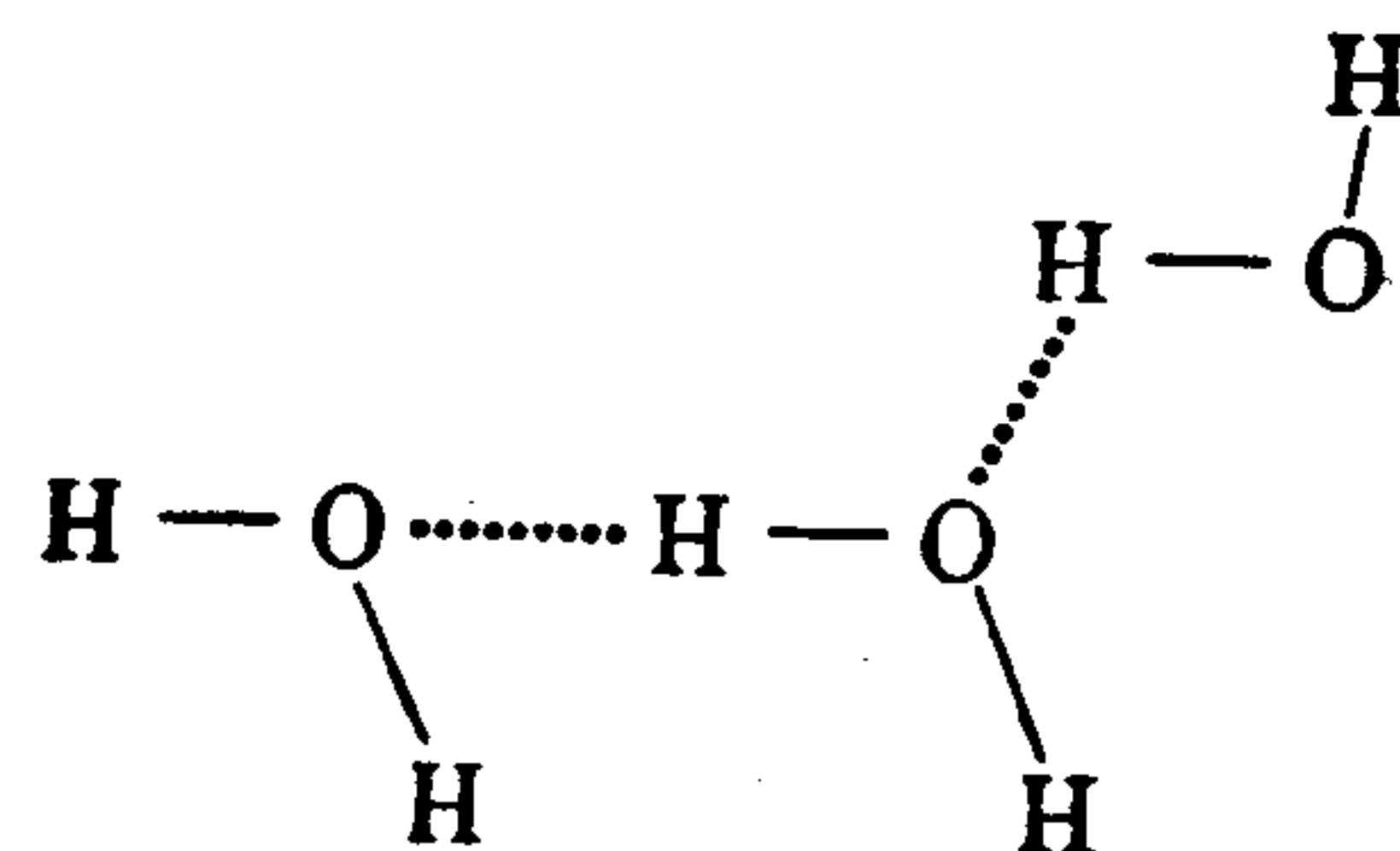
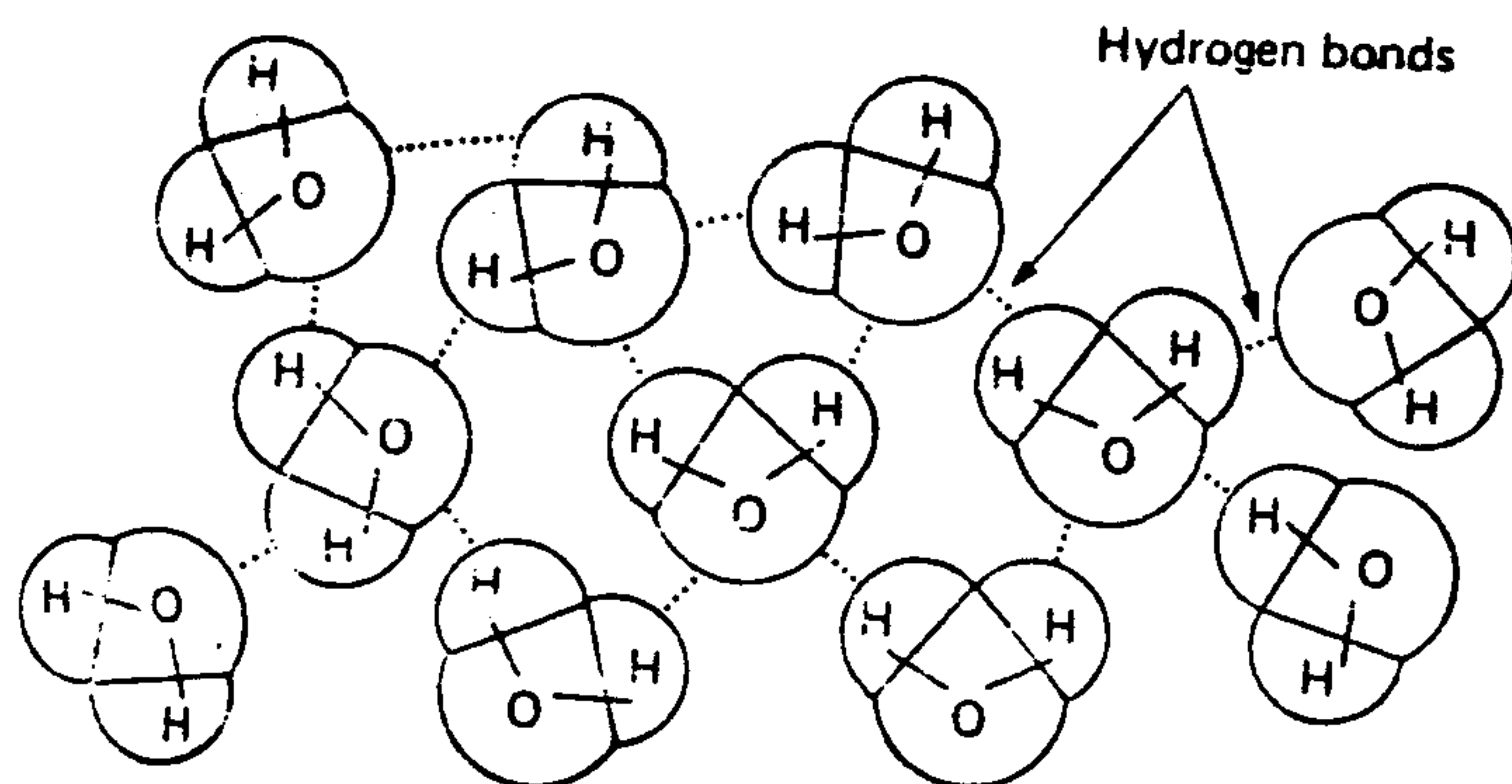
Hydrogen bonds are intermolecular forces of attraction.

Hydrogen bonds usually occur between compounds whose molecules contain hydrogen bonded to fluorine, oxygen or nitrogen.

The hydrogen atom involved in a hydrogen bond is bonded to two atoms. It is bonded covalently to an atom in its own molecule, and through the hydrogen bond, to an atom in a neighboring molecule.

The strength of the hydrogen bond increases as the electronegativity of the atom to which hydrogen is bonded increases.

The strength of the hydrogen bond decreases as the size of the atom to which hydrogen is bonded increases.



Effect of Hydrogen Bonding on Physical Properties of Compounds

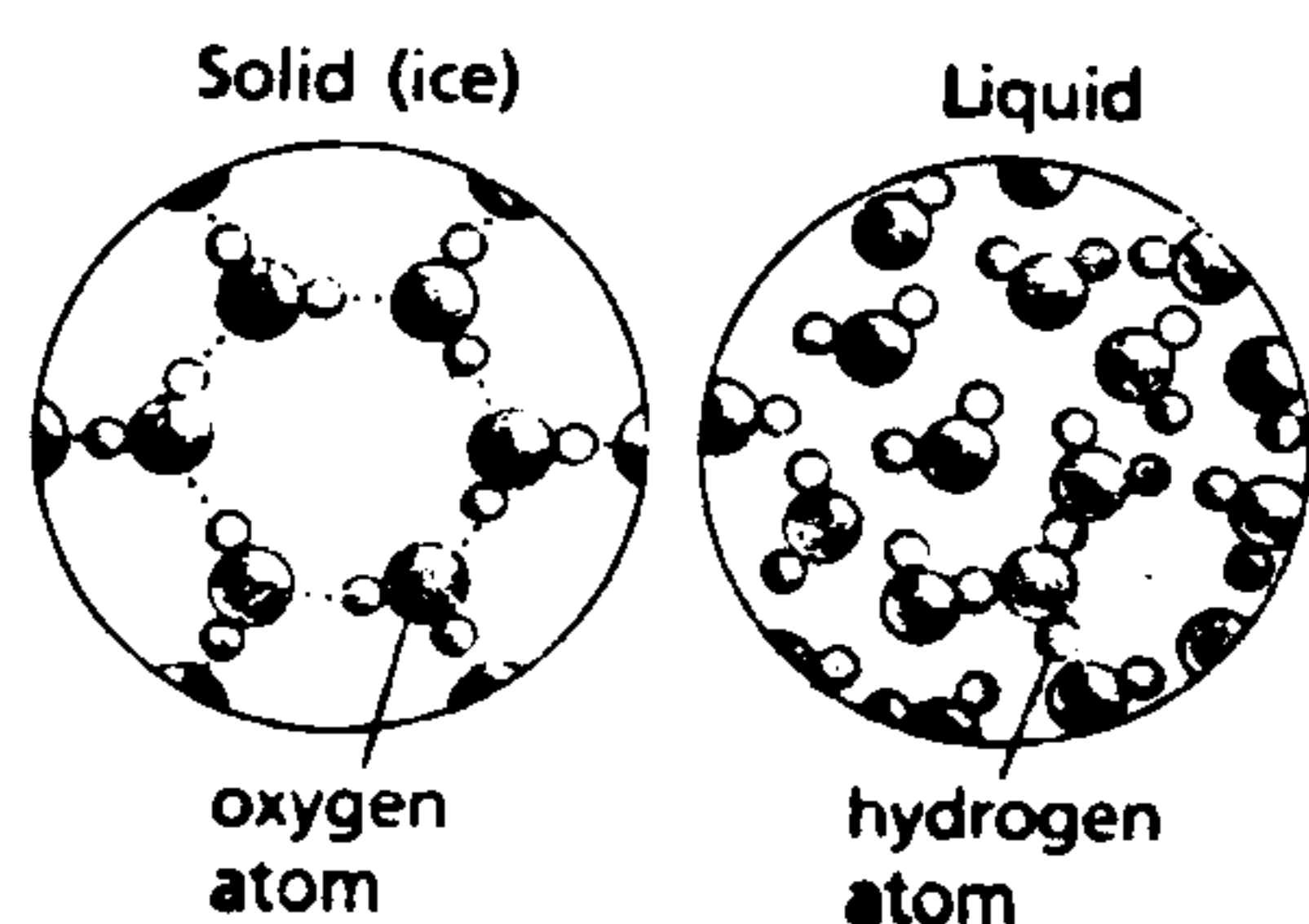
Hydrogen bonding will increase boiling point .

Hydrogen bonding will increase melting point .

Hydrogen bonding will decrease vapor pressure .

Hydrogen bonding will increase heat of vaporization .

Hydrogen bonding will cause the density of the solid state of a compound to be lower than the density of the liquid state of the same compound .



The structure of water in the solid and liquid phases. Hydrogen bonding between water molecules in ice gives a more open structure than the structure of liquid water. Hence, while the solid phase of most substances is more dense than the liquid phase, the opposite is true for water.

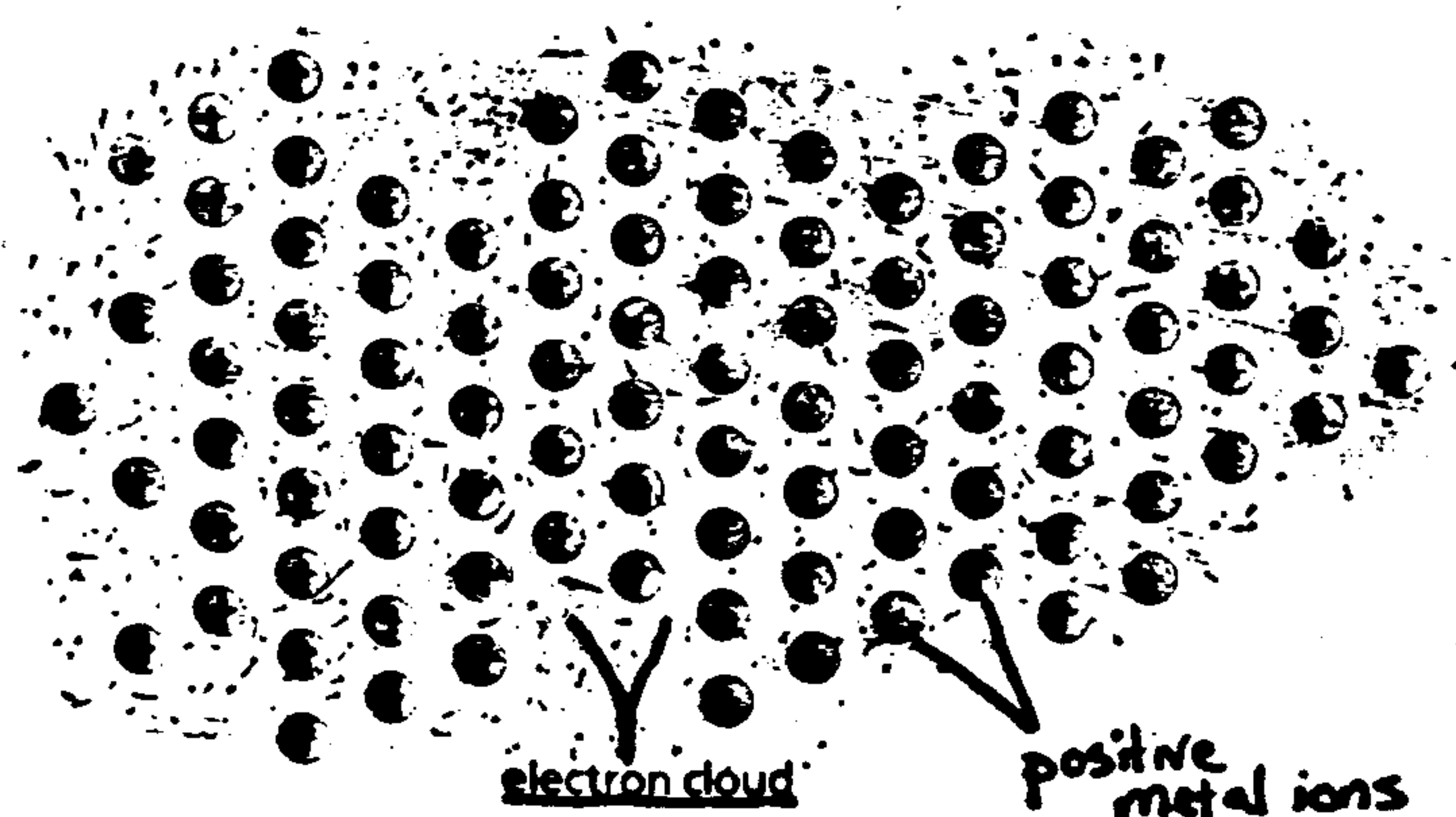
Metallic Bonding

Metallic bonding occurs between metal atoms. Most metals have only one or two valence electrons which are not tightly bound to the atom. (Recall that metals tend to have low electronegativities and tend to give away their valence electrons to nonmetals in ionic bonding.)

When metals bond to other metals, their valence electrons do not seem to belong to any individual atoms but move easily from one atom to another. Therefore they can be considered to be a part of the whole metal crystal. In a sense, this means that all of the valence electrons are shared by all of the atoms in the metal.

Metals, therefore, can be viewed as positive ions immersed in a "sea" of mobile electrons. These mobile electrons exert an attractive force on the positive ions thus helping to fix their positions.

The shared attraction that all of the positive metal ions have for the sea of valence electrons that surround them is the attractive force that binds the metal atoms together and is known as the **metallic bond**.



The nature of the metallic bond (especially the mobility of valence electrons) is what gives metals their special properties.

Properties of Metals

Metals are good conductors of heat and electricity because of the mobility of their valence electrons.

The binding action of the valence electrons determines the hardness of metals. (The weaker the binding forces, the softer the metal will be.)

Metals have high malleability, ductility, and sectility because the metal atoms can slide past one another yet remain bonded.

van der Waals Forces

These types of forces of attraction are intermolecular (between molecules).

There are two general groups of van der Waals forces:

1. dipole-dipole forces - These intermolecular bonds occur between **polar** molecules.
2. London forces - These intermolecular bonds occur between **nonpolar** molecules.

Dipole-dipole forces

This group of intermolecular bonds includes the **hydrogen bond**. Yet the hydrogen bond is a special type of dipole-dipole force that only occurs in molecules that contain the H-F, H-O, or H-N polar covalent bond. For all other types of polar molecules that do not contain these three types of bonds the intermolecular bonds that will occur between them are not strong enough to be considered hydrogen bonds and will be referred to simply as other dipole-dipole forces.

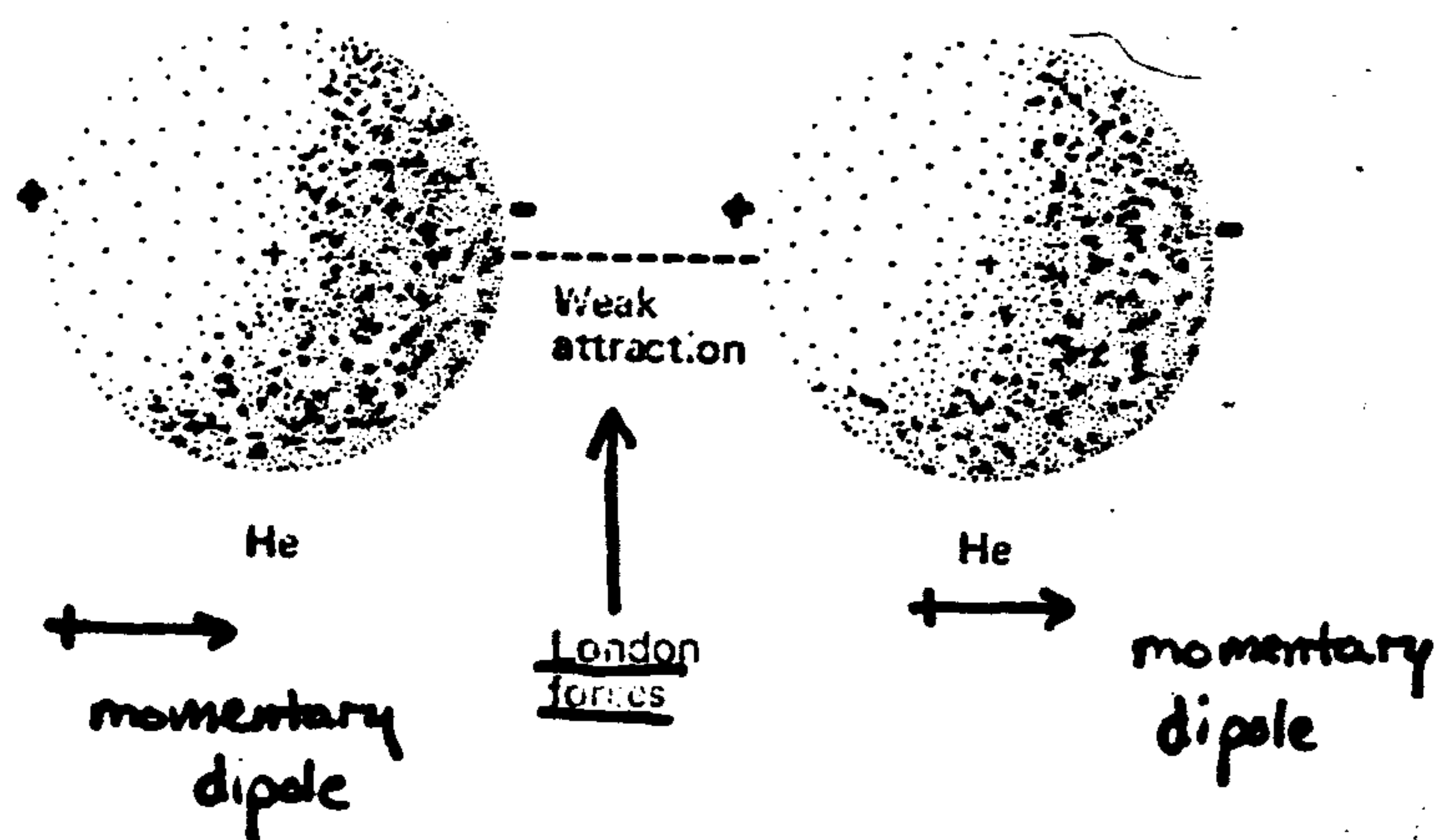
London forces

When nonpolar molecules come close enough together, electrostatic forces of attraction can develop between them. These forces, known as London forces, are much weaker than those that exist in between atoms that have intramolecular bonds (ionic bonds, covalent bonds) and those that exist between polar molecules (dipole-dipole bonds).

Nonpolar molecules do not have a permanent or net dipole; Yet, as mentioned earlier they can develop electrostatic forces of attraction for each other. **London forces arise as a result of shifts in the positions of electrons within the molecule.**

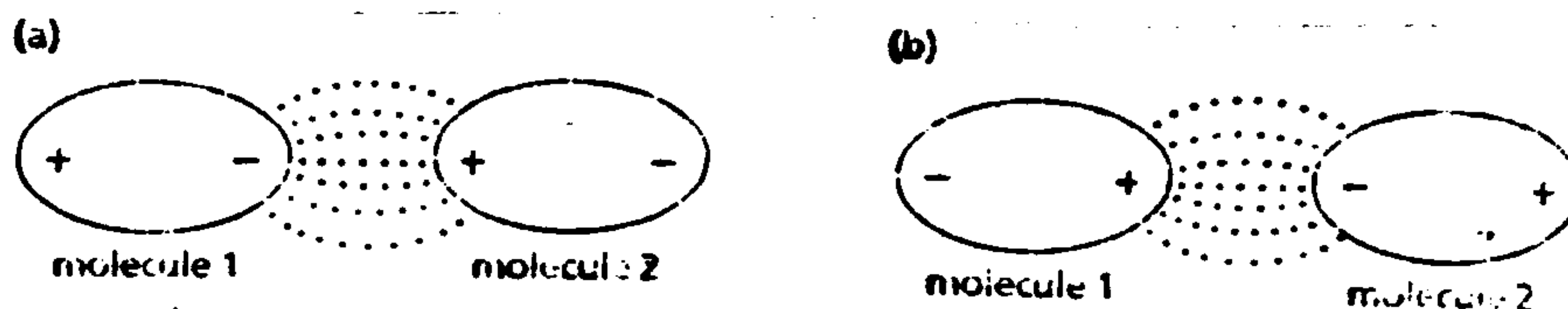
In terms of probability, the electrons can be thought of being evenly distributed, on the average, about the atoms in a nonpolar molecule so there will be no permanent dipole. But, at any given instant, the distribution may not be even and atoms can have a **momentary dipole**. The shifting of electrons will have produced an uneven distribution of charge. One portion of the molecule becomes temporarily negative and, by repelling electrons in a neighboring molecule, it makes the near end of the neighboring molecule temporarily positive. The attraction of these opposite charges acts to hold the molecules together. Also, the second molecule may have a similar effect on a third molecule and so on and so on..... Although the charge distributions are constantly shifting, the net effect will be an overall attraction between the molecules. **The attractive forces promoted by the existence of momentary dipoles are the London forces.**

When two helium atoms approach each other, it is possible that the electrons of one helium atom are attracted to the nucleus of the other atom for a fraction of an instant. The attractions resulting from momentary dipoles in helium are very weak, but they are enough to lead to the formation of helium liquid at a very low temperature, 4.2 K.

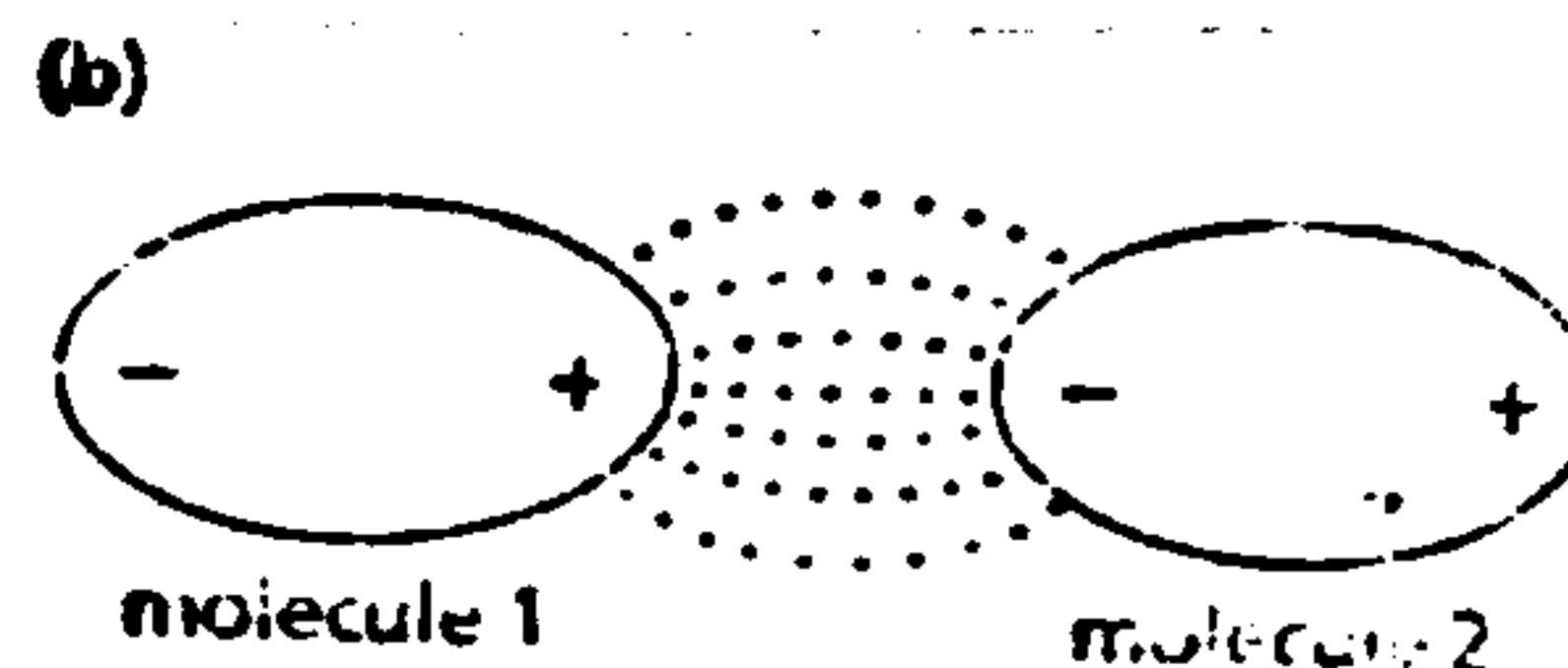


Weak forces between molecules.

(a) At a particular instant, molecule 1 has more electrons on the right side. The negative charge on the right side of molecule 1 repels the electrons in molecule 2. The negative end of molecule 1 and the positive end of molecule 2 attract each other as shown by the dotted lines.



(b) An instant later, as electrons shift again, the left side of molecule 1 may develop a slight negative charge, causing the charge distribution in the neighboring molecule to shift. This electrostatic attraction between molecules, which provides a cohesive force between molecules, is one of the van der Waals forces.



The strength of van der Waals forces

Hydrogen bonds are the strongest of the van der Waals forces.
(refer to earlier notes on differences in H-bond strengths)

Other dipole-dipole bonds are weaker than H-bonds but stronger than London forces. As bond polarity is increased in polar molecules, the dipole-dipole bond strength increases. In a family of related polar molecules, dipole-dipole bond strength will increase as molecular mass increases.

London forces are the weakest of the van der Waals forces.

The strength of London forces is directly related to the number of electrons present in a molecule. Therefore, the larger the molecule, the stronger the London force. London forces also increase in strength as the distance between molecules decreases.

Hybridization

Some atoms form a different number of covalent bonds than the electron configurations of those atoms suggests they should form.

Carbon (C), Boron (B), and Beryllium (Be) are three atoms that are known to undergo hybridization when they bond to other atoms.

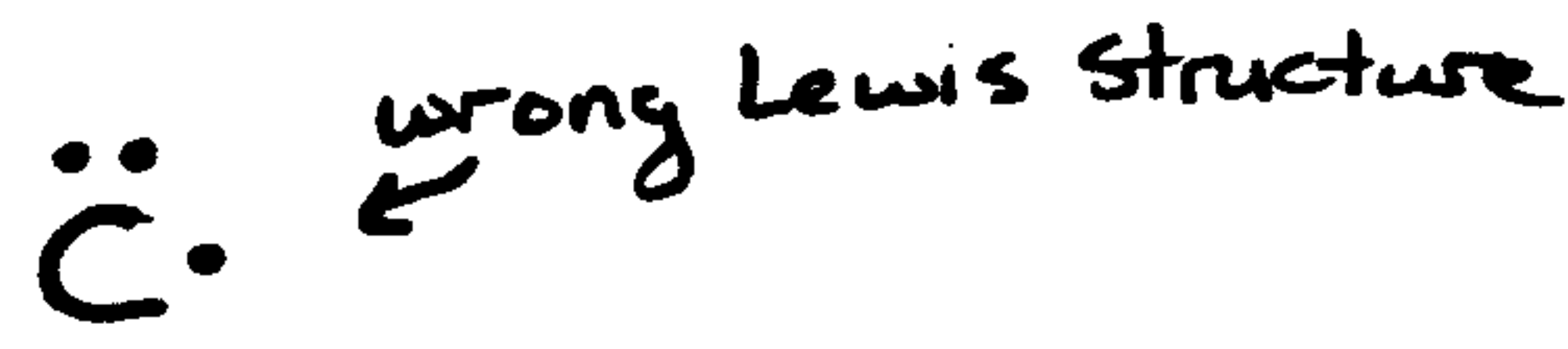
Hybridization is the rearrangement of electrons within the valence orbitals of atoms during bonding.

Carbon hybridization

The electron configuration for carbon shows that it has four valence electrons. Two of these fill the 2s orbital and each of the remaining two is in a half filled 2p orbital. This suggests that carbon forms two bonds with other atoms by sharing its two unpaired electrons.



2 unpaired orbitals



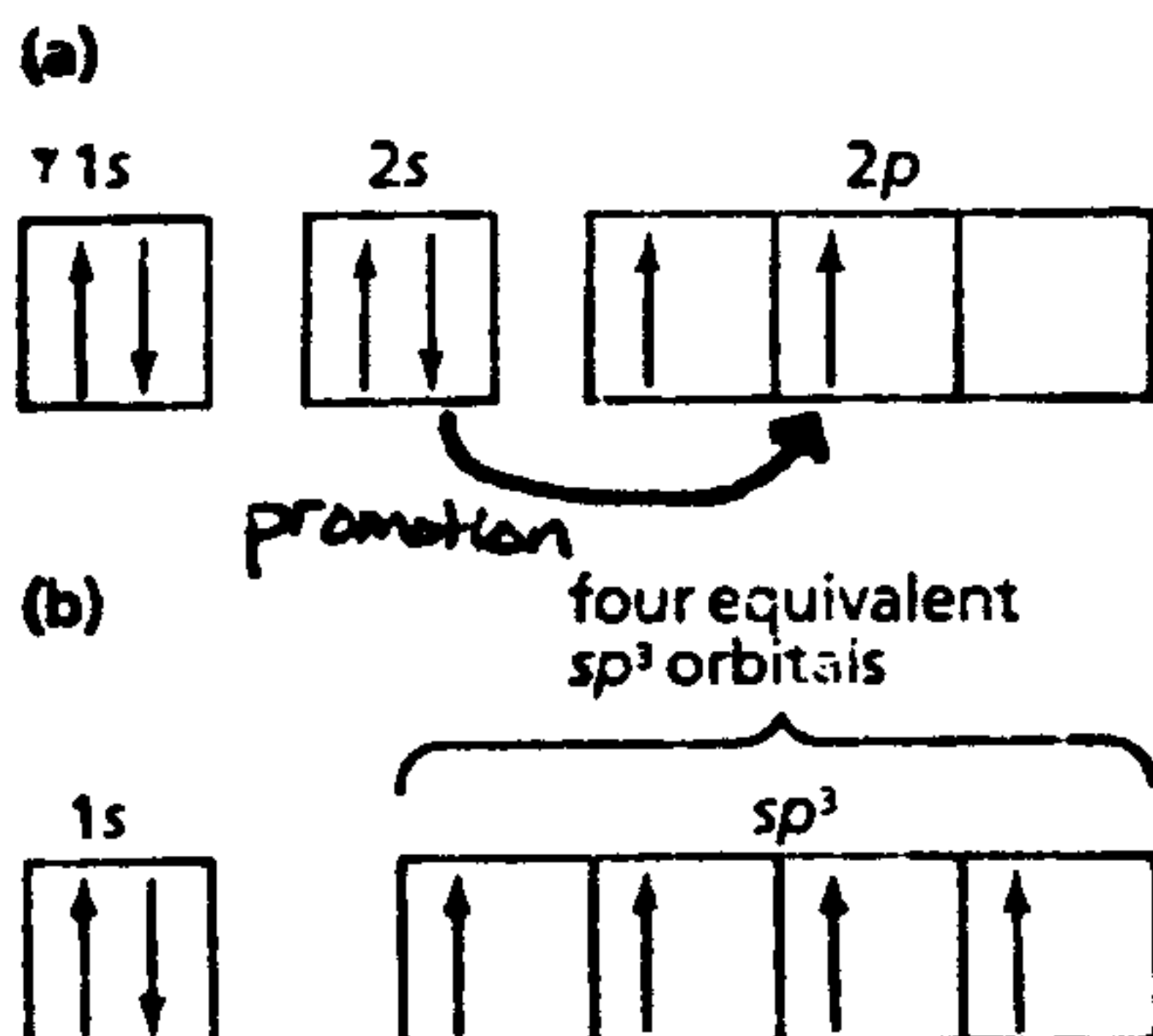
However, experimental evidence shows that carbon forms four identical covalent bonds. The carbon atom appears to behave as though it has four unpaired electrons instead of two.

The hybridization of carbon can be explained in the following manner:

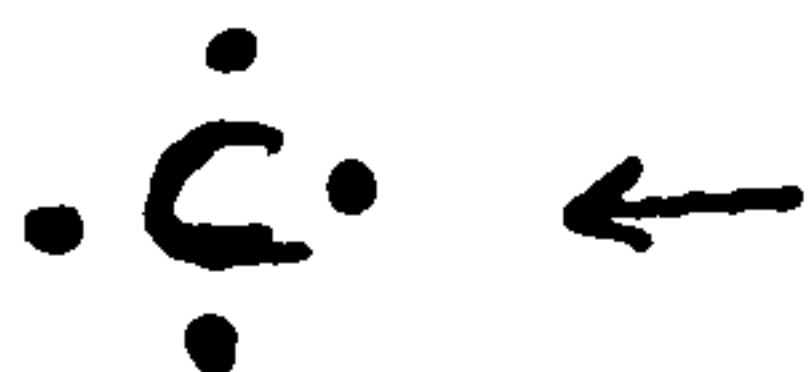
Assume that one of the atom's 2s electrons leaves the 2s orbital and enters the empty 2p orbital when the atom is approached by atoms of an element with which it will react.

The 2s electron that enters the empty 2p orbital is said to have been **promoted**.

After promotion occurs, the 2s and 2p orbitals are **hybridized** and rearranged into four half-filled orbitals of equal energy. Each of these four orbitals is called an **sp³ hybrid orbital**. All four of these hybrid orbitals have new bond characteristics that are different from those of simple s and p orbitals.



(a) The electron configuration of a carbon atom ($Z = 6$). (b) The electron configuration of a carbon atom after hybridization—that is, after a 2s electron has been "promoted" to a 2p orbital. After hybridization, the electrons in all four orbitals, called sp³ hybrid orbitals, have identical energies.



actual Lewis structure

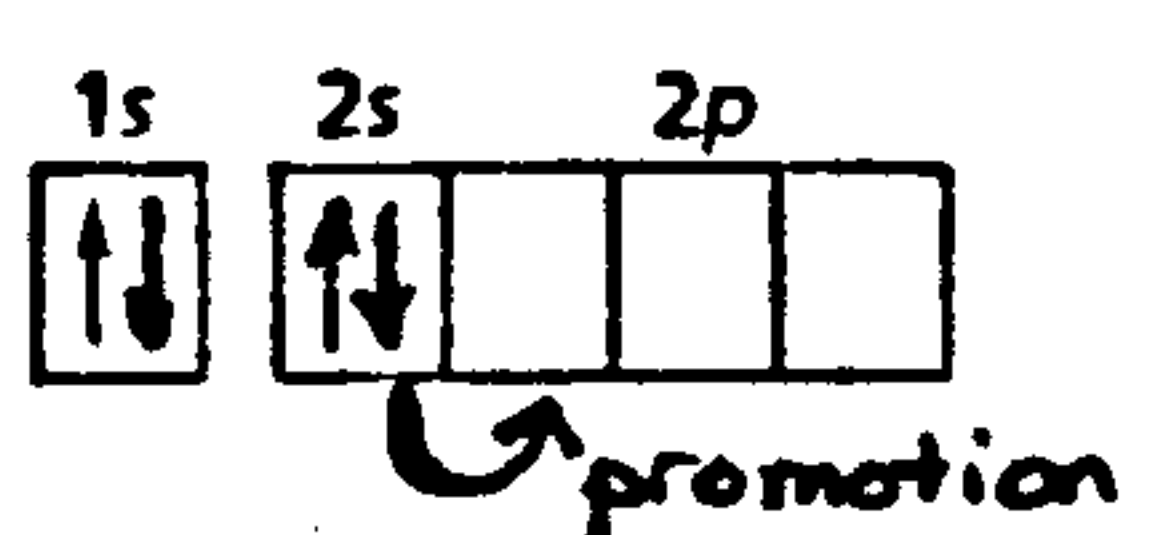
Beryllium hybridization

The electron configuration of beryllium shows that it has two valence electrons which are both in the 2s orbital. It has no half-filled orbitals to pair covalently with the half-filled orbitals of other atoms.

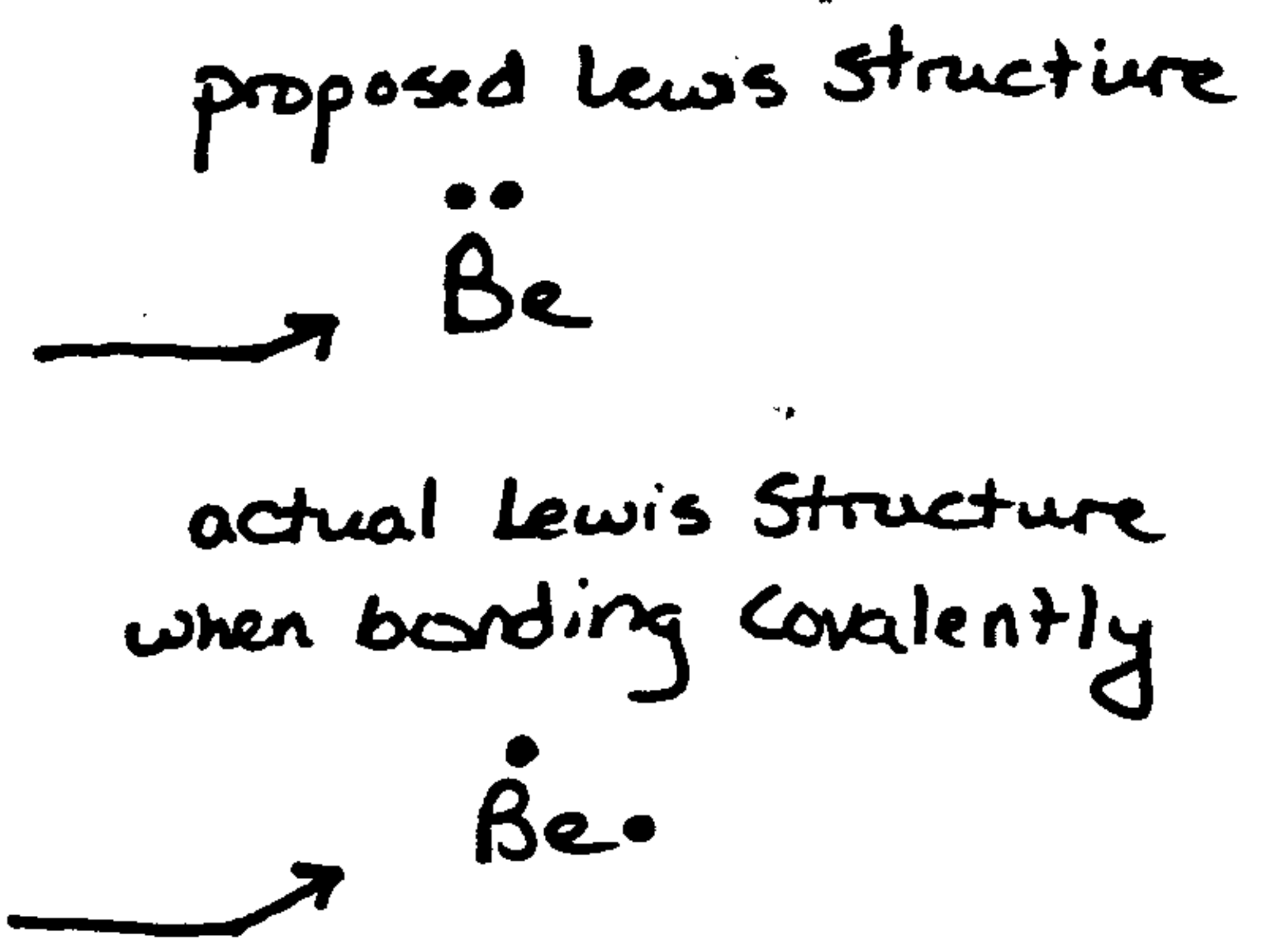
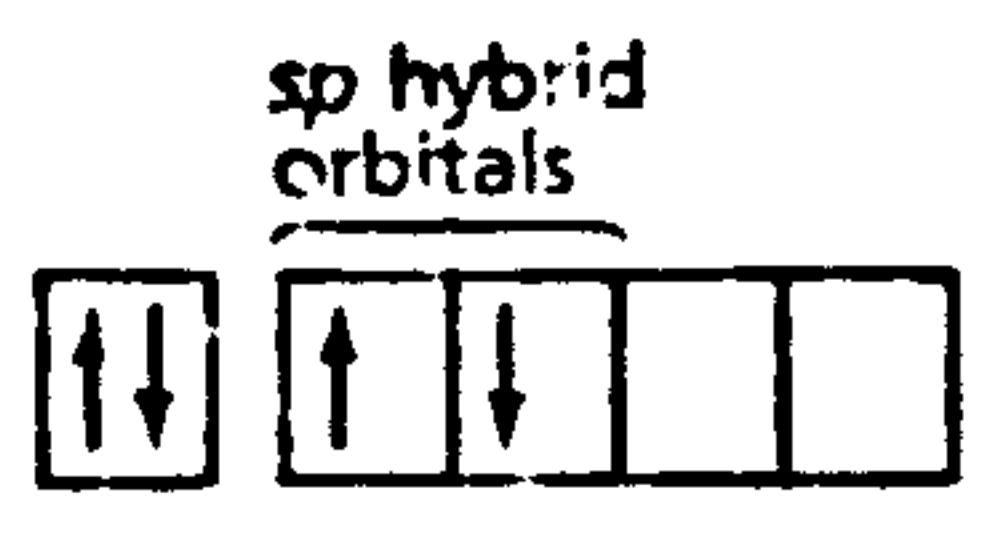
However, beryllium has been shown to form two covalent bonds in compounds. This means that beryllium must undergo hybridization when it is involved in covalent bonding.

One of its 2s electrons is promoted to one of its empty 2p orbitals. After promotion occurs, the 2s and 2p orbitals are hybridized and rearranged into two half-filled orbitals of equal energy. Each of these two new orbitals is called an **sp hybrid orbital**.

(a) Beryllium atom



(b) Beryllium atom after promotion of a 2s electron



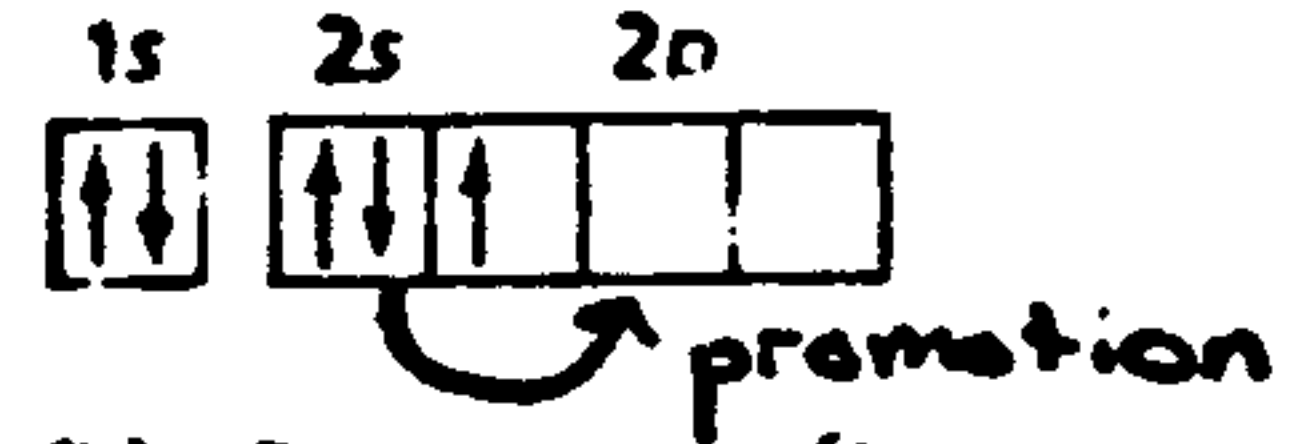
Boron hybridization

The electron configuration of boron shows that it has three valence electrons. Two of these valence electrons fill the 2s orbital. The third electron is in a half-filled 2p orbital. This suggests that boron would tend to form a single covalent bond.

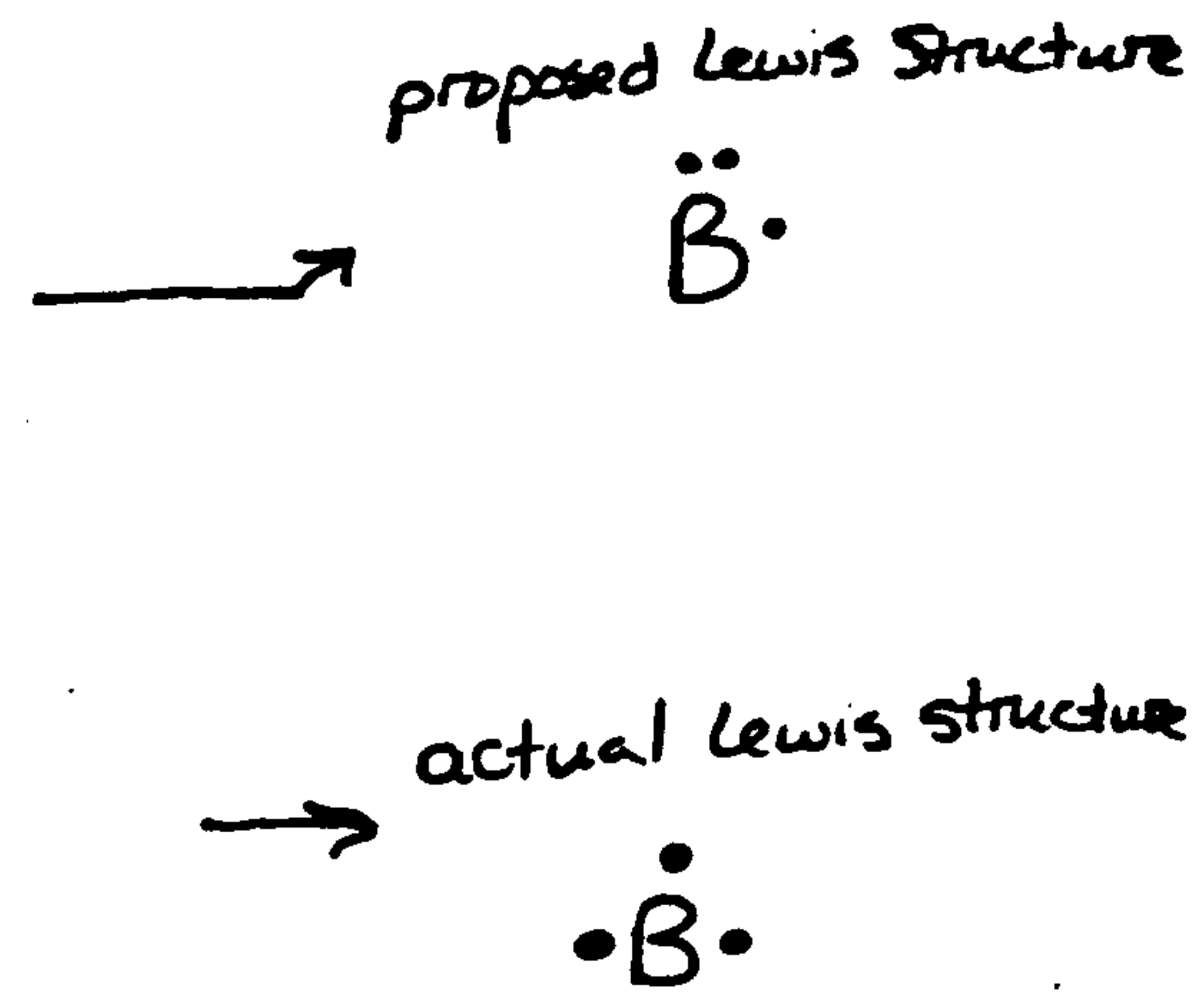
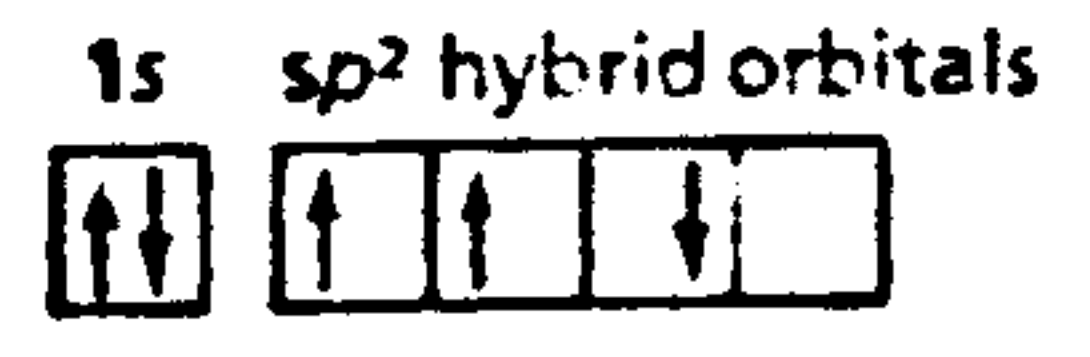
However, boron has been shown to form three covalent bonds in compounds. This means that boron must undergo hybridization when it bonds to other atoms.

One of its 2s electrons is promoted to one of its empty 2p orbitals. After promotion occurs, the 2s and 2p orbitals are hybridized and rearranged into three half-filled orbitals of equal energy. Each of these three new orbitals is called an **sp² hybrid orbital**.

(a) Boron atom



(b) Boron atom after promotion of a 2s electron to a 2p orbital



Molecular Shapes – VSEPR Models

VSEPR Model = valence-shell electron-pair repulsion model


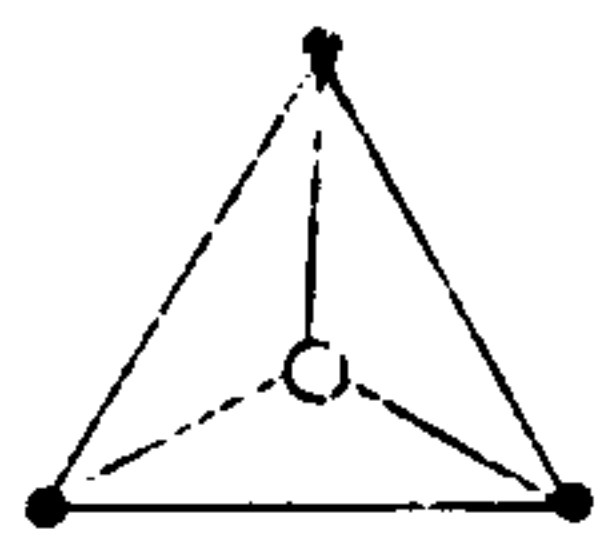
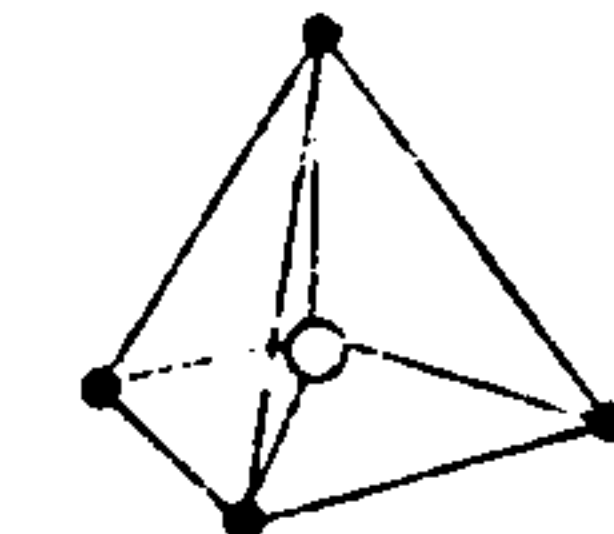
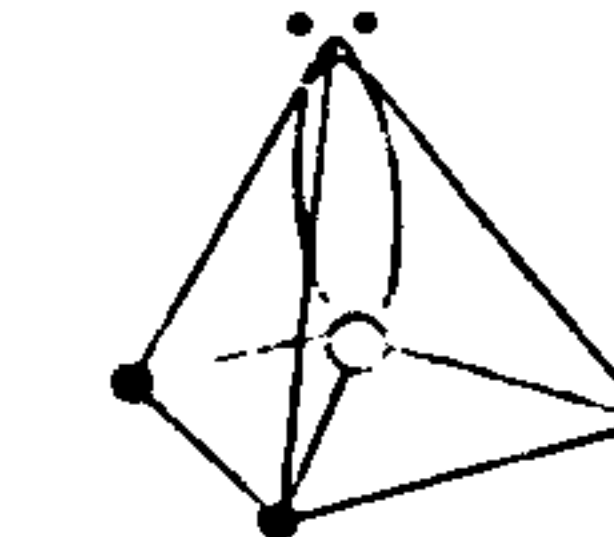
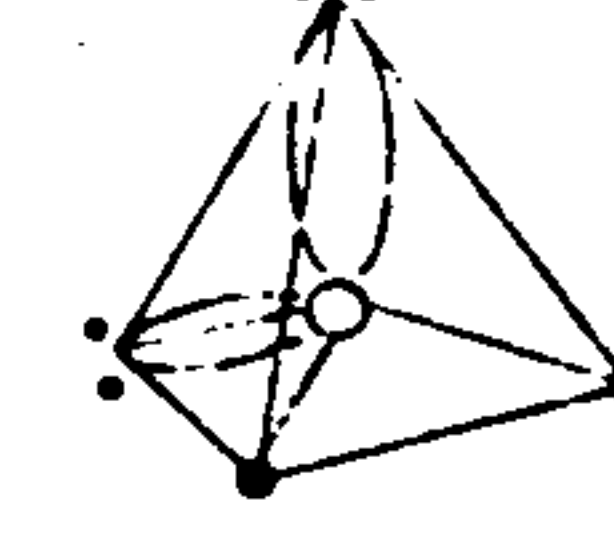
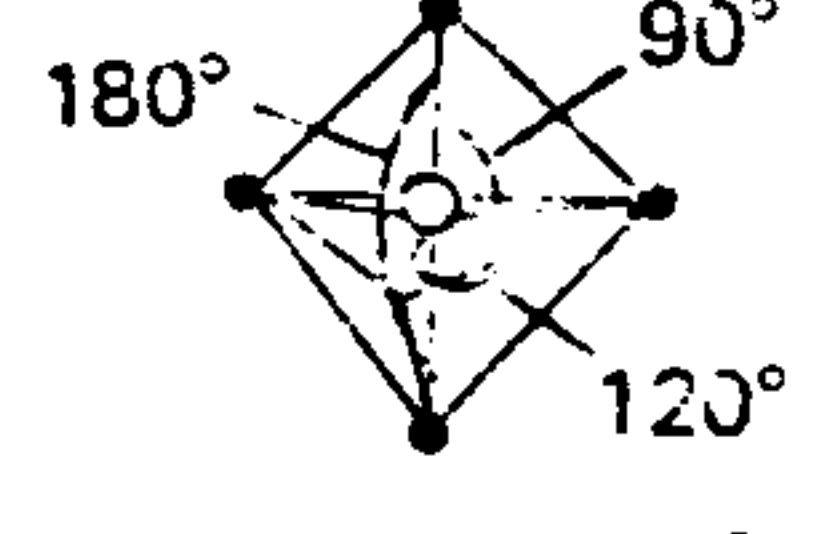

The VSEPR model provides a way to predict the geometric shape of molecules due to their internal bonding arrangements.

Predicting the shapes of molecules is very important because the shape of a molecule can affect its properties.

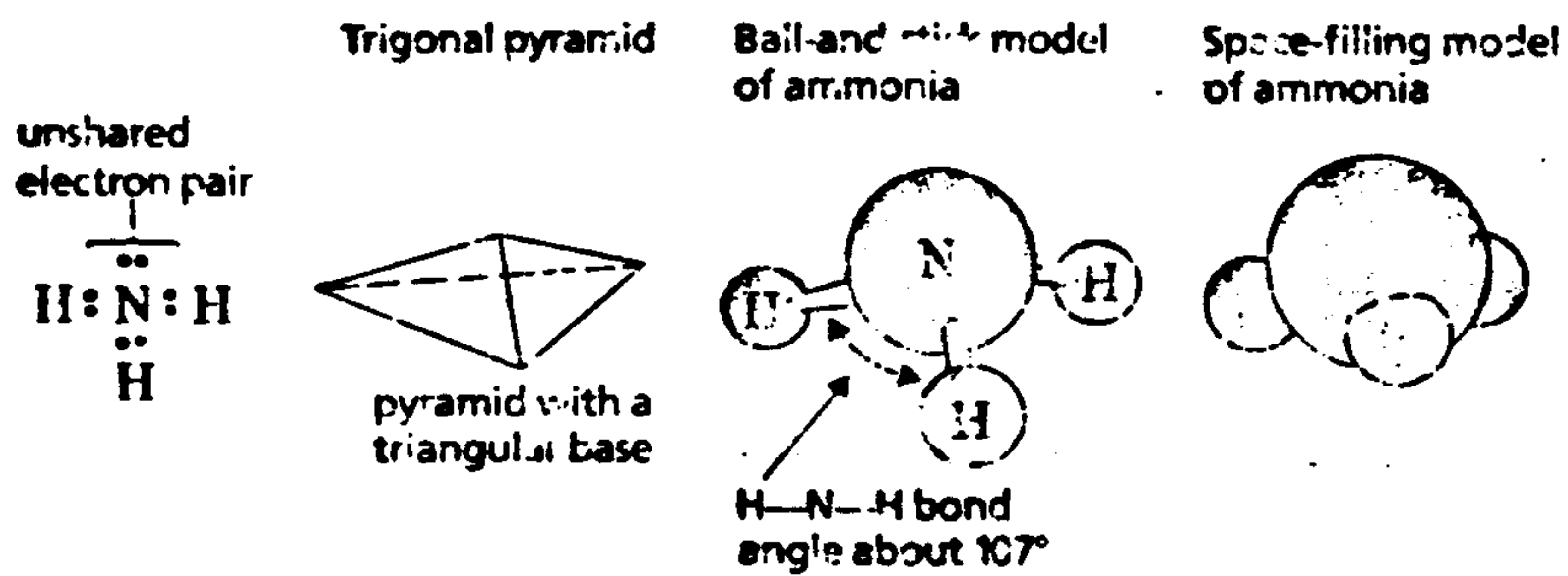
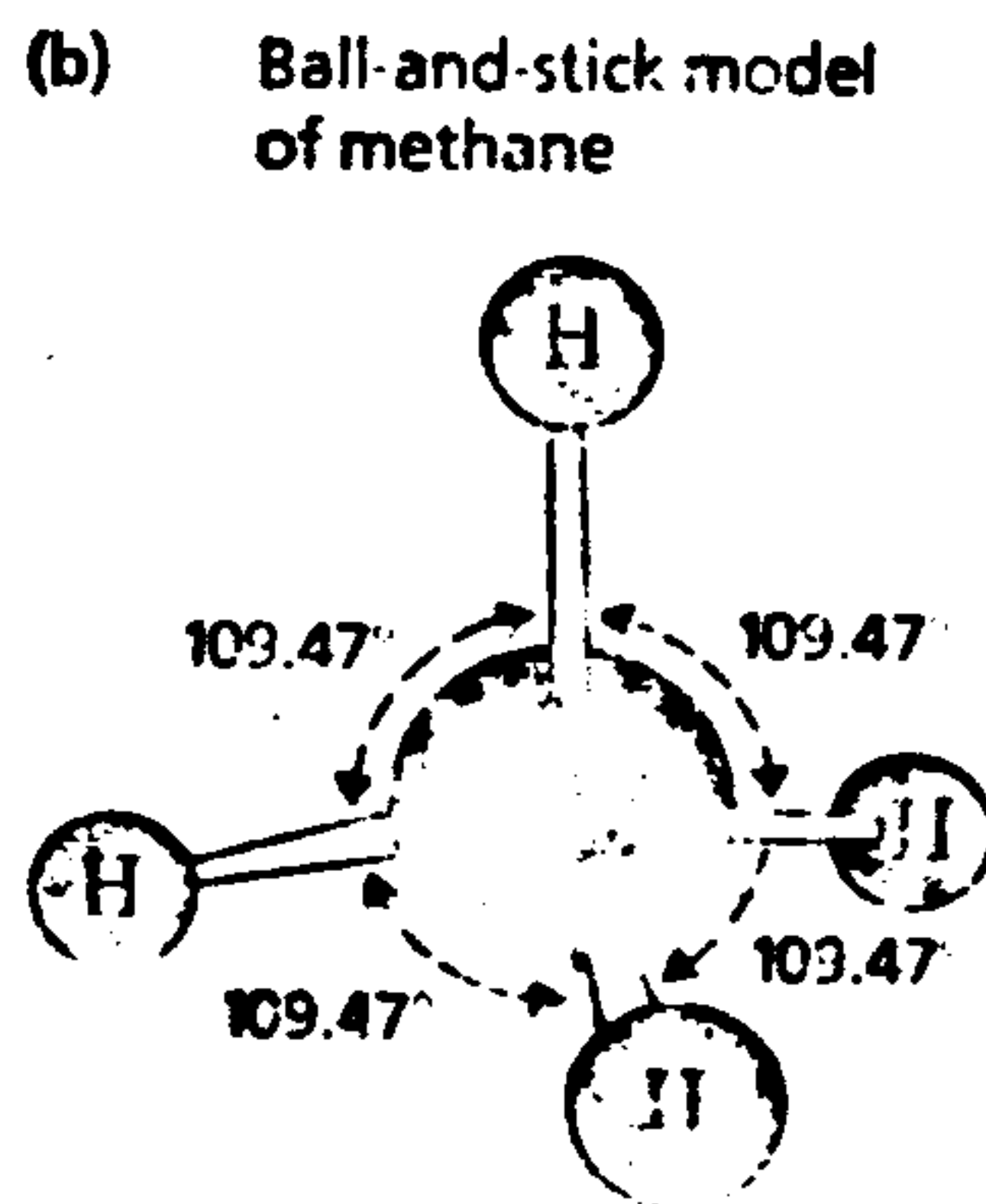
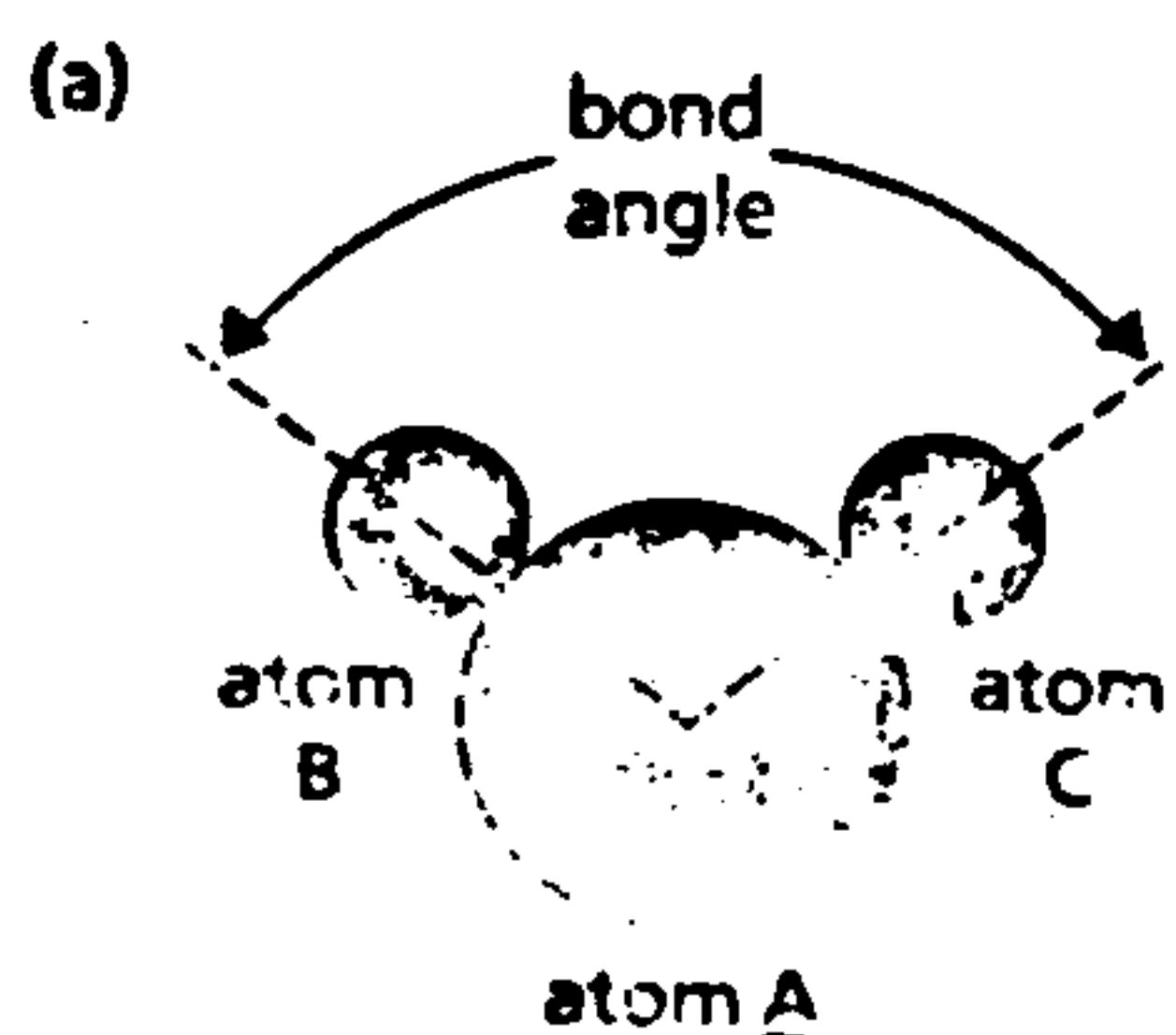
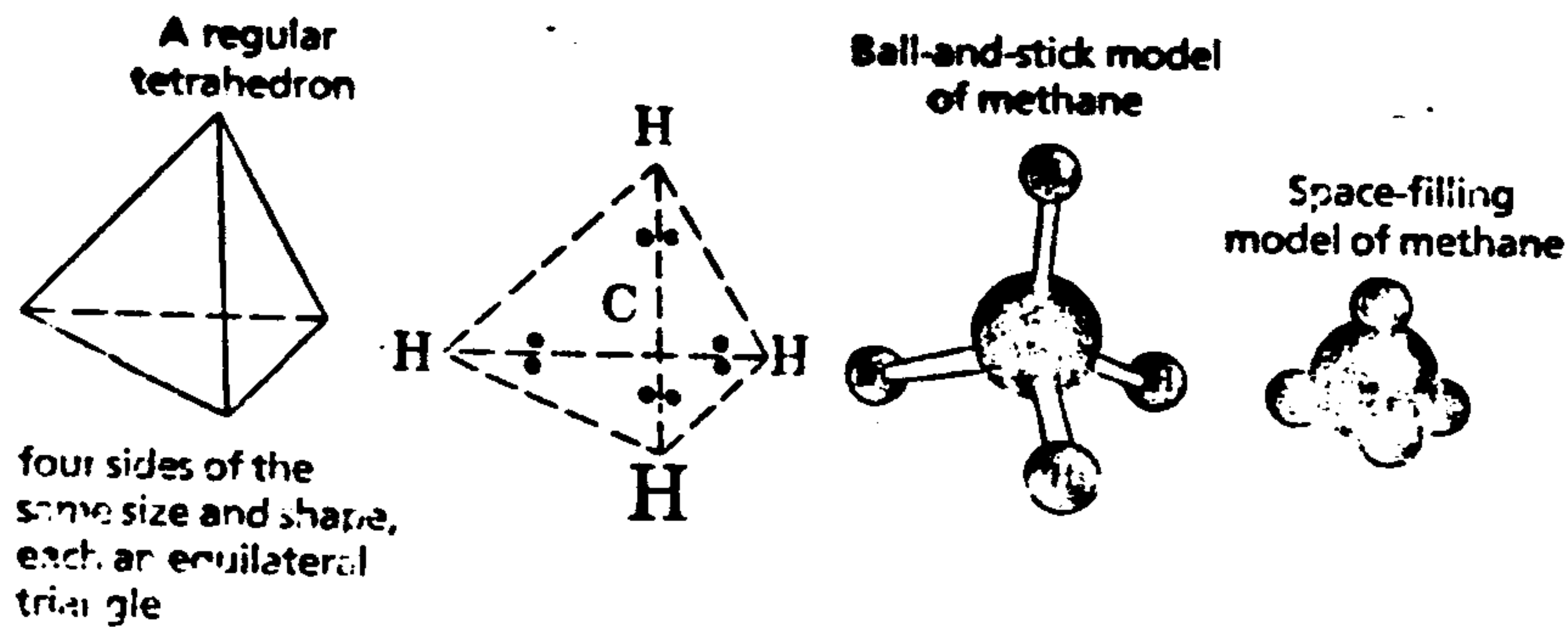
According to the VSEPR model, the shape of a molecule depends on the number of atoms bonded to the central atom and the number of unshared pairs of electrons around the central atom.

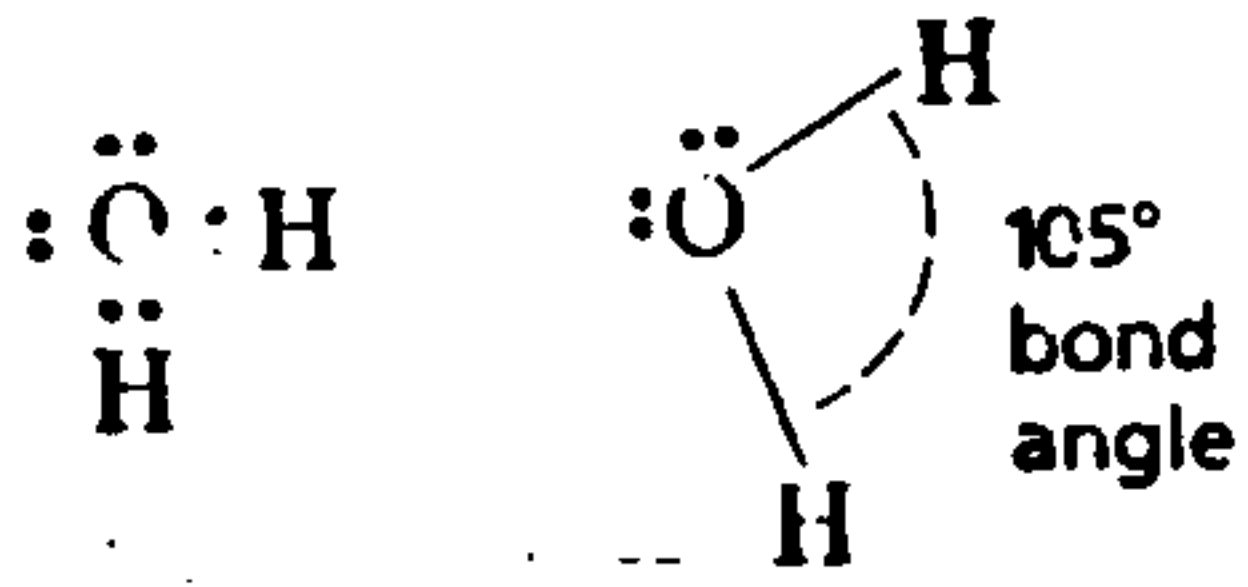
Each pair of electrons surrounding the central atom is considered to repel all of the other electron pairs around that atom. This repulsion causes each electron pair to take a position about the central atom as far away as possible from the other electron pairs.

Use the following chart to help you predict molecular shapes:

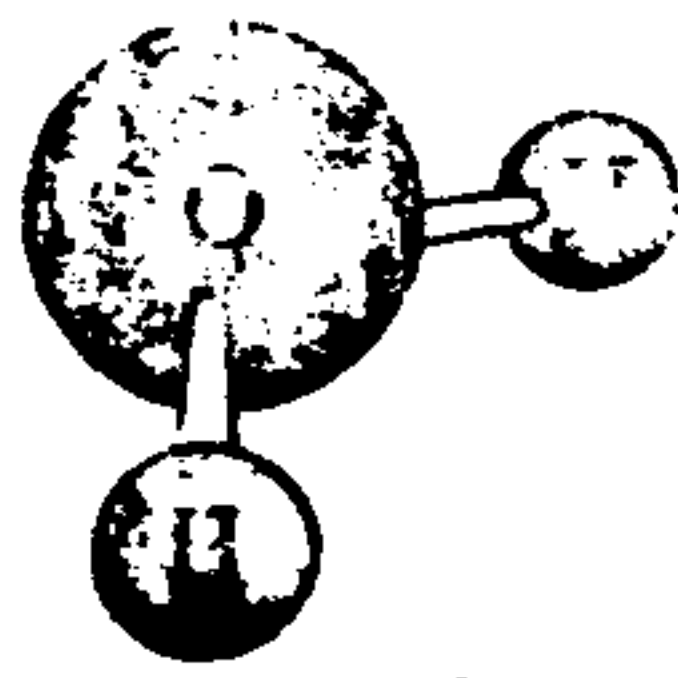
NAME	STRUCTURAL SHAPE	EXAMPLES OF MOLECULAR SHAPES			EXAMPLE	
		ATOMS BONDED TO CENTRAL ATOM	LONE PAIRS OF ELECTRONS	BOND ANGLE	FORMULA	ELECTRON DOT DIAGRAM
Linear		2	0	180°	BeH_2	$\text{H}:\text{Be}:\text{H}$
Trigonal planar		3	0	120°	BF_3	$\begin{array}{c} :\ddot{\text{F}}: \\ \\ \text{B} \\ \\ :\ddot{\text{F}}: \\ \\ :\ddot{\text{F}}: \end{array}$
Tetrahedral		4	0	109.5°	CH_4	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$
Trigonal pyramidal		3	1	107°	NH_3	$\begin{array}{c} :\ddot{\text{N}}: \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$
Angular		2	2	104.5°	H_2O	$\begin{array}{c} :\ddot{\text{O}}: \\ \\ \text{H}-\text{O}-\text{H} \end{array}$
Trigonal bipyramidal		5	0	90° 120° 180°	PCl_5	$\begin{array}{c} :\ddot{\text{Cl}}: \\ \\ :\ddot{\text{Cl}}-\text{P}-\ddot{\text{Cl}}: \\ \\ :\ddot{\text{Cl}}: \end{array}$
Octahedral		6	0	90° 180°	SF_6	$\begin{array}{c} :\ddot{\text{F}}: \\ \\ :\ddot{\text{F}}-\text{S}-\ddot{\text{F}}: \\ \\ :\ddot{\text{F}}: \end{array}$

examples of molecular shapes:

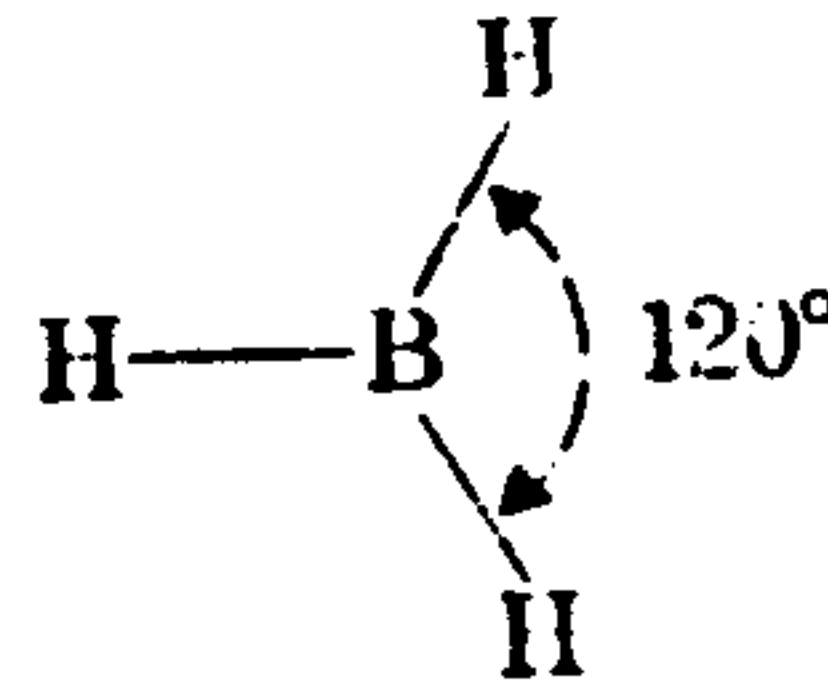
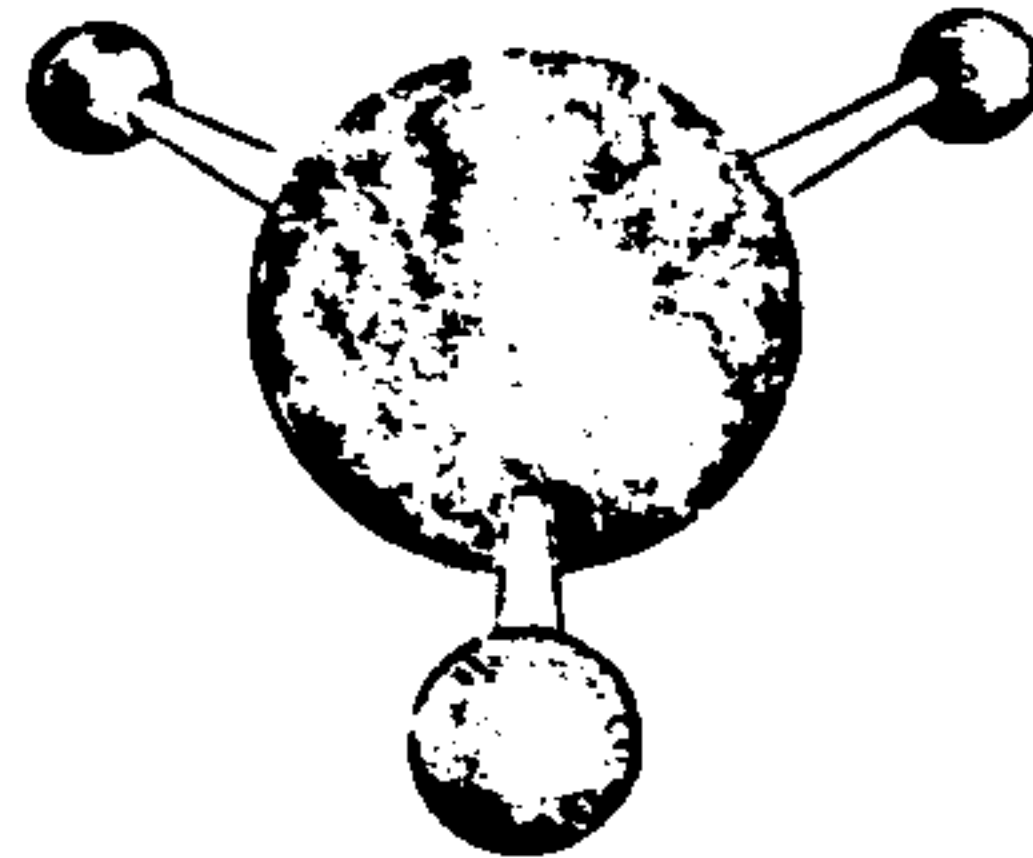




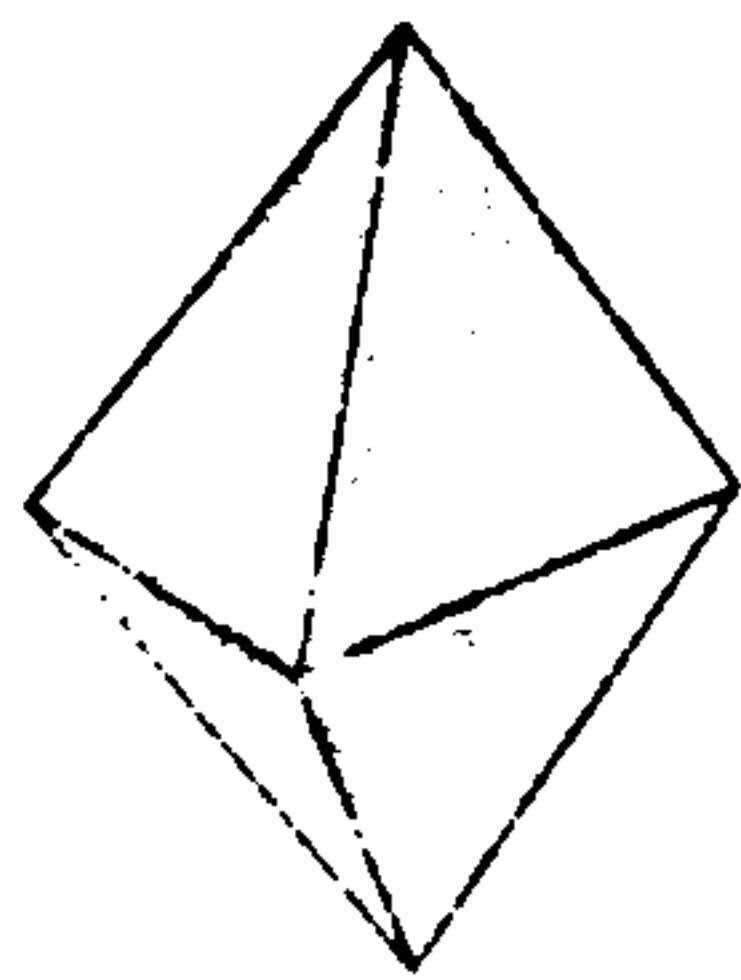
Ball-and-stick model of water



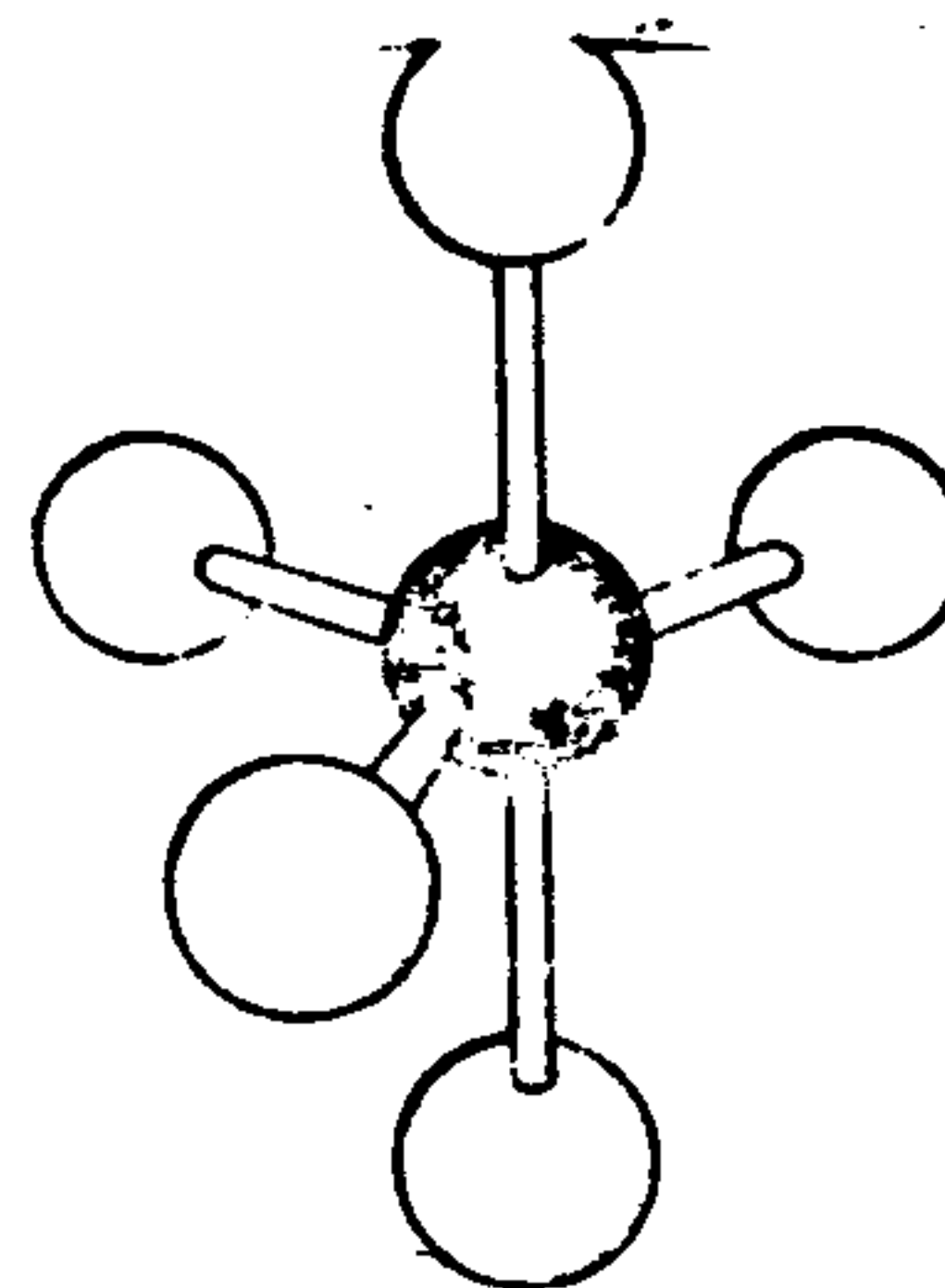
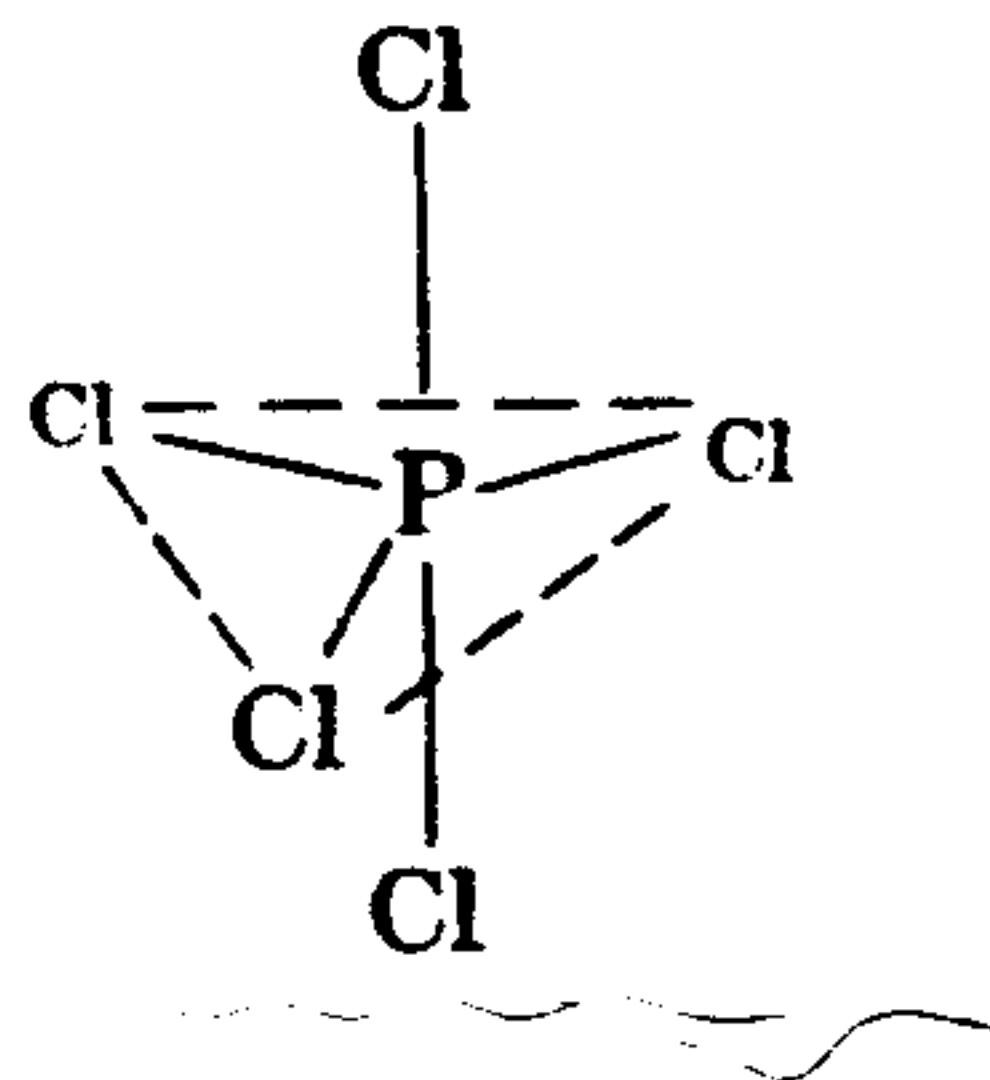
Space-filling model of water



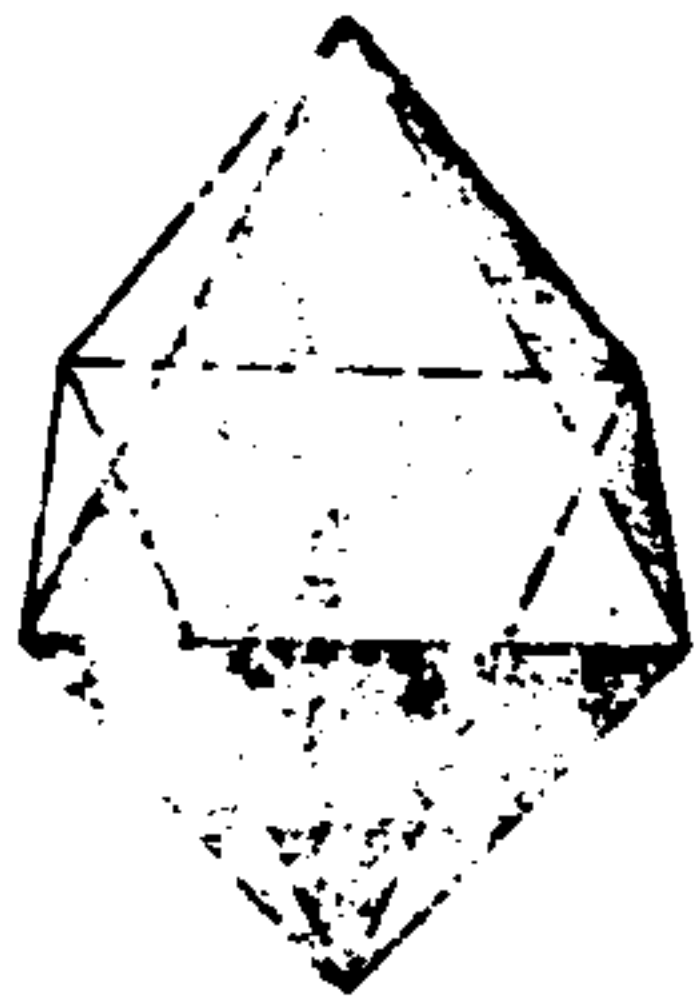
Shape: trigonal planar
(all four atoms lie in the same plane)



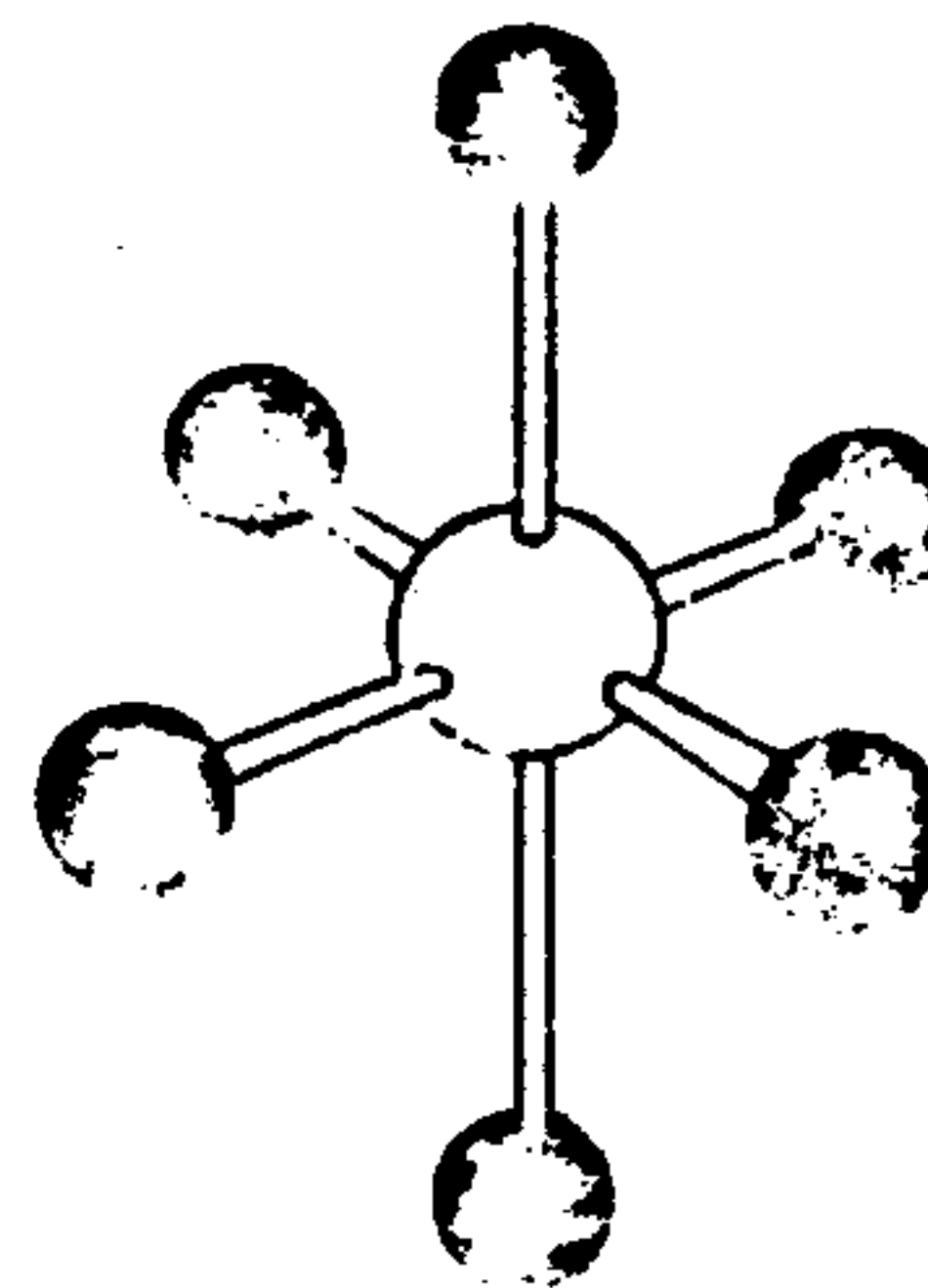
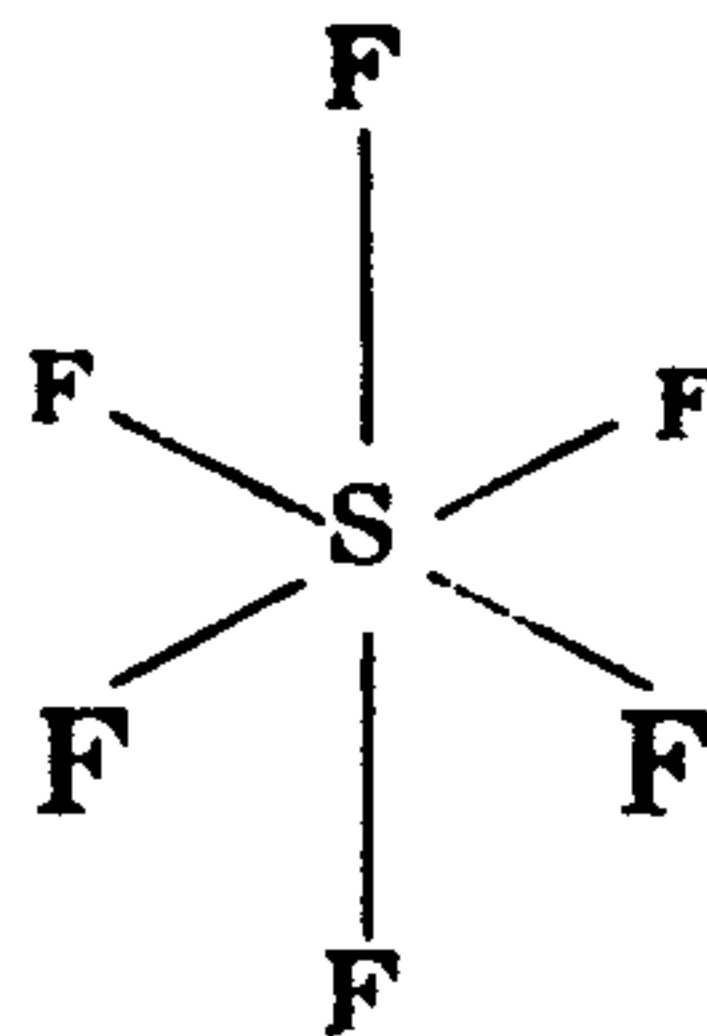
A trigonal bipyramid



Ball-and-stick model of PCl_5



An octahedron



Ball-and-stick model of SF_6

Exceptions to the Octet Rule

The octet rule can not be used to explain the bonding of all molecules. Although most molecules do follow this rule in bonding, molecules exist that do not form stable octets in their molecular structure yet they are stable molecules nonetheless. (This is known from experimental evidence that proves their existence and stability.)

Group 13 Elements

Boron (B), a group 13 element, forms stable compounds even though it does not form a stable octet. Because of its small size, the boron atom can accommodate only three pairs of electrons.

Recall that boron undergoes hybridization to form three sp^2 hybrid orbitals, each of which will be half-filled with one of boron's three valence electrons, thus allowing boron to form three covalent bonds.

According to VSEPR theory, the molecules of boron compounds will therefore have a trigonal planar shape (3 atoms bonded to the central boron atom; 0 lone pairs).

Group 15, 16, and 17 Elements

Sometimes atoms of these groups will have bonding characteristics that do not follow the octet rule. These exceptions are best explained in terms of "expanded" valence shells.

Expanded valence shell- a valence shell that holds more than an octet of electrons as a result of one or more d orbitals being used by an atom to form covalent bonds in addition to the s and p orbitals

Phosphorus (P) is a group 15 element that is capable of forming expanded octets. This means that phosphorus can form more than the three covalent bonds normally predicted.

In its "expanded" form, phosphorus is capable of forming five covalent bonds. According to VSEPR theory, these "expanded" phosphorus compounds will therefore have a trigonal bipyramidal shape (5 atoms bonded to the central phosphorus atom; 0 lone pairs).

Sulfur (S) is a group 16 element that is capable of forming expanded octets. This means that sulfur can form more than the two covalent bonds normally predicted.

In its "expanded" form, sulfur is capable of forming six covalent bonds. According to VSEPR theory, these "expanded" sulfur compounds will therefore have an octahedral shape (6 atoms bonded to the central sulfur atom; 0 lone pairs).

The fact that phosphorus and sulfur can form "expanded octets" suggests that these elements are capable of hybridization. If this is the case what would we call their hybrid orbitals ?

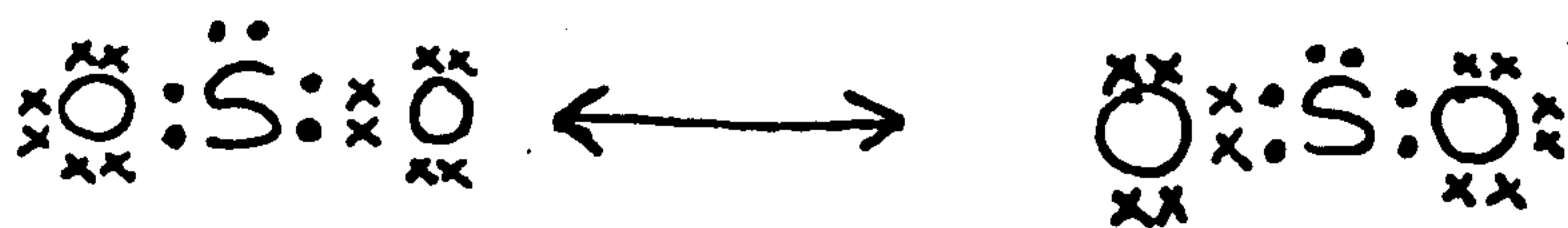
Resonance

Sometimes reasonable Lewis structures that follow the octet rule fail to give an accurate representation of the actual bonding in a molecule. In these cases, experimental evidence suggests that the actual nature of the intramolecular bonding within a molecule is quite different than the bonding predicted by a Lewis dot diagram. The concept known as resonance is used to help explain this phenomenon and to help make dot diagrams more accurate in describing the properties of a substance.

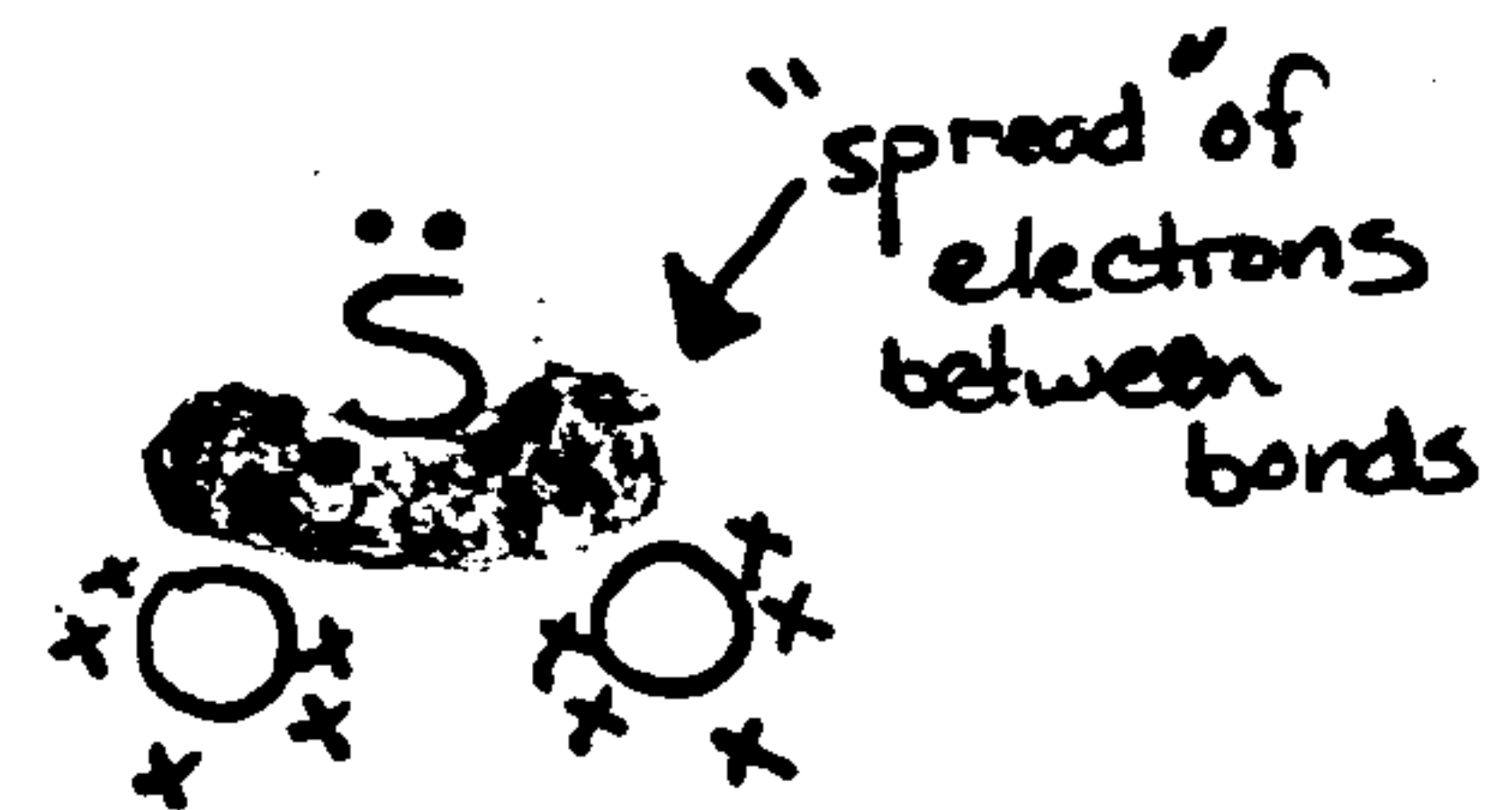
Originally, it was believed that valence electrons in a resonance structure moved back and forth from one bond location to another. Because the electrons appeared to resonate (vibrate) between different bonds, this behavior was called resonance. Today, it is believed that certain valence electrons are "spread" across the locations of the bonds in which resonance is occurring.

A good example of resonance can be seen in the sulfur dioxide (SO_2) molecule. The Lewis diagram of this molecule suggests one coordinate covalent bond and one double bond; yet, experimental evidence shows that both S-O bonds are the same. Each bond has properties characteristic of a single bond and other properties characteristic of a double bond. There is no way to show this using a single dot diagram based on the octet rule. Instead all of the possible dot diagrams for the molecule are shown and are connected by a double ended arrow that indicates that they are resonance structures.

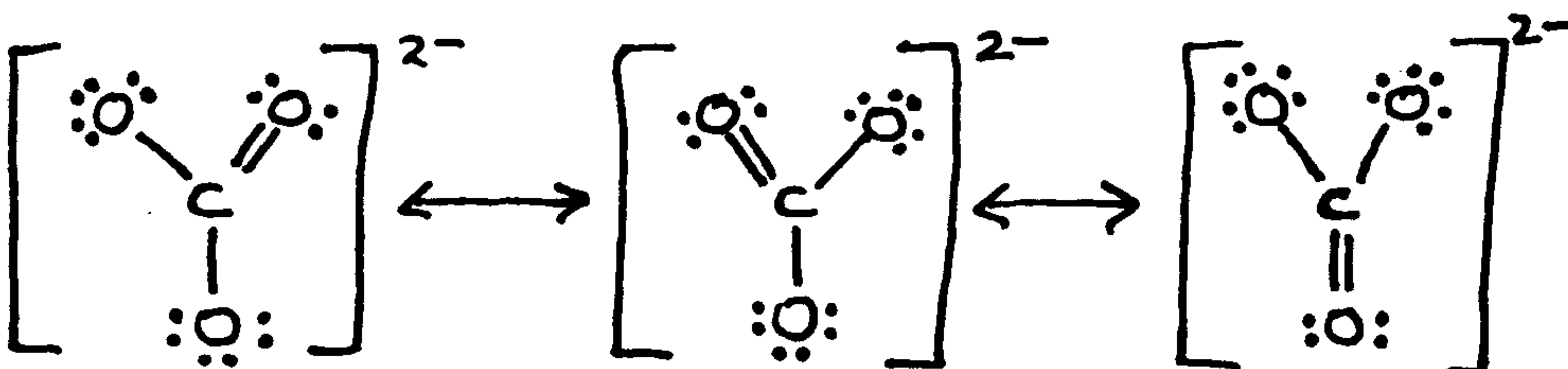
Resonance structures are not meant to imply that there is more than one molecular structure but rather that no single structure adequately represents the molecule.



Resonance Structures



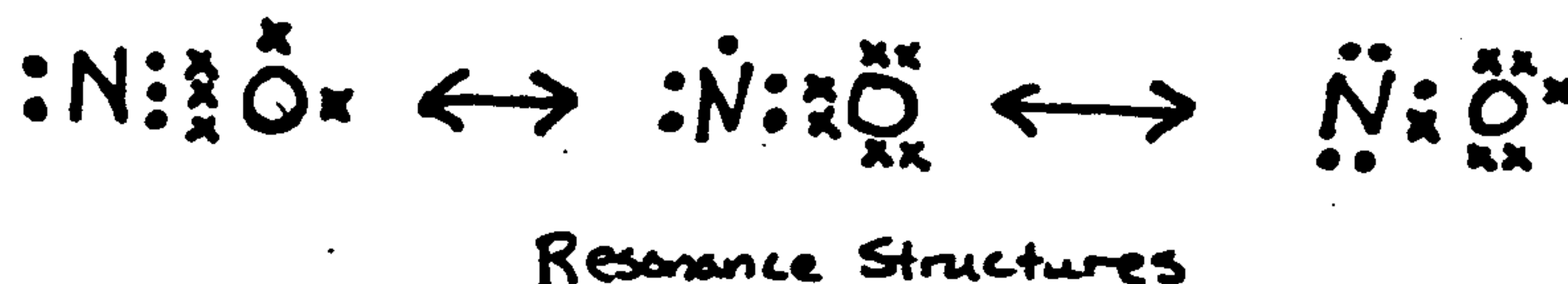
other examples of resonance:



Molecules With an Odd Number of Valence Electrons

A small number of stable molecules have an odd number of valence electrons. This means that an electron will not be paired. In these cases, no Lewis dot diagram can be drawn that follows the octet rule—it is impossible. In order to represent the bonding in these molecules, resonance structures that break the octet rule are used.

A good example of this type of situation is a molecule of nitrogen oxide (NO).



Polarity in Molecules

In terms of electron distribution in a molecule, molecules are considered to be either polar or nonpolar.

polar molecule- a molecule will be polar when there is an uneven distribution of electrons in the molecule caused by an uneven distribution of one or more polar bonds (net dipole) therefore the whole molecule will behave as a dipole (as if one end is positive and one end is negative)

nonpolar molecule- A molecule will be nonpolar when the distribution of electrons in the molecule is even (no net dipole)

Diatomic Molecules

Diatomic molecules are molecules that have only two atoms in their structure.

In any diatomic molecule, the polarity of the bond between the two atoms will determine the polarity of the molecule. **If the bond is polar, the molecule will be polar. If the bond is nonpolar, the molecule will be nonpolar.**

Molecules That Have More Than Two Atoms

When a molecule is made up of more than two atoms, both the shape of the molecule and the type(s) of intramolecular bonds determine the polarity of the molecule.

If all the bonds within a molecule are nonpolar, the molecule will be nonpolar.

If only one of the bonds within a molecule is polar, the molecule will be polar.

When two or more of the bonds within a molecule are polar, the shape of the molecule determines its polarity.

If all of the polar bonds are symmetrically distributed, the molecule will be nonpolar because all of the dipoles will cancel each other out. Linear, tetrahedral, and trigonal planar shapes are symmetrical and generally lead to nonpolarity in molecules.

(exception: If one of the bonds is much more highly polar than the others, the molecule will be polar because the molecule's shape will become distorted and will no longer be symmetrical.)

If the polar bonds are not symmetrically distributed, the molecule will be polar because all of the dipoles will not cancel and the molecule will have a net dipole. Trigonal pyramidal and angular(bent) shapes generally lead to polarity in molecules.

Molecular Substances

Molecular substances are defined as substances whose separate units are made from atoms covalently bonded together (molecules).

The individual molecules that comprise a molecular substance may be either polar or nonpolar and this will have a direct bearing on the physical properties of molecular substances. If the molecules of a substance are polar, then the forces of attraction that hold them together will be stronger than those that hold together similar nonpolar molecules (see van der Waals forces). As a result of their polarity, polar substances will have higher boiling points, higher melting points, higher heats of vaporization, and lower vapor pressures than nonpolar substances of similar molecular mass. For example, polar substances are usually liquids or solids at room temperature whereas most nonpolar substances are gases at room temperature.

Network Solids

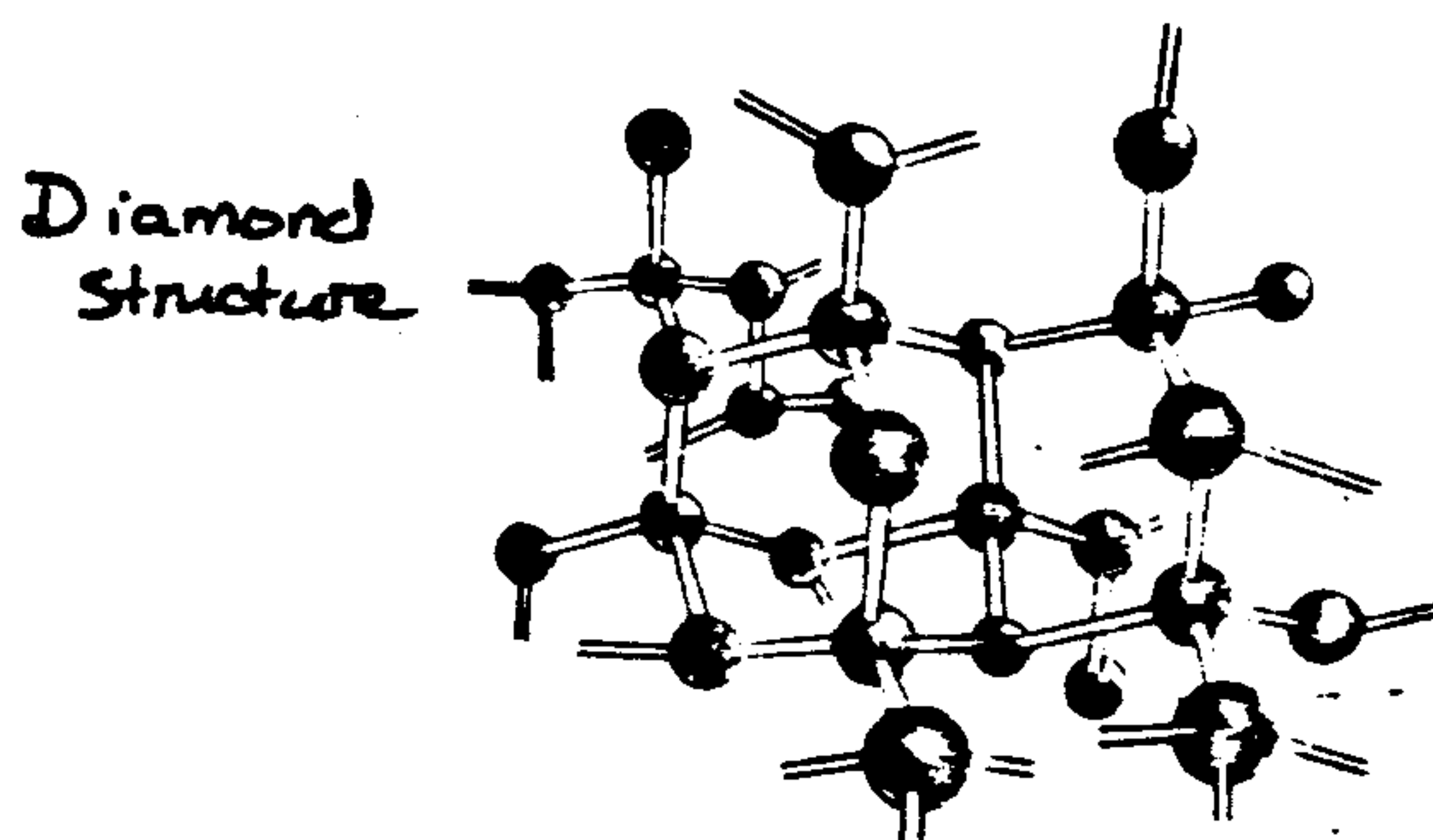
Network solids are also known as covalent solids or covalent crystals.

These substances are not made up of separate, distinct molecules. Instead, they appear to be a single, giant molecule (macromolecule) in which covalent bonds extend from one atom to another in a continuous pattern throughout the entire substance.

Properties of network solids

- Very high melting and boiling points.
- Poor heat and electrical conductors.
- Extreme hardness.

examples: Diamond (pure carbon)
 Silicon carbide (silicon and carbon)
 Silicon dioxide (silicon and oxygen) [also known as quartz]



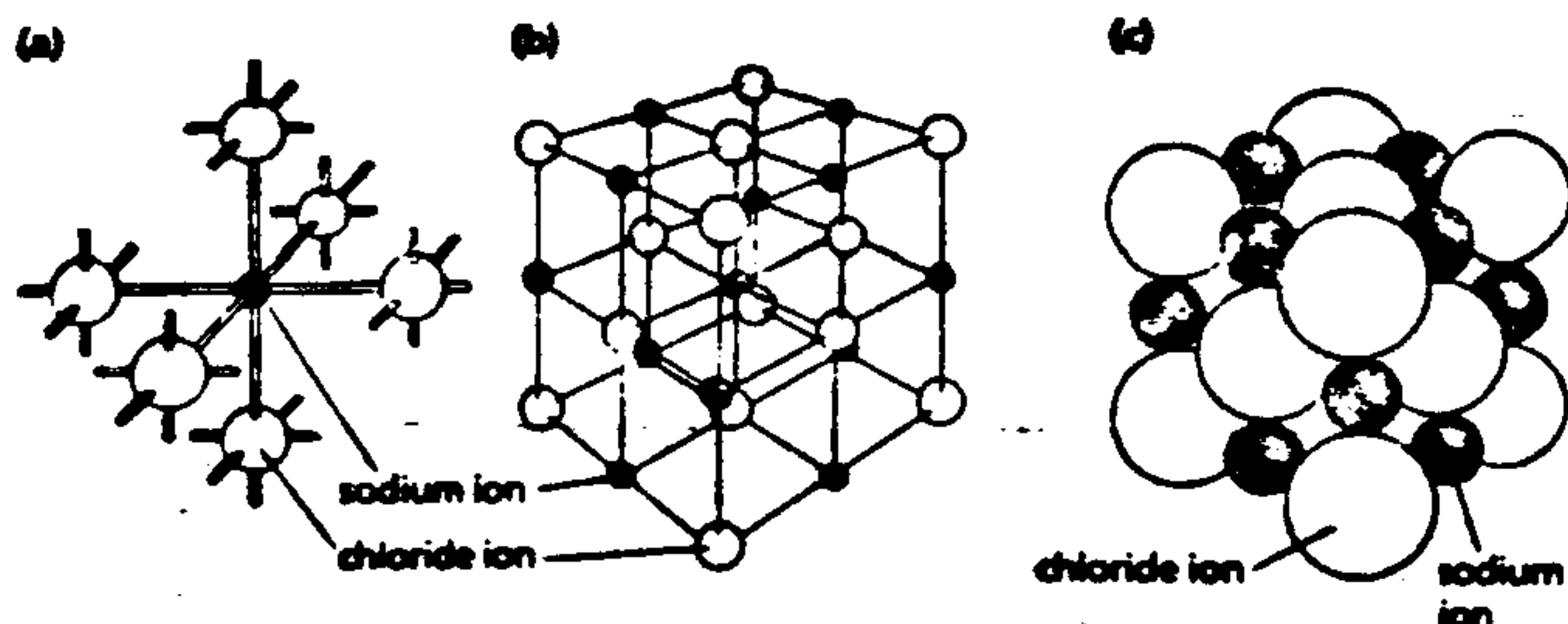
Ionic Crystals

Ions, not atoms, are the basic units that make up an ionic crystal (substance). Cations and anions are arranged into a regular pattern resulting from a balance of forces of attraction and repulsion of opposite and like charges on the ions. This regular pattern of ions is called an ionic crystal or a crystal lattice.

The ions in a crystal lattice structure are strongly held in fixed positions by the electrostatic forces of attraction of surrounding ions. Thus, a large amount of energy is required to break up an ionic crystal.

Properties of ionic crystals

- High melting and boiling points.
- High solubility in water.
- Nonconductor of electricity in solid form.
- High conductor of electricity in melted or solution form.



The sodium chloride crystal. (a) A portion of a crystal, showing a sodium ion and the six chloride ions that surround it. (b) A larger portion of the crystal. (c) Another way of representing a sodium chloride crystal. The arrangement of the ions gives sodium chloride crystals their cubic shape. In ionic crystals, the basic units making up the crystals are ions. In the crystal, there are no groups of bonded atoms that fit the definition of a molecule.

Bond Energy / Bond Strength

The strength of a chemical bond can be expressed in terms of the amount of energy needed to break the bond and separate the atoms.

bond energy- the amount of energy required to break a chemical bond
(measured in kilojoules per mole)

Bond energy is used as a measure of bond strength. **As bond energy increases, bond strength increases. As bond energy decreases, bond strength decreases.**

bond length- the distance between the nuclei of two bonded atoms

Bond energy is used a relative measure of bond length. **As bond energy increases, bond length decreases. As bond energy decreases, bond length increases.**

Bond Strength and Stability of Compounds

As stability increases (potential energy decreases), bond strength increases.
As stability decreases (potential energy increases), bond strength decreases.

Bond Energy and Chemical Change

Generally, chemical change will only take place if the change leads to a lower state of potential energy, and, therefore to a more stable structure.

In **exothermic reactions** energy is released (net output) because the potential energy of the products is less than that of the reactants. This means that the products will be more stable and have stronger bonds (higher bond energy) than the reactants from which they were formed.

In **endothermic reactions** energy is absorbed (net input) because the products have higher potential energy than the reactants. This means that the products will be less stable and have weaker bonds (lower bond energy) than the reactants from which they were formed.

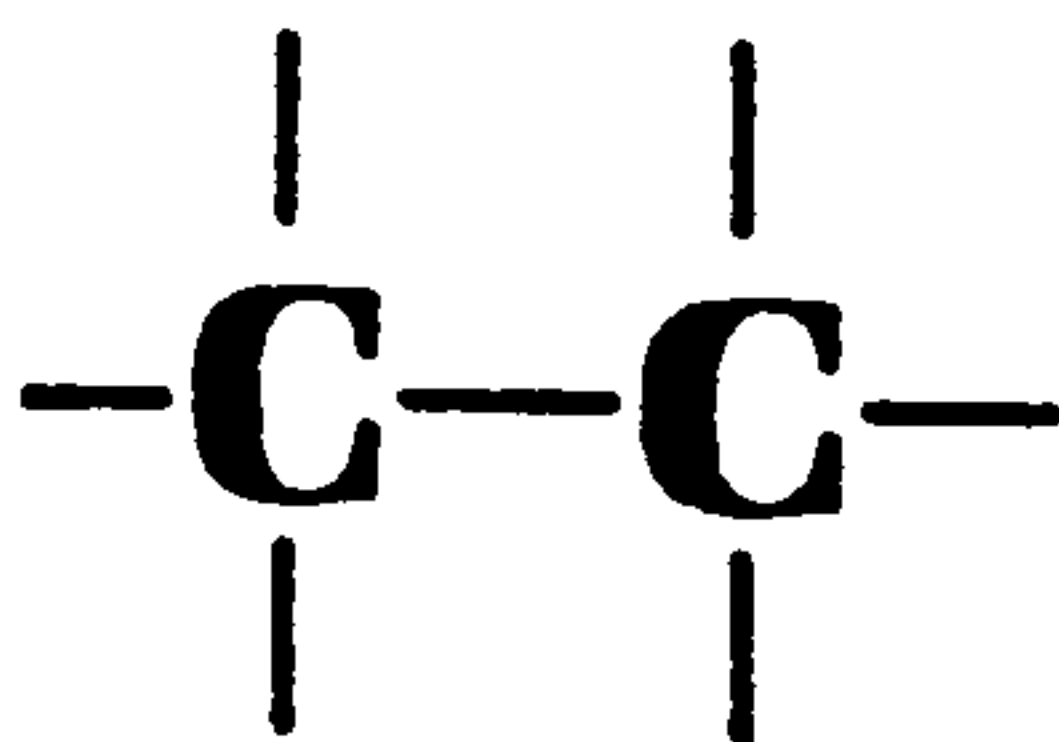
examples of bond energies:

BOND ENERGIES (kJ/mol)*

H—H	436	H—Cl	431
C—H	414	H—Br	364
C—C	347	H—I	299
C=C	619	N—N	159
C≡C	812	N≡N	941
O—O	138	N—H	389
O=O	494	Cl—Cl	243
O—H	463	Br—Br	193
C—O	335	I—I	151
C=O	707	C—Cl	326
H—F	569	C—Br	276

*The bond energies in the table are averages. Values vary depending on the structure of the molecule.

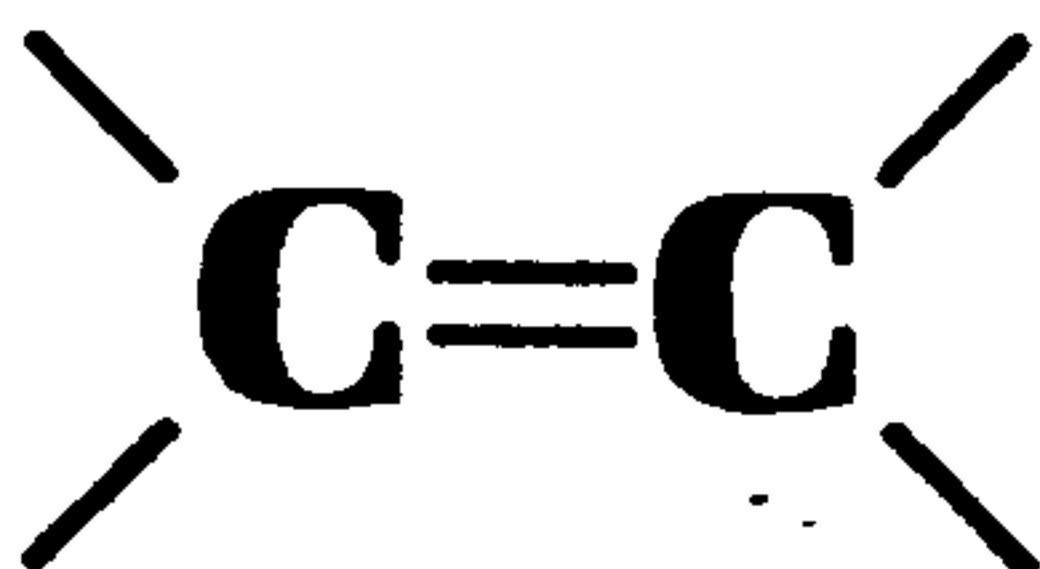
Single bond



0.154 nm

bond lengths

Double bond



0.134 nm

Triple bond



0.120 nm

A carbon atom is capable of a single, double, or triple bond with another carbon atom. Triple bonds are the strongest and shortest of the three carbon-carbon bonds.

d →
gths

d
rgies →

347 kJ/mol

bond energies

619 kJ/mol

812 kJ/mol

In comparing the bond energies / bond lengths of the carbon-carbon single, double, and triple bond it becomes evident that the strength of the double bond is greater than that of the single bond and that the triple bond has the greatest strength of the three types.

Looking carefully, it is interesting to note that the bond energy of the double bond is not twice as great as the energy of the triple bond and that the energy difference between the triple and double bonds is even less than that between the double and single bond. What does this imply?

This data suggests that all of the bonds that make up a multiple bond are not of equal strength. In a double bond, the second bond is not as strong as the first and, in a triple bond, the second bond is weaker than the first bond with the third bond being the weakest of all three bonds.

What does this imply about the chemical reactivity of multiple bonds?