

Chapter 8 - Covalent Bonding

Section 8.1 - Molecular Compounds

Valence electrons - outermost electrons. Able to be gained, lost, or shared to form a bond.

1. Ionic Compounds and Molecular Compounds

a. Ionic Compounds

- Crystalline solids with high melting points
- Bonding occurs when electrons are transferred between atoms (from a cation to an anion)
- Composed of cations and anions but have an overall neutral charge (oppositely charged ions)
- Can conduct an electric current when melted or dissolved in water
- Tend to form between a metal and a nonmetal.
- Smallest representative unit is a Formula unit.
 - Formula unit describes the smallest whole number ratio of ions involved in the ionic compound.
 - A formula unit exists as an array of ions.

b. Molecular Compounds

- Molecular compounds tend to have relatively lower melting and boiling points than ionic compounds.
- At room temperature can be liquids (water, H₂O) or gases (carbon dioxide, CO₂, and nitrous oxide, N₂O).
- Bonding occurs when atoms share electrons (valence electrons)
- Held together by covalent bonds.
 - Covalent bond - a bond formed by the sharing of electrons between atoms
- Have an overall neutral charge.
- Tend to form between two or more nonmetals.
- Smallest representative unit is a molecule.
 - A molecule is a neutral group of atoms joined together by covalent bonds.

2. Molecules and Molecular Compounds

a. In nature, only the Noble Gas elements exist as uncombined atoms.

- They are monatomic as they consist of single atoms (He, Ne, Ar, Kr, Xe, Rn)

- b. Some atoms exist as diatomic molecules
- Diatom molecule - a molecule consisting of 2 atoms.
 - O₂ represents two oxygen atoms that are bonded together
 - Other examples include H₂, N₂, and the halogens (F₂, Cl₂, Br₂, I₂, At₂)
- c. Molecular compounds refer to Compounds made of atoms of different elements (held together by covalent bonds)
- Molecular compound - a compound that is composed of molecules

Examples:

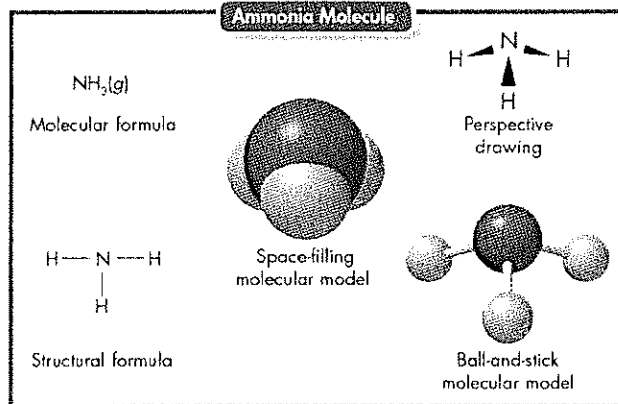
- H₂O, water
 - CO₂, carbon dioxide
 - NH₃, ammonia
 - C₂H₆O, ethanol
 - O₃, ozone
- d. A molecular formula is the chemical formula of a molecular compound
- The molecular formula shows the Kinds and numbers of atoms present in a molecule of a compound.
 - Molecular formula reflects the actual number of atoms in each molecule
 - Ionic compounds' formula units showed the lowest whole-number ratio of ions involved.
 - A molecule is made up of two or more atoms that act as a unit.
 - Examples:
 - H₂O = 2 hydrogens and 1 oxygen in each molecule of water
 - C₄H₁₀ = 4 carbons and 10 hydrogens in each molecule of butane
 - O₂ = 2 oxygen atoms in each molecule of atmospheric oxygen
 - The molecular formula does not tell you about a molecule's structure.

1. It doesn't show either the arrangement of the various atoms in space or which atoms are covalently bonded to one another.

iii. Representing Molecules

1. A variety of diagrams and molecular models can be used to show the arrangement of atoms in a molecule

- a. Molecular formula
b. Structural formula
c. Space filling molecular model
d. Ball + stick molecular model
e. Perspective drawing



2. Molecular structure refers to the arrangement of atoms within a molecule.

Section 8.2 – The Nature of Covalent Bonding

3. In covalent bonds, electron sharing usually occurs so that atoms attain the electron configurations of Noble Gases
- a. Combinations of atoms of the nonmetals and metalloids are likely to form covalent bonds. The combined atoms usually acquire a total of 8 electrons, or an octet, by sharing electrons.
4. The octet rule states that each of the atoms joined by a covalent bond usually acquires eight valence electrons. Most noble gases have eight valence electrons.
5. Single covalent bond – two atoms held together by sharing 1 pair of electrons
- a. H₂ – hydrogen gas consists of diatomic molecules whose atoms share only one pair of electrons, forming a single covalent bond.
- i. The two hydrogen atoms share electrons to form a covalent bond in a diatomic hydrogen molecule
- ii. Each hydrogen attains the electron configuration of Helium (2 electrons)

b. Electron dot structures

i. Show the electrons available to each atom. Helps identify the electrons that are shared

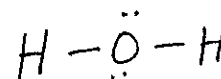
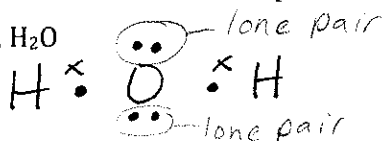
ii. H:H (H_2)

c. Structural formula - represents the covalent bonds as dashes and shows the arrangement of covalently bonded atoms.

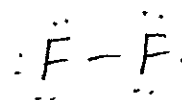
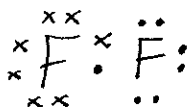
i. H-H (H_2)

d. Unshared pair - valence electrons that are not shared between atoms. Can also be called "lone pair" electrons or nonbinding pairs.

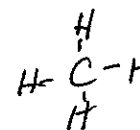
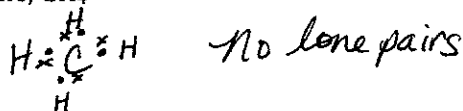
i. Water, H_2O



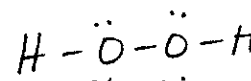
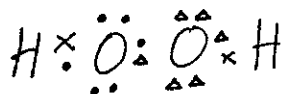
ii. Fluorine gas, F_2



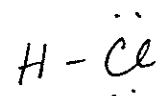
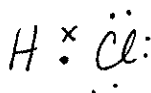
iii. Methane, CH_4



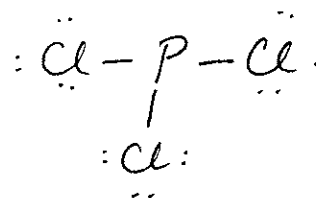
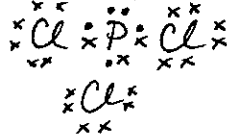
iv. Hydrogen peroxide, H_2O_2



v. Hydrochloric acid, HCl



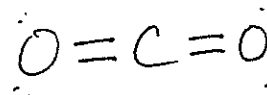
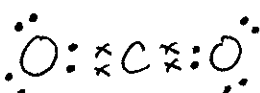
vi. Phosphorous trichloride, PCl_3



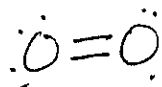
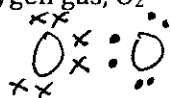
6. Other types of covalent bonds

a. Double covalent bonds - atoms form double covalent bonds if they can attain a noble gas structure by sharing 2 pairs of electrons

i. Carbon dioxide, CO_2

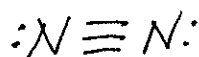
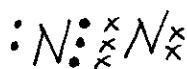


ii. Oxygen gas, O₂



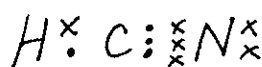
b. Triple covalent bonds – atoms form triple covalent bonds if they can attain a noble gas structure by sharing 3 pairs of electrons

i. Nitrogen gas, N₂



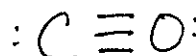
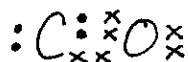
c. Sometimes, molecules can contain a variety of bonds

i. Hydrogen cyanide, HCN



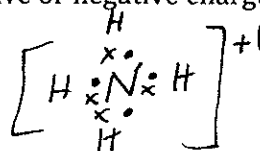
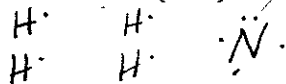
d. Coordinate covalent bond – a covalent bond in which one atom contributes both bonding electrons. The shared electron pair comes from one of the bonding atoms.

i. Carbon monoxide, CO

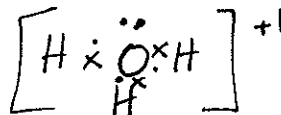
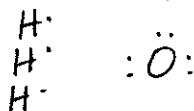


e. Polyatomic ions – atoms joined by covalent bonds that have an overall positive or negative charge. They need additional electrons or fewer to satisfy the octet rule. Many polyatomic ions contain covalent and coordinate covalent bonds. Can also be described as a tightly bound group of atoms that behave as a unit and has a positive or negative charge.

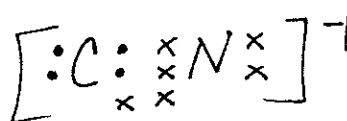
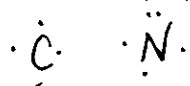
i. Ammonium (NH₄)⁺¹



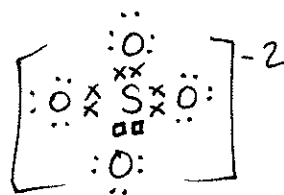
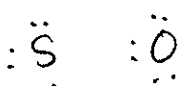
ii. Hydronium (H₃O)⁺¹



iii. Cyanide (CN)⁻¹



iv. Sulfate (SO₄)⁻²



7. Bond dissociation energies

- a. The strength of a covalent bond is related to its bond dissociation energy
- Bond dissociation energy - the energy required to break the bond between two covalently bonded atoms. Units are KJ/mol, which is the energy needed to break one mole of bonds.
 - A large bond dissociation energy corresponds to a strong covalent bond.
- b. There are listed in Table 8.3 on page 236 of our online textbook.

8. Resonance structures

- a. Resonance structures are structures that occur when it is possible to draw 2 or more valid electron dot structures that have the same number of electron pairs for a molecule or ion.
- b. Chemists use resonance structures to envision the bonding in molecules that cannot be adequately described by a single structural formula.
- They don't always accurately represent actual bonding but they are a way to envision the bonding in certain molecules. The actual bonding is a hybrid, or mixture, of the extremes represented by the resonance forms.

c. Ozone, O₃

Section 8.3 - Bonding Theories

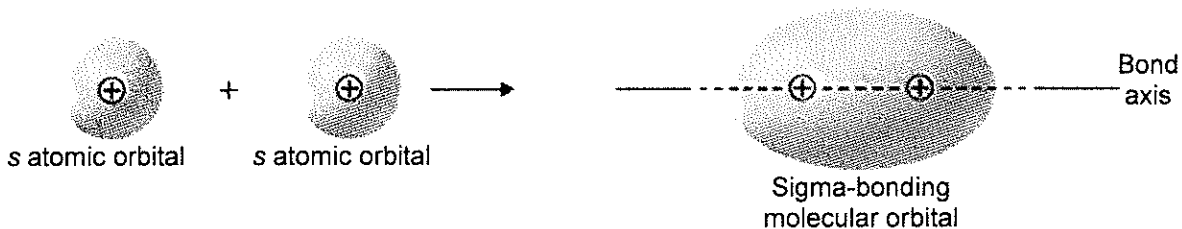
9. Molecular orbitals of electrons

- a. Just as an atomic orbital belongs to a particular atom, a molecular orbital belongs to a molecule as a whole.
- Atomic orbitals are filled when they contain 2 electrons.
 - Molecular orbital that can be occupied by two electrons of a covalent bond is called a bonding orbital. The energy is less than that of the atomic orbitals from which it formed.
- b. Drawings can show molecular orbitals, which are the areas where bonding electrons are most likely to be found.
- c. The quantum mechanical model of bonding assumes that atomic orbitals overlap to produce molecular orbitals.

d. Sigma bonds (Greek letter sigma, σ)

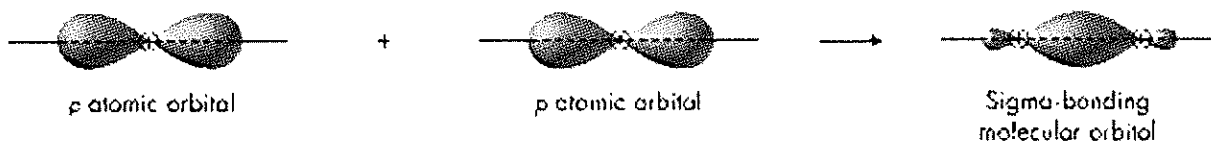
- i. When two atomic orbitals combine to form a molecule orbital that is symmetrical around the axis connecting two atomic nuclei, a sigma bond is formed.
- ii. Covalent bonding results from an imbalance between the attractions and repulsions of the nuclei and electrons involved
 1. The nuclei and electrons attract each other
 2. Nuclei repel other nuclei
 3. Electrons repel other electrons
- iii. Two s atomic orbitals can combine to form a molecular orbital (as in the case of hydrogen, H_2). In a bonding molecular orbital, the electron density between the nuclei is high.
- iv. In sigma bonds, bonding electrons are most likely found between the positively charged nuclei of the atoms bonded together.

\oplus represents the nucleus



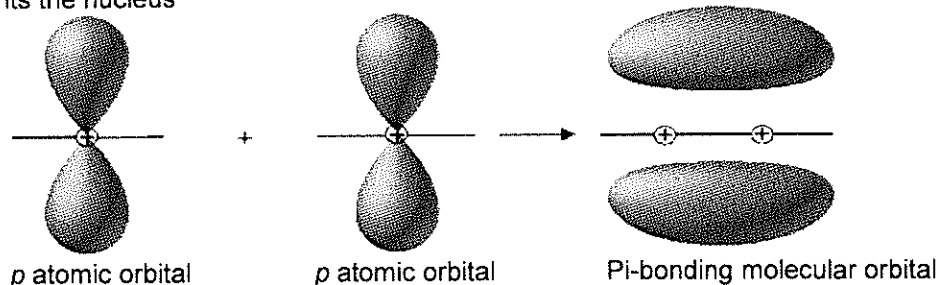
- v. Atomic p orbitals can also overlap to form molecular orbitals. The overlap of the p orbitals produces a bonding molecular orbital that is symmetrical and connects the nuclei.

\oplus represents the nucleus.



- e. Pi bonds (Greek letter pi, π)
- Some orbitals can overlap side to side. When a pi molecular orbital is filled with two electrons, a pi bond will result.
 - Atomic orbitals in pi bonding overlap less than in sigma bonding. Pi bonds tend to be weaker than sigma bonds.

⊕ represents the nucleus



- The bonding electrons are most likely to be found in the regions above and below the bond axis of the bonded atoms.

10. VSEPR Theory

- Electron dot structures fail to reflect the 3-dimensional shapes of molecules.
 - The electron dot structure and structural formulas show the molecule as if it were flat and merely 2-dimensional
 - In reality, molecules are 3-dimensional
- In order to explain the three-dimensional shape of molecules, scientists use valence shell electron pair repulsion theory (VSEPR theory)
 - VSEPR theory states that the repulsion between electron pairs causes molecular shapes to adjust so that the valence electron pairs stay as far apart as possible.
 - Unshared pairs of electrons are also important in predicting the shapes of molecules.

creates minimal amount of repulsion

c. Common molecular shapes

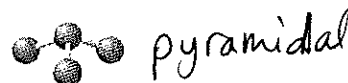
Linear



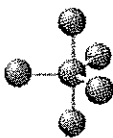
Trigonal planar



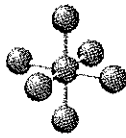
Bent



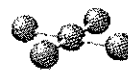
Tetrahedral



Trigonal bipyramidal



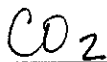
Octahedral



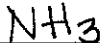
Square planar

d. Examples:

i. Linear -



ii. Pyramidal -



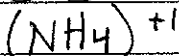
iii. Bent -



iv. Trigonal planar -



v. Tetrahedral -



11. Hybrid Orbitals

a. The VSEPR theory works well when accounting for molecular shapes, but it does not help much in describing the types of bonds formed.

b. Orbital hybridization provides information about both molecular bonding and molecular shape.

i. In hybridization, several atomic orbitals mix to form the same total number of equivalent hybrid orbitals.

c. sp³ hybridization

i. Carbon's electron configuration is 1s² 2s² 2p², so it has 4 valence electrons to use for bonding. Orbital notation = ↑↓ ↑↓ ↑ ↑

1. The one 2s orbital and the three 2p orbitals of a carbon atom mix to form four sp³ hybrid orbitals (Tetrahedral shape, with each angle at 109.5°)

2. In methane, CH₄, each sp³ hybrid orbital of carbon overlaps with a 1s orbital of hydrogen, forming sigma bonds.

3. The sp^3 orbitals extend farther into space than either s or p orbitals, allowing a great deal of overlap with the hydrogen 1s orbitals.
- a. The extent of overlap results in unusually strong covalent bonds.
- d. Hybridization involving double bonds
- i. Ethene (C_2H_4)
1. sp^2 hybrid orbitals form from the combination of one 2s and two 2p atomic orbitals of carbon. Each hybrid orbital will be separated from the other two by 120° .
2. In an ethane molecule, two sp^2 hybrid orbitals of each carbon form sigma bonding molecular orbitals with the four available hydrogen 1s orbitals.
- a. The third sp^2 orbitals of each of the two carbons overlap to form a sigma bonding orbital
- b. The 2p carbon orbitals overlap side by side to form a pi bonding orbital.
- e. Hybridization involving triple bonds
- i. Ethyne or acetylene (C_2H_2)
1. It has two sp hybrid orbitals for each carbon as one 2s atomic orbital mixes with only one of the three 2p atomic orbitals.
2. In an acetylene molecule, one sp hybrid orbital from each carbon overlaps with a 1s orbital of hydrogen to form a sigma bond.
- a. The other sp hybrid orbital of each carbon overlaps to form additional sigma bonds
- b. The two p atomic orbitals from each carbon also overlap.
- f. Types of hybrid orbitals
- i. One atom combining with 3 other atoms
1. sp^3 (one 2s and three 2p orbitals will form 4 sp^3 orbitals)
- ii. One atom combining with 2 other atoms
1. sp^2 (one 2s and two 2p orbitals will form 3 sp^2 orbitals)
- iii. One atom combining with 1 other atom
1. sp (one 2s and one 2p orbitals will form 2 sp orbitals)

Section 8.4 – Polar Bonds and Molecules

12. Bond Polarity

a. Covalent bonds differ in terms of how the bonded atoms share the electrons

i. The character of the molecule depends on the kind and number of atoms joined together. These features determine the molecular properties.

ii. The bonding pairs of electrons in covalent bonds are pulled between the nuclei of the atoms sharing the electrons.

1. The nuclei of atoms pull on the shared electrons (tug of war)

b. Nonpolar covalent bond – when the atoms in the bond pull equally, the bonding electrons are shared equally. Likely to occur when identical atoms are bonded.

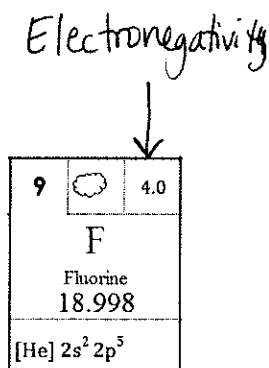
c. Polar covalent bond (polar bond) – covalent bond between atoms in which the electrons are shared unequally. (unequal attraction)

i. The more electronegative atom attracts more strongly and gains a slightly negative charge. The less electronegative atom has a slightly positive charge.

ii. The higher the electronegativity value, the greater the ability of an atom to attract electrons to itself.

d. We can use electronegativity values between two elements to determine what kind of bond is likely to form.

Electronegativity difference range (absolute value)	Most probable type of bond
0.0–0.4	Nonpolar covalent
0.4–1.0	Moderately polar covalent
1.0–2.0	Very polar covalent
≥ 2.0	ionic



- i. There is no sharp boundary between ionic and covalent bonds
1. As the electronegativity difference between two atoms increases, the polarity of the bond increases.
 2. If the difference is more than 2.0, the electrons will likely be pulled away completely by one of the atoms. In that case, an ionic bond will form.

e. Examples:

i. Indium (In) and Tin (Sn)

1. In has an electronegativity of 1.7
2. Sn has an electronegativity of 1.8
3. Electronegativity difference is 0.1 and the bond will be nonpolar.

ii. Hydrogen (H) and Chlorine (Cl)

1. H has an electronegativity of 2.1
2. Cl has an electronegativity of 3.0
3. Electronegativity difference is 0.9 and the bond will be moderately polar.

iii. Gallium (Ga) and Bromine (Br)

1. Ga has an electronegativity of 1.6
2. Br has an electronegativity of 2.8
3. Electronegativity difference is 1.2 and the bond will be very polar.

iv. Potassium (K) and Fluorine (F)

1. K has an electronegativity of 0.8
2. F has an electronegativity of 4.0
3. Electronegativity difference is 3.2 and the bond will be ionic.

v. Identifying Bond Type. Which type of bond will form between each of the following pairs of atoms?

1. N and H 0.9 mod. polar
2. F and F 0 nonpolar
3. Ca and Cl 2.0 ionic
4. Al and Cl 1.5 very polar

13. Describing Polar Covalent Bonds

- a. In a polar molecule, ^{one} end of the molecule is slightly negative and the other end is slightly positive.
- b. The lowercase Greek letter delta (δ) denotes that atoms with a slight charge
- $\delta+$ is used to show the atom in a polar covalent bond that has a slightly positive charge (due to a lower electronegativity value)
 - $\delta-$ is used to show the atom in a polar covalent bond that has a slightly negative charge (due to a higher electronegativity value).
 - HCl forms a moderately polar covalent bond. The H is slightly positive and the Cl is slightly negative (based on their electronegativity differences). The electrons between H and Cl are more likely to be pulled towards Cl

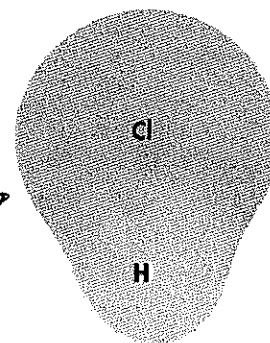
 $\delta+$ $\delta-$

1. H - Cl

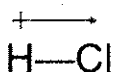
- c. These partial charges are
- ^{shown}
- ~~shows~~
- as clouds of electron

density.

This picture shows that the chlorine atom attracts the electron cloud more than the hydrogen atom does.



- d. The polar nature of the bond may also be represented by an
- arrow
- pointing to the more electronegative atom



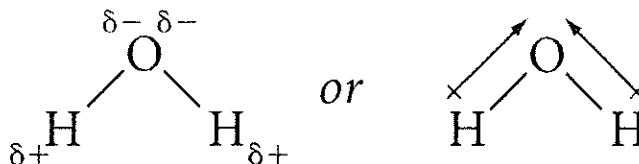
- e. In the hydrogen chloride molecule, the partial charges on the H and Cl atoms are electrically charged regions, or
- poles
- .

- i. A molecule that has two poles is called a dipolar molecule or
- dipole
- . HCl is an example of a dipole.

- f. The bonds in a water molecule are also
- polar
- .

- i. The highly electronegative oxygen (3.5) partially pulls the bonding electrons away from hydrogen (2.0)

- ii. The oxygen acquires a slightly
- negative
- charge. Each hydrogen is left with a slightly
- positive
- charge.



14. Attractions Between Molecules

- a. Molecules can be attracted to each other by a variety of different forces.
- b. Intermolecular attractions are weaker than either ionic or covalent bonds.
 - i. These attractions are responsible for determining whether a molecular compound is a gas, a liquid, or a solid at a given temperature.
- c. Van der Waals forces
 - i. Named after the Dutch chemist Johannes van der Waals
 - ii. Weakest attractions between molecules
 - iii. These forces consist of dipole interactions and dispersion forces.
 1. Dipole interactions occur when polar molecules are attracted to one another.
 - a. The electrical attraction occurs between the oppositely charged regions of polar molecules.
 - b. The slightly negative region of a polar molecule is weakly attracted to the slightly positive region of **another** polar molecule
 2. Dispersion forces are the weakest of all molecular forces and are caused by the motion of electrons. They can occur between polar and nonpolar molecules.
 - a. When the moving electrons happen to be momentarily more on the side of a molecule closest to a neighboring molecule, their electric force influences the neighboring molecule's electrons to be momentarily more on the opposite side.
 - b. The strength of dispersion forces generally increases as the number of electrons in a molecule increases.
 - iv. These attractions are responsible for determining whether a molecular compound is a gas, a liquid, or a solid at a given temperature.
 1. Fluorine and Chlorine have relatively few electrons and are gases at ordinary room temperature and pressure because of their especially weak dispersion forces.

2. Bromine molecules therefore attract each other sufficiently to make bromine a liquid under ordinary room temperature and pressure.
 3. Iodine, with a still larger number of electrons, is a solid at ordinary room temperature and pressure.
- d. Hydrogen bonds
- i. The dipole interactions in water produce an attraction between water molecules
 1. Each O—H bond in the water molecule is highly polar and the oxygen acquires a slightly negative charge because of its greater electronegativity.
 2. The hydrogen in water molecules acquire a slightly positive charge.
 3. The positive region of one water molecule attracts the negative region of another water molecule.
 4. This relatively strong attraction, which is also found in hydrogen-containing molecules other than water, is called a hydrogen bond.
 - ii. Hydrogen bonds are attractive forces in which a hydrogen covalently bonded to a very electronegative atom is also weakly bonded to an unshared electron pair of another electronegative atom.
 1. The other atom may be in the same molecule or in a nearby molecule.
 2. Hydrogen bonding always involves hydrogen.
 - iii. A hydrogen bond has about 5 percent of the strength of the average covalent bond.
 1. Hydrogen bonds are the strongest of the intermolecular forces.
 2. They are extremely important in determining the properties of water and biological molecules.
 - a. A snowflakes shape is determined by the interactions of hydrogen bonds during its formation.
 - b. Water has many unique properties due to hydrogen bonding. It has surface tension, is able to form droplets, and exhibits capillarity.

15. Intermolecular Attractions and Molecular Properties

- a. At room temperature, some compounds are gases, some are liquids, and some are solids.
- The physical properties of a compound depend on the type of bonding it displays—in particular, on whether it is ionic or covalent.
 - The diversity of physical properties among covalent compounds is mainly because of widely varying intermolecular attractions.
- b. The melting and boiling points of most compounds composed of molecules are low compared with those of ionic compounds.
- In most solids formed by molecules, only the weak attractions between molecules need to be broken.
 - A few solids that consist of molecules do not melt until the temperature reaches 1000°C or higher.
 - Most of these very stable substances are network solids (or network crystals), solids in which all of the atoms are covalently bonded to each other.
 - Melting a network solid would require breaking covalent bonds throughout the solid.
 - Diamond is an example of a network solid.
 - Each carbon atom in a diamond is covalently bonded to four other carbons, interconnecting carbon atoms throughout the diamond.
 - Diamond does not melt; rather, it vaporizes to a gas at 3500° C and above.

16. Differences between ionic and covalent (molecular) substances

Characteristics of Ionic and Molecular Compounds		
Characteristic	Ionic Compound	Molecular Compound <i>Covalent</i>
Representative unit	Formula unit	Molecule
Bond formation	Transfer of one or more electrons between atoms <i>(gain + lose electrons)</i>	Sharing of electron parts between atoms <i>equal sharing = nonpolar</i> <i>unequal sharing = polar</i>
Type of elements	Metallic and nonmetallic	Nonmetallic
Physical state	Solid	Solid, liquid, or gas
Melting point	High (usually above 300° C)	High (usually below 300° C)
Solubility in water	Usually high	High to low
Electrical conductivity of aqueous solution	Good conductor	Poor to nonconducting

"Crystal lattice"

Examples

LiF, NaCl

H₂O, CH₄