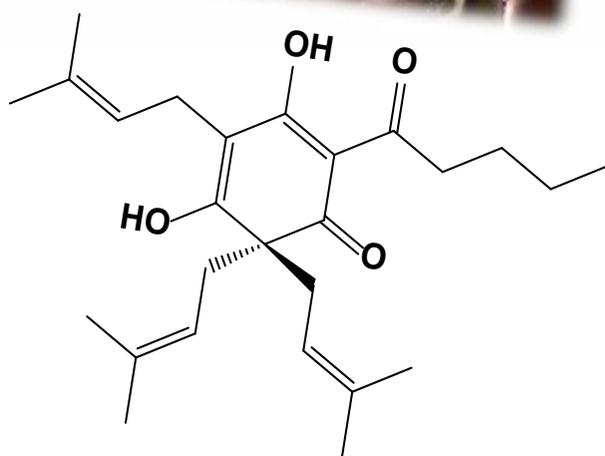
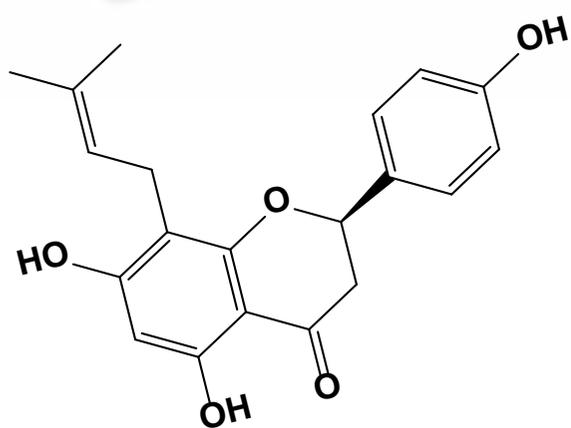


Consumer Chemistry: How Organic Chemistry Impacts Our Lives



Abozenadah

Bishop

Bittner

Flatt



To Share or Adapt this Content please Reference:

Abozenadah, H., Bishop, A., Bittner, S. and Flatt, P.M. (2017) Consumer Chemistry: How Organic Chemistry Impacts Our Lives. CC BY-NC-SA. Available at:

Cover photo adapted from:

1. Rovinetti, R. (2014). Available at: https://en.wikipedia.org/wiki/VSEPR_theory

Chapter 4: The Shape and Characteristics of Compounds

Chapter 4 materials have been adapted from the following creative commons resources unless otherwise noted:

1. Organic Chemistry Portal. WikiUniversity. Available at: https://en.wikiversity.org/wiki/Portal:Organic_chemistry
2. Anonymous. (2012) *Introduction to Chemistry: General, Organic, and Biological (V1.0)*. Published under Creative Commons by-nc-sa 3.0. Available at: <http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/index.html>
3. Poulsen, T. (2010) *Introduction to Chemistry*. Published under Creative Commons by-nc-sa 3.0. Available at: <http://openedgroup.org/books/Chemistry.pdf>
4. OpenStax (2015) Atoms, Isotopes, Ions, and Molecules: The Building Blocks. OpenStax CNX. Available at: <http://cnx.org/contents/be8818d0-2dba-4bf3-859a-737c25fb2c99@12>.
5. Wikipedia, Ionic Compound. Available at: https://en.wikipedia.org/wiki/Ionic_compound

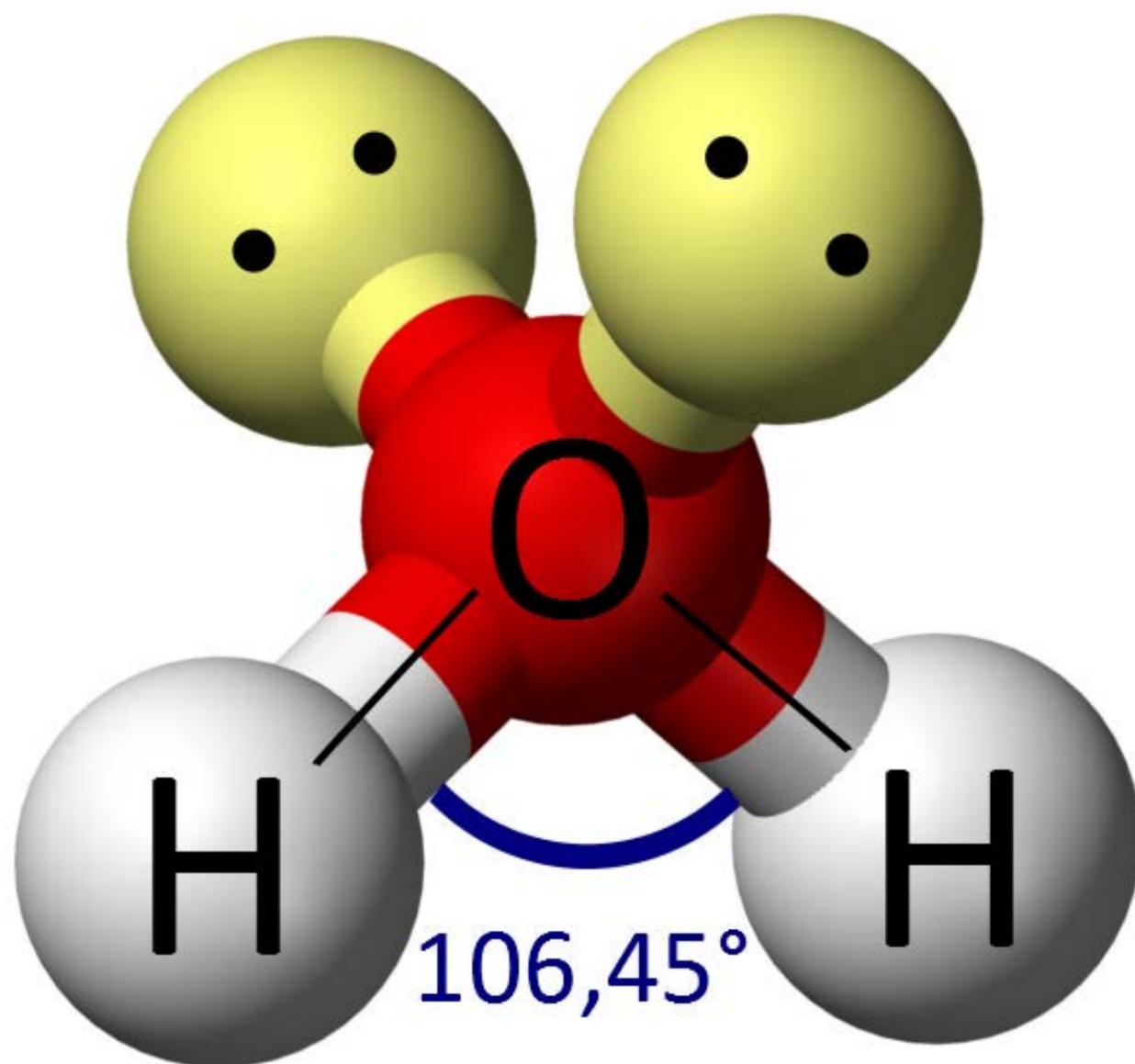


Table of Contents

4.1 Molar Mass	6
4.2 Electronegativity and Bond Polarity	6
4.3 Shape of Ionic Compounds	13
4.4 Shape of Covalent Compounds:	
VSEPR Theory	14
Predicting the Shape: The AXE Method	15
4.5 Intermolecular Interactions	22
Chapter Summary	35

Chapter 4: The Shape and Characteristics of Compounds

4.1 Molar Mass

The **molar mass** of an ionic or covalent compound is simply the sum of the masses of its atoms. To calculate a molar mass, it is important that you keep track of the number of atoms of each element in the chemical formula to obtain the correct molecular mass.

For Example:

A molecule of NaCl contains 1 Na⁺ and 1 Cl⁻. Thus, we can calculate the molar mass of this compound by adding together the atomic masses of sodium and chlorine, as found on the periodic table (Figure 4.1).

Na Atom	Cl Atom	Na + Cl
22.990	35.453	58.443

For a larger molecule, like glucose (C₆H₁₂O₆) that has multiple atoms of the same type, simply multiply the atomic mass of each atom by the number of atoms present in the chemical formula, and then add up all the atomic masses to get the final molecular mass.

Atom	Carbon	Hydrogen	Oxygen	Glucose (C ₆ H ₁₂ O ₆)
# atoms	6	12	6	6 + 12 + 6
atomic mass	12.011	1.0079	15.999	6(12.011) + 12(1.0079) + 6(15.999)
total mass	72.066	12.095	95.994	180.155

4.2 Electronegativity and Bond Polarity

Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, there will always be one atom that attracts the electrons in the bond

more strongly than the other atom does, as shown in Figure 4.2. When such an imbalance occurs, there is a resulting buildup of some negative charge (called a partial negative charge and designated δ⁻) on one side of the bond and some positive charge (designated δ⁺) on the other side of the bond. A covalent bond that has an unequal sharing of electrons, as in part

Test Yourself:

Use the atomic masses in Fig 4.1 (rounded to two decimal places) to determine the formula or molecular mass for each compound.

Remember that numbers in parenthesis are distributive....

$$2\text{Al} + 3\text{S} + 12\text{O} = \text{Al}_2(\text{SO}_4)_3$$

TiO₂

Au(NO₃)₃

CH₃OH

N₂O₅

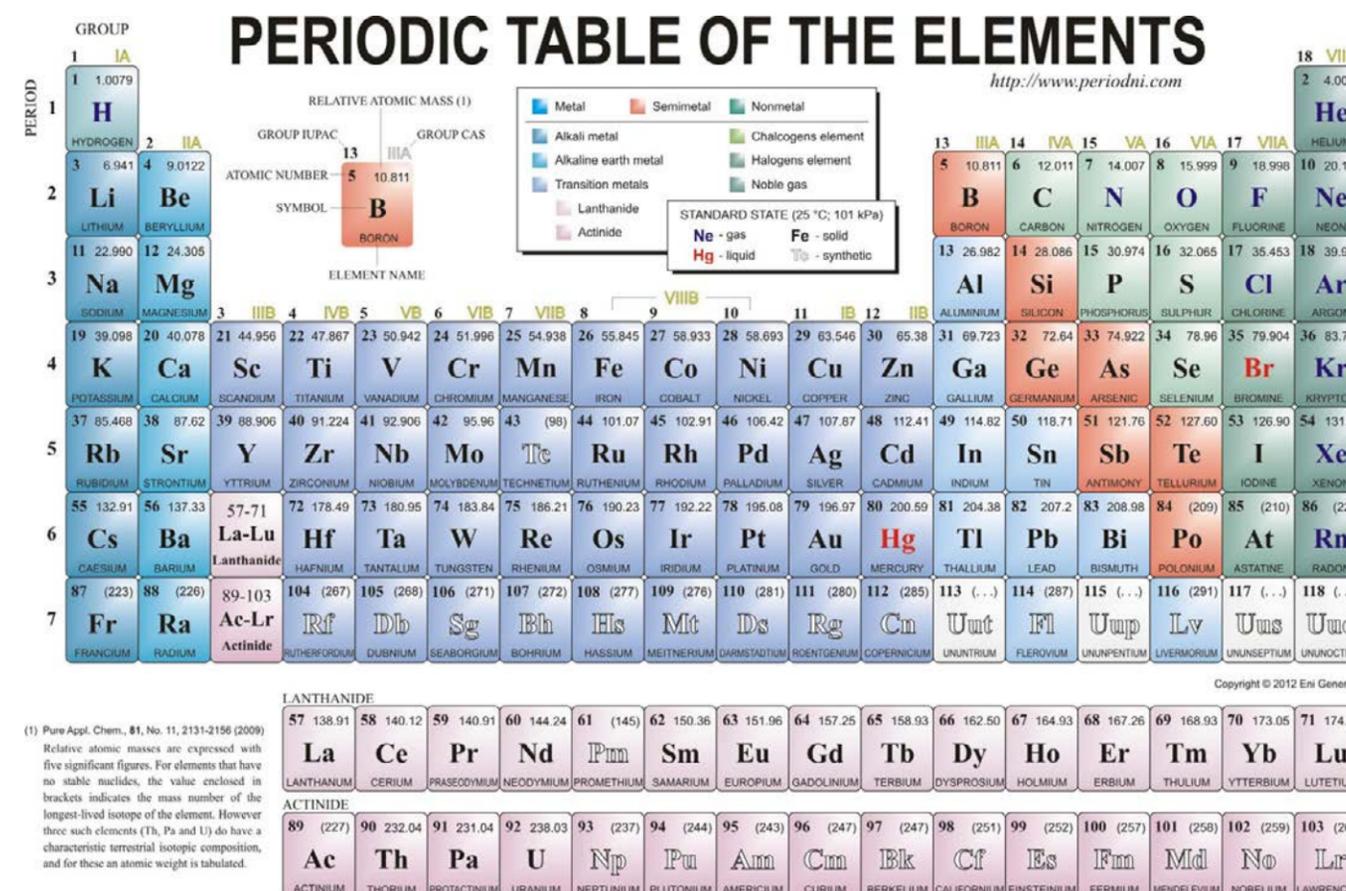


Figure 4.1 Periodic Table of the Elements

(b) of Figure 4.2, is called a **polar covalent bond**. A covalent bond that has an equal sharing of electrons (part (a) of Figure 4.2) is called a **nonpolar covalent bond**.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred completely rather than shared. To judge the relative polarity of a covalent bond, chemists use **electronegativity**, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

There are various numerical scales for rating electronegativity. Figure 4.3 shows one of the most popular—the **Pauling scale**. The polarity of a covalent bond can be judged by determining the difference in the electronegativities between the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in

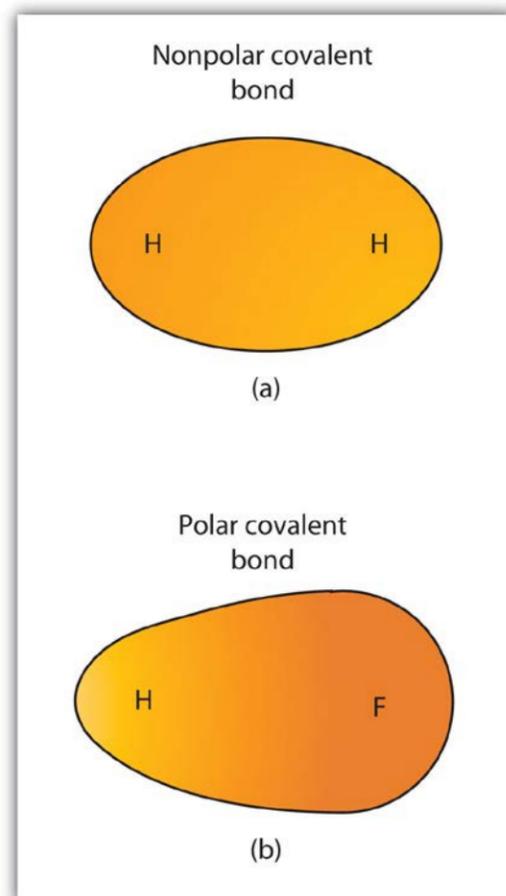


Figure 4.2 Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The fluorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

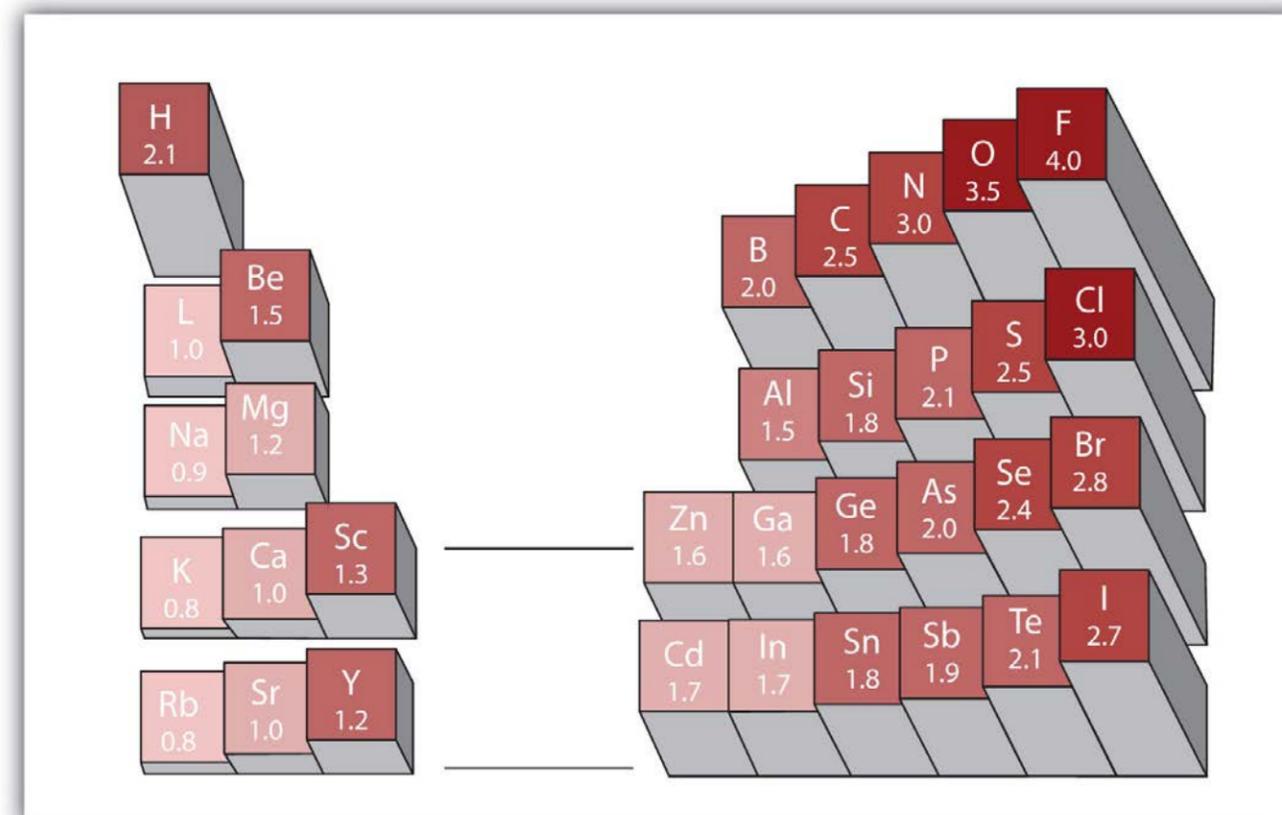


Figure 4.3 Electronegativities of Various Elements. The Pauling Scale for electronegativities has the value for fluorine atoms set at 4.0, the highest value.

the bond. Although there are no hard and fast rules, the general rule is that a difference in electronegativity less than 0.4 indicates the bond is nonpolar; when the difference is greater than 0.4, the bond is considered polar. When the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond. Examples of electronegativity difference are shown in Figure 4.4.

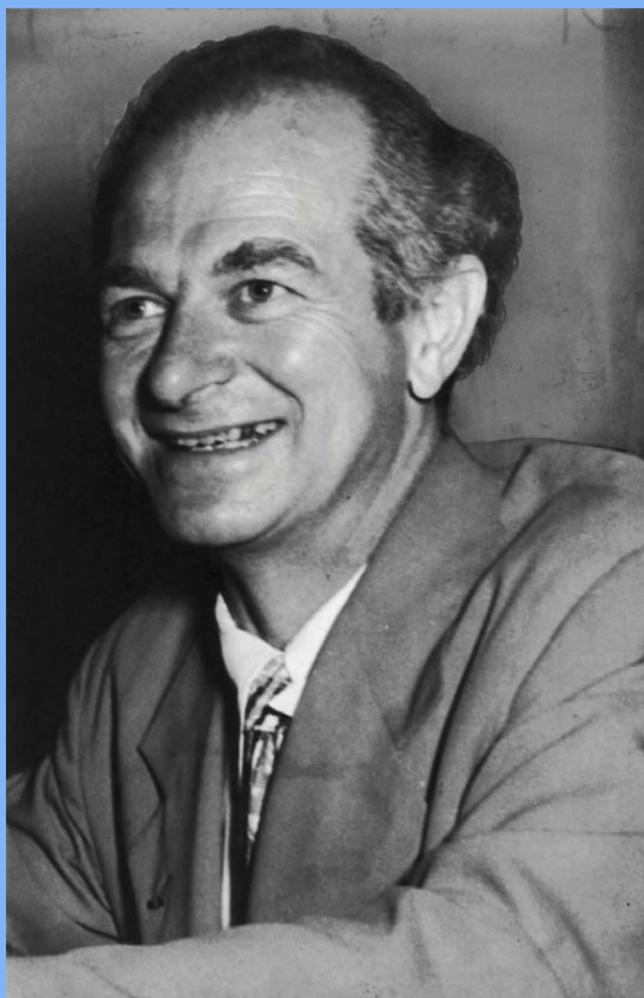
Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–94) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.

Linus Pauling was one of the most influential chemists of the 20th century.



When a molecule's bonds are polar, the molecule as a whole can display an uneven distribution of charge, depending on how the individual bonds are oriented. For example, the orientation of the two O–H bonds in a water molecule (Figure 4.5) is bent: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule itself is polar. The polarity of water has an enormous impact on its physical and chemical properties. (For example, the boiling point of water [100°C] is high for such a small molecule and is due to the fact that polar molecules attract each other strongly.) In contrast, while the two C=O bonds in carbon dioxide are polar, they lie directly opposite each other and so cancel each other's effects. Thus, carbon dioxide molecules are nonpolar overall. This lack of polarity influences some of carbon dioxide's properties. (For example, carbon dioxide becomes a gas at -77°C, almost 200° lower than the temperature at which water boils.)

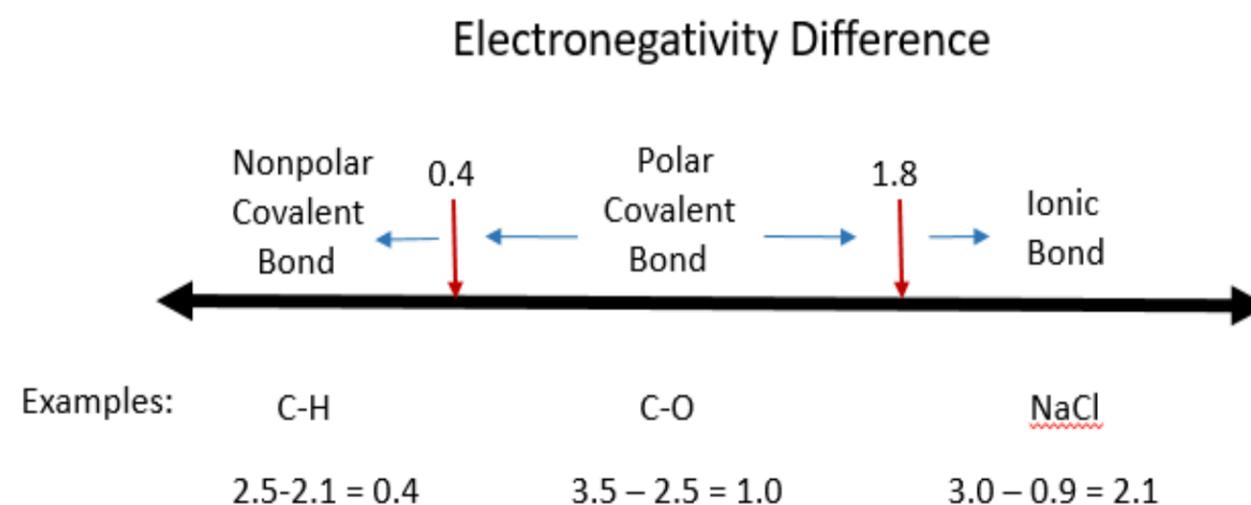


Figure 4.4 Electronegativity Difference Diagram. The diagram above is a guide for discerning what type of bond forms between two different atoms. By taking the difference between the electronegativity values for each of the atoms involved in the bond, the bond type and polarity can be predicted.

Concept Review:

1. Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

- A. C and N
- B. H and H
- C. Na and F
- D. O and H

Answers:

Solution

- A. Carbon has an electronegativity of 2.5, while the value for nitrogen is 3.0. The difference is 0.5, which is just slightly polar.
- B. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
- C. Sodium's electronegativity is 0.9, while fluorine's is 4.0. The difference is 3.1, which is very high, and so sodium and fluorine form an ionic compound.
- D. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. We would expect a very polar bond, but not so polar that the O–H bond is considered ionic.

Test Yourself:

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

C and P

K and Br

N and N

Cs and F

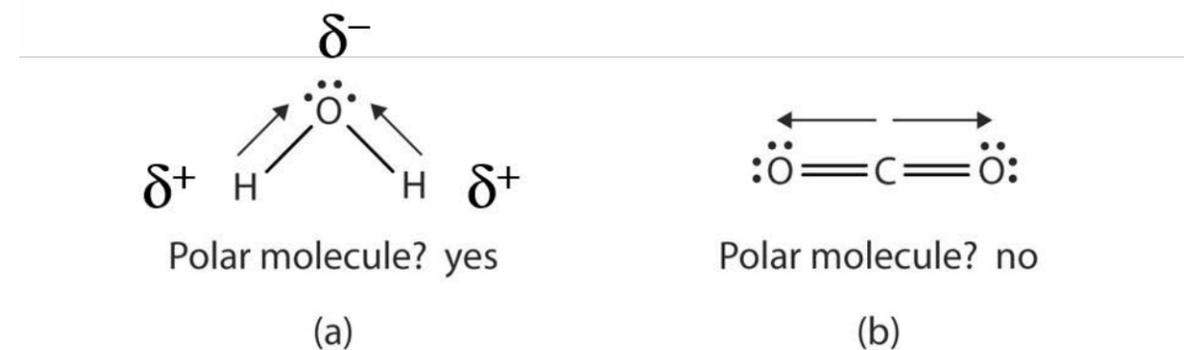


Figure 4.5 Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their molecular polarities. Note that the arrows in the diagram always point in the direction where the electrons are more strongly attracted.

4.3 Shape of Ionic Compounds

In chemistry, an ionic compound is a chemical compound comprised of ions held together by electrostatic forces, termed ionic bonding. The compound is neutral overall, but consists of positively charged cations and negatively charged anions. These can be simple ions such as the sodium (Na⁺) and chloride (Cl⁻) in sodium chloride, or polyatomic species such as the ammonium (NH₄⁺) and carbonate (CO₃⁻²) ions in ammonium carbonate. Individual ions within an ionic compound usually have multiple nearest neighbours, so are not considered to be part of molecules, but instead part of a continuous three-dimensional network, usually in a crystalline structure. Figure 4.6 shows the structure of sodium chloride (NaCl).

Ionic compounds containing hydrogen ions (H⁺) are classified as **acids**, and those containing hydroxide (OH⁻) or oxide (O₂⁻) ions are classified as **bases**. Ionic compounds without these ions are known as **salts**.

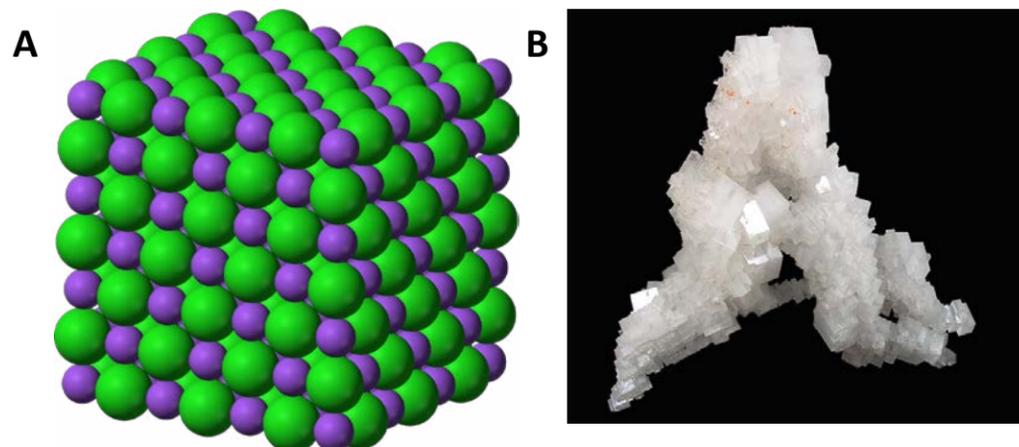


Figure 4.6 Crystal Lattice. (A) The crystal structure of sodium chloride, NaCl, a typical ionic compound. The purple spheres represent sodium cations, Na⁺, and the green spheres represent chloride anions, Cl⁻. (B) Halite, the mineral form of sodium chloride, forms when salty water evaporates leaving the ions behind.

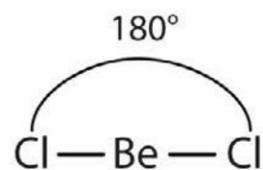
Source: (A) Benjah-bmm27 (2010). (B) Lavisky, R. (2010) Both (A) and (B) Available at: https://en.wikipedia.org/wiki/Ionic_compound

Ionic compounds typically have high melting and boiling points, and are hard and brittle. As solids, they are most often electrically insulating, but when melted or dissolved they become highly conductive, because the ions are mobilized.

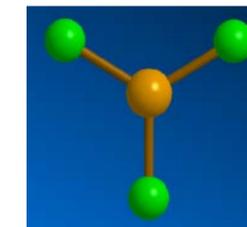
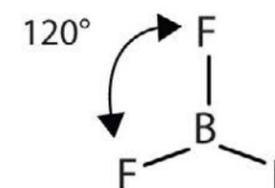
4.4 Shape of Covalent Compounds: VSEPR Theory

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of shared negatively charged electrons, tend to repel one another. This concept is called the valence shell electron pair repulsion (VSEPR) theory. For example, the two covalent bonds in BeCl₂ stay as far from each other as possible, ending up 180° apart from each other.

The result is a linear molecule:

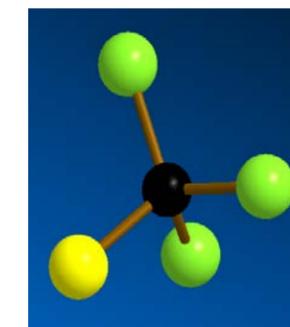
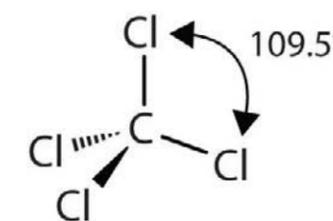


Similarly, the three covalent bonds in BF₃ repel each other to form 120° angles in a plane, in a shape called trigonal planar:



The molecules BeCl₂ and BF₃ actually violate the octet rule; however, such exceptions are rare and will not be discussed further in this text.

The four covalent bonds in CCl₄ arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5°:



Predicting the Shape: The AXE Method

So, how can this theory of electron repulsion be used in a simple way to predict the shape of a molecule? First, it is necessary to understand how many electron pairs are involved and whether or not those electron pairs are in bonded relationships between two atoms (**Bonded Pairs**) or whether they are nonbonding pairs (**Lone Pairs**). To make this determination, it is useful to draw the Lewis Structure for the molecule and show all of the bonding groups and lone pair electrons. Note that in VSEPR theory that a double or triple bond are treated as a single bonding group, because all of the electrons involved in the bond are shared with only a single atom. The sum of the number of atoms bonded to a central atom and the number of lone pairs formed by the nonbonding valence electrons is known as the central atom's steric number. Once the Lewis Structure is drawn and the central atom's steric number is known, the AXE method can be used to predict the overall shape of the molecule.

Everyday Uses for Ionic Compounds

Ionic compounds have long had a wide variety of uses and applications. Many minerals are ionic. Humans have processed common salt (sodium chloride) for over 8000 years, using it first as a food seasoning and preservative, and now also in manufacturing, agriculture, water conditioning, for de-icing roads, and many other uses. Many ionic compounds are so widely used in society that they go by common names unrelated to their chemical identity. Examples of this include borax, calomel, milk of magnesia, oil of vitriol, and saltpeter.

Mercury (I) Chloride (Hg_2Cl_2) or Calomel is a unique compound, because the mercury forms a metallic bond with the other mercury atom, and then forms an ionic interaction with each of the chloride ions (Cl-Hg-Hg-Cl). Calomel was once used as a treatment for infectious diseases such as syphilis, cholera, and malaria. It was used in the United States from the late 1700s to the 1860s. Use was discontinued due to the neurotoxicity of mercury and the discovery of safer and more effective treatments.

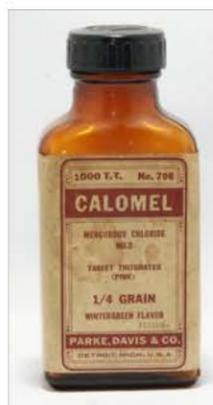
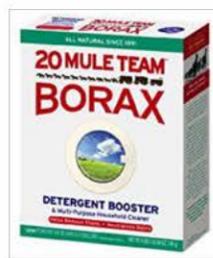


Photo from: The Herb Museum. Available at: <http://www.herbmuseum.ca/content/parke-davis-co-calomel-wintergreen-flavor>

Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) or Borax has many uses. It is used in detergents, cosmetics, and enamel glazes. It is also used in biochemistry to make buffer solutions, has been used as a flame retardant, and an antifungal compound. It was first discovered in dry lake beds in Tibet where it was transported via the Silk Road. Discovery in the deserts of California and Nevada in the late 1800s made borax readily available in the United States.



Rio Tinto Borax Mine Pit, Boron, CA
Source: Wichary, M. (2012)
<https://en.wikipedia.org/wiki/Borax>

Everyday Uses for Ionic Compounds

Magnesium Hydroxide [$\text{Mg}(\text{OH})_2$] or Milk of Magnesia is a basic ionic compound that is a common component of antacids and laxatives. As an antacid, milk of magnesia simply reduces the acidity of the stomach through an acid-base neutralization reaction: $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$. As a laxative, Mg^{2+} is poorly absorbed from the intestinal tract, so it draws water from the surrounding tissue by osmosis.



Sulfuric Acid (H_2SO_4) or Oil of Vitriol is a highly corrosive acid that can be derived from a category of glassy minerals originally called green vitriol (iron sulfate – FeSO_4). Sulfuric acid is a highly utilized industrial compound with approximately 180 million tons produced annually. Most is used in the production of fertilizers (~60%). It is also required for the production of many detergents, synthetic resins, dyes, pharmaceuticals, insecticides, and antifreeze, among others.



Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration.

Photo By Toxic Walker - Own work, CC BY-SA 3.0,
<https://commons.wikimedia.org/w/index.php?curid=19343915>

Potassium Nitrate (KNO_3) or Saltpeter has found major uses in fertilizers providing a major source of nitrogen. As an oxidizing agent, it is used in rocket propellants, fireworks, and as a major constituent of gunpowder (blackpowder). It has also found use as a food preservative. As a preservative, it prevents the germination of the bacterium, *C. botulinum*, in meat products, reducing botulism poisoning (although the use of KNO_3 for this purpose has largely been replaced by other nitrates and preservatives).



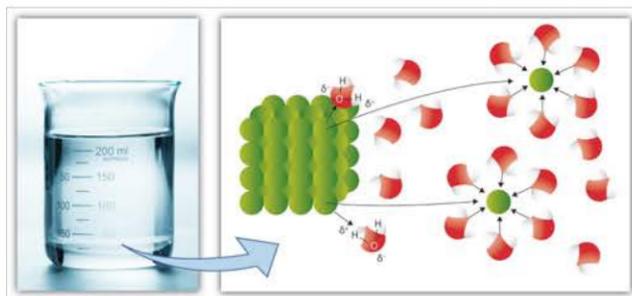
Saltpeter powder, KNO_3

Photo By w:User:Walkerma, Public Domain,
<https://commons.wikimedia.org/w/index.php?curid=184556>

Everyday Uses for Ionic Compounds

Soluble ionic compounds like table salt (NaCl) can easily be dissolved to provide **electrolyte solutions** (solutions that contain charged ions). Rehydration fluids and many sports drinks contain required electrolytes (Na⁺, K⁺, Mg²⁺, Ca²⁺ and Cl⁻) that are used in nerve impulse conduction and other important biological processes. Infections like cholera can be deadly due to dehydration and loss of electrolyte balance in the body.

Specific properties of solutions depend on the concentration of dissolved particles within the solution. These properties are called **colligative properties** and include increasing the osmotic pressure, and causing freezing-point depression and boiling-point elevation. Because the particles are charged ions they also increase the electrical conductivity of the solution. Due to these properties, salts are used for many purposes, including roadway de-icing in the winter. By placing salt on the road, the freezing point of water is depressed.



When a salt dissolves in water, the individual ions of the salt become surrounded by water molecules. Eventually the ion detaches from the remaining solid, and floats suspended by the surrounding water molecules in solution. These charged particles floating in solution are known as electrolytes.



Cholera patient drinking and oral rehydration electrolyte solution to reduce dehydration.

Source: Centers for Disease Control and Prevention.
<https://commons.wikimedia.org/w/index.php?curid=1312984>



De-icing roadways with salt

Source: <http://www.treehugger.com/environmental-policy/americas-dairyland-wisconsin-using-cheese-brine-deice-roads.html>



Mounds of road salt used in the winter

Source: https://en.wikipedia.org/wiki/Sodium_chloride

Everyday Uses for Ionic Compounds

The chemical identity of the ions is important in many uses. For example, fluoride compounds are used in dentistry to help strengthen tooth enamel. Salts containing fluoride are often dissolved in municipal water supplies for water fluoridation. This aims to help prevent tooth decay.

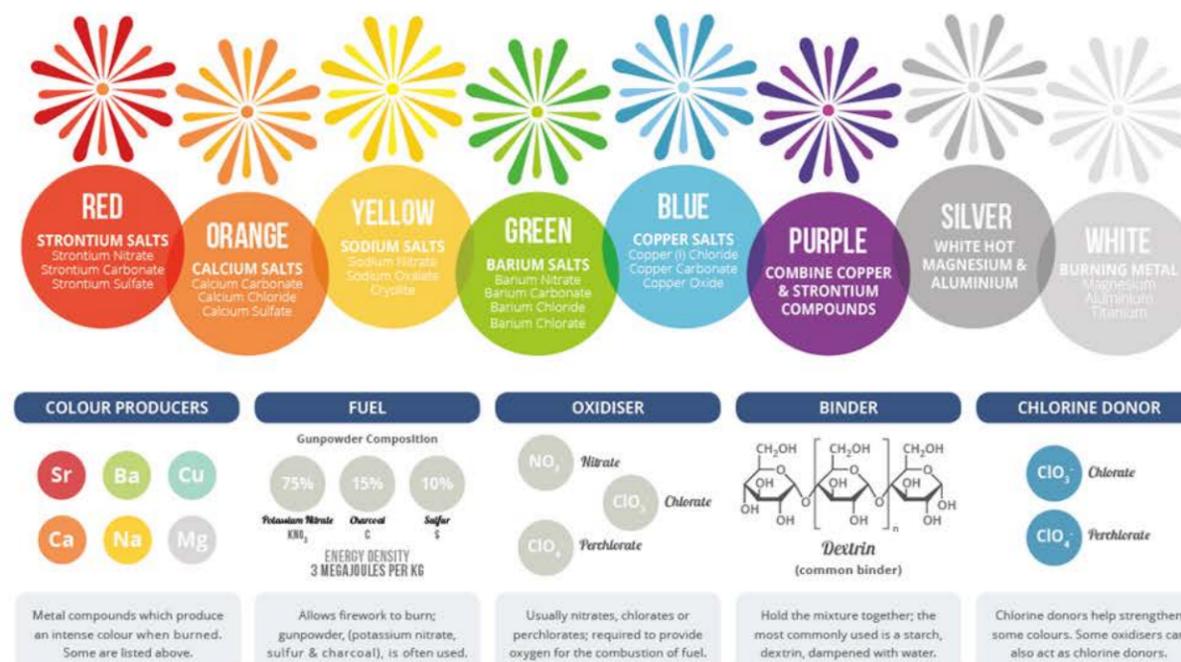


Dentistry trays filled with fluoride foam

Source: https://en.wikipedia.org/wiki/Tooth_enamel

Solid ionic compounds have long been used as paint pigments and are resistant to organic solvents, but are sensitive to acidity or basicity. Since 1801 pyrotechnicians, who build fireworks, have described and widely used metal-containing ionic compounds as sources of color in fireworks. Under intense heat, the electrons in the metal ions or small molecules can be excited. These electrons later return to lower energy states, and release light with a color spectrum characteristic of the metal ion present.

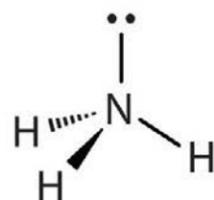
THE CHEMISTRY OF FIREWORK COLOURS



© COMPOUND INTEREST 2015 - WWW.COMPOUNDCHEM.COM | Twitter: @compoundchem | Facebook: www.facebook.com/compoundchem
 This graphic is shared under a Creative Commons Attribution-NonCommercial-NoDerivatives licence.

Source for Everyday uses for ionic compounds: https://en.wikipedia.org/wiki/Ionic_compound

In the AXE method of electron counting, the 'A' refers to the central atom in the molecule, 'X' is the number of bonded atoms connected to the central atom, and 'E' are the number of lone pair electrons present on the central atom. Note that 'X' and 'E' only refer to the electron pairs associated with the central atom 'A'. The number of connected atoms, 'X', and lone pair electrons, 'E' are then written as a formula. For example, if you have a molecule of NH₃:



We can see that there are three atoms of hydrogen bonded to the central nitrogen atom. Thus, 'X' = 3 bonded atoms. We can also see that the central nitrogen has one lone pair of electrons extended off of the top of the atom. Thus, 'E' = 1 lone pair of electrons. We derive two important pieces of information from this. First, we can add 'X' + 'E' to determine the steric number of our central atom. In this case, the nitrogen has a steric number of 4 = (3 + 1). Second, we can solve our overall AXE formula by writing in the subscripts for 'X' and 'E'. For NH₃, the AXE formula is AX₃E₁. With the steric number and AXE formula calculated, we can now use Table 4.1 'AXE Model of Molecular Shapes' to predict the molecular geometry or shape of the overall molecule.

In Table 4.1, scroll down to the correct steric number row, in this case, row 4, and then scan across to find the correct AXE formula for your compound. In this case, the second selection is correct: AX₃E₁. So we can see from this table that the shape of NH₃ is trigonal pyramidal (or it looks like a pyramid with three corners with a hydrogen at each one). Notice that a lone pair electrons on the central atom affect the shape by their presence by pushing the hydrogens below the central plain of the molecule, but that it is not included in the overall shape of the molecule (Figure 4.7).

Table 4.1: AXE Model of Molecular Shapes

Steric Number	Molecular Geometry (0 Lone Pairs)	Molecular Geometry (1 Lone Pair)	Molecular Geometry (2 Lone Pairs)	Molecular Geometry (3 Lone Pairs)
2	Linear, AX ₂ 			
3	Trigonal Planar, AX ₃ 	Bent, AX ₂ E ₁ 		
4	Tetrahedral, AX ₄ 	Trigonal Pyramidal, AX ₃ E ₁ 	Bent, AX ₂ E ₂ 	
5	Trigonal Bipyramidal, AX ₅ 	Seesaw, AX ₄ E ₁ 	T-shaped, AX ₃ E ₂ 	Linear, AX ₂ E ₃
6	Octahedral, AX ₆ 	Square Pyramidal, AX ₅ E ₁ 	Square Planar, AX ₄ E ₂ 	
7	Pentagonal Bipyramidal, AX ₇ 	Pentagonal Pyramidal, AX ₆ E ₁ 	Pentagonal Planar, AX ₅ E ₂ 	

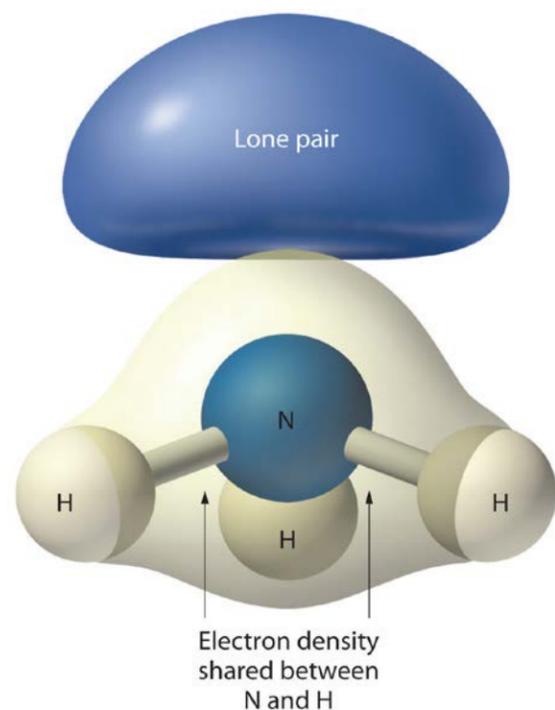
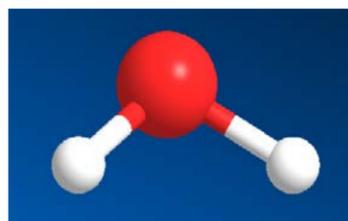
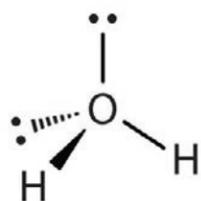


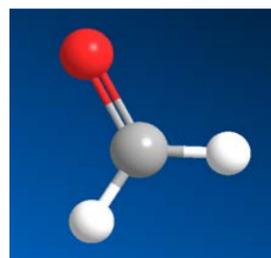
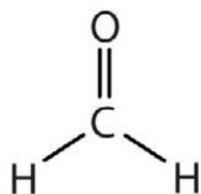
Figure 4.7 The Molecular Geometry of Ammonia (NH₃). The lone pair density in NH₃ contributes to the overall shape of the molecule by pushing the hydrogens below the plane of the nitrogen central atom. However, they are not visible in the final molecular geometry, which is trigonal pyramidal.

Source: <http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/index.html>

In a water molecule, oxygen has 2 Lone Pairs of electrons and 2 bonded hydrogen atoms, giving it a steric number of 4 and an AXE formula of AX₂E₂. Using Table 4.1, we see that the shape of H₂O is bent.



How about the shapes of molecules with multiple bonds? They are determined by treating the multiple bonds as one bonding group. Thus, CH₂O has a shape similar to that of BF₃:



This is because CH₂O has three bonded atoms, or an 'X' = 3, and carbon has no lone pairs, so 'E' = 0. The steric number is 3, and the AXE formula is AX₃E₀. Since 'E' = 0, we can drop it from the equation to give AX₃.

Concept Review:

1. Describe the shape of each molecule.



Answers:

Solution

The Lewis diagram for PCl₃ is as follows:

The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like NH₃, this molecule is trigonal pyramidal. (AXE = AX₃E)

The Lewis diagram for CO₂ is as follows:

The multiple bonds are treated as one group. Thus, CO₂ has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO₂ molecules are linear. (AXE = AX₂)

Test Yourself:

2. Describe the shape of each molecule using the AXE formula.



4.5 Intermolecular Interactions

In addition to learning about the bond characteristics and shapes of molecules, it is also very important to learn about how molecules interact with other molecules around them. This type of interaction, known as an **intermolecular interaction**, is important for determining broader characteristics of the molecule including reactivity and function.

Intermolecular interactions between molecules are dependent on the phase that the molecule exists. A **phase** is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. As mentioned in Chapter 1, science recognizes three stable phases: **the solid phase**, in which individual particles can be thought of as in contact and held in place (defined volume and shape); **the liquid phase**, in which individual particles are in contact but moving with respect to each other (defined volume but, shape of the container); and **the gas phase** (no defined shape or volume), in which individual particles are separated from each other by relatively large distances. Not all substances will readily exhibit all phases on the Earth. For example, carbon dioxide does not exhibit a liquid phase on Earth unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose or breakdown at higher temperatures, rather than becoming a liquid or a gas. For example, think about roasting a marshmallow. If it gets too close to the flames it will become charred and blackened, breaking down the sugar molecules inside. The sugar is not converted into the liquid or gaseous phase. Thus, water is very unique in its ability to exist on the Earth in all three phase states (solid ice - liquid water - water vapor)..

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H₂O exists in the solid form as ice. When it is warmer, the liquid phase of H₂O is present. At even higher temperatures, H₂O boils and becomes steam (gaseous phase).

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather

Table 4.2 Temperature Ranges for the Three Phases of Various Substances

	Melting Point		Boiling Point
	Solid Below	Liquid Above	Gas Above
Hydrogen (H ₂)	-259°C	-259°C	-253°C
Water (H ₂ O)	0°C	0°C	100°C
Sodium Chloride (NaCl)	801°C	801°C	1413°C

extreme. Table 4.2 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges. Recall that the **melting point** of a substance is the temperature that separates a solid and a liquid. The **boiling point** of a substance is the temperature that separates a liquid and a gas.

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the intermolecular interactions between the particles of substances. (Although ionic compounds are not composed of discrete molecules, we will still use the term intermolecular to include interactions between the ions in such compounds.) Substances that experience strong intermolecular interactions require higher temperatures to become liquids and, finally, gases. Substances that experience weak intermolecular interactions do not need

much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at lower temperatures.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

Substances with the highest melting and boiling points have **covalent network bonding**. This type of interaction is actually a covalent bond. In these substances, all the atoms in a sample are covalently bonded to the other atoms; in effect, the entire sample is essentially one large molecule. Many of these substances are solid over a large temperature range because it takes a lot of energy to disrupt all the covalent bonds at once. One example of a substance that shows covalent network bonding is diamond (Figure 4.8), which is a form of pure carbon. At temperatures over 3,500°C, diamond finally vaporizes into gas-phase atoms.

For interactions between different molecules, the strongest force between any two particles is the **ionic bond**, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 4.9) is an example of a substance

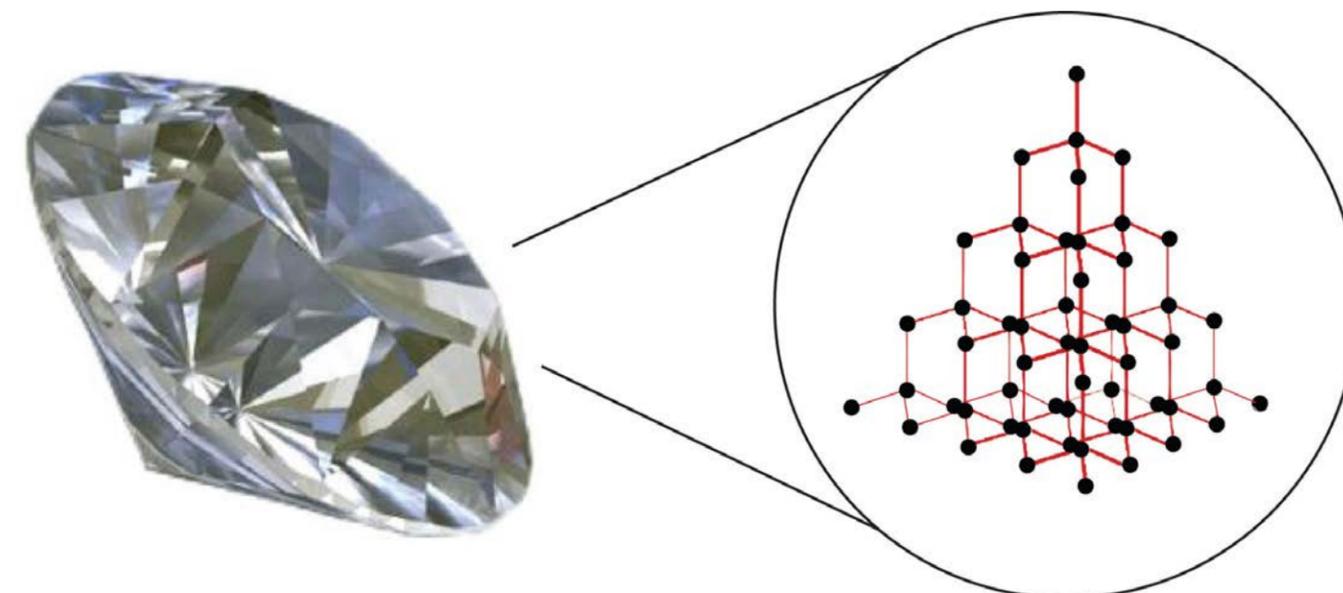
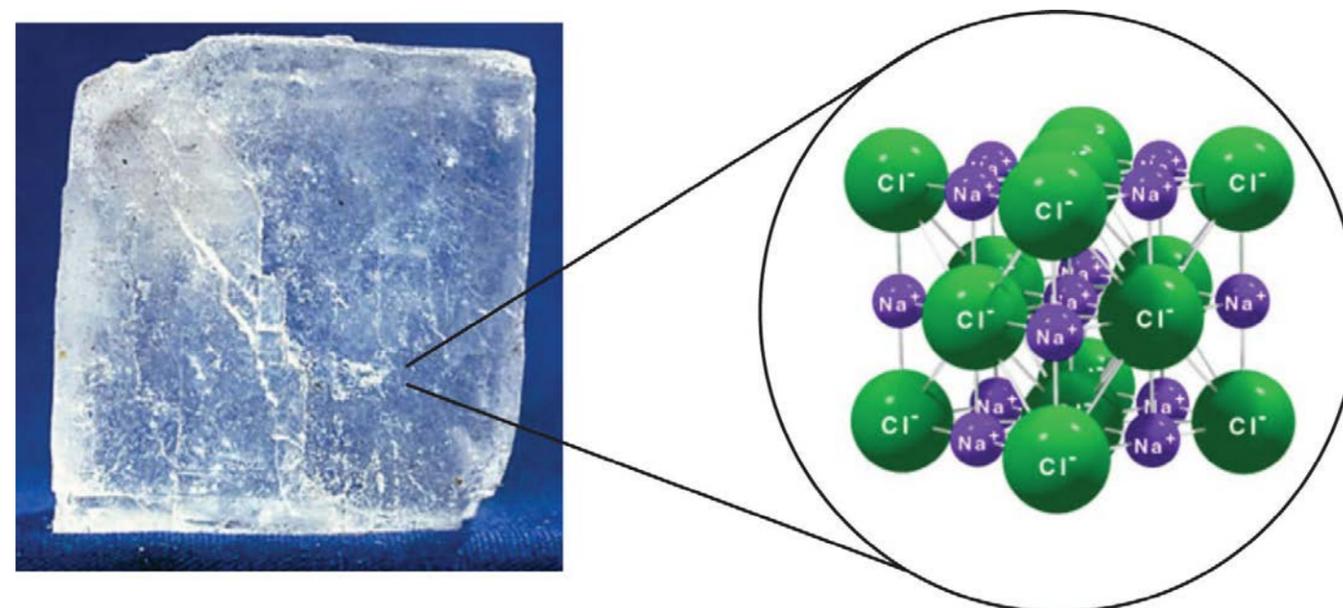


Figure 4.8. Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state.

Source: Photo © Thinkstock



whose particles experience ionic interactions (Table 4.2).

Figure 4.9 Sodium Chloride. Solid NaCl is held together by ionic intermolecular forces.

Source: Photo © Thinkstock

Many substances that experience covalent bonding exist as discrete molecules and do not

engage in covalent network bonding. Thus, most covalently bonded molecules will also experience intermolecular forces. These intermolecular forces are weaker than those found in ionic interactions and depend on the polarity of the covalent bond. Recall that in polar covalent bonds, the electrons that are shared in a covalent bond are not shared equally between the two atoms in the bond. Typically, the atom displaying higher electronegativity attracts the electrons more strongly than the other, leading to the unequal sharing of electrons in the bond. This sets up a permanent dipole within the molecule, where one end of the molecule has a partial negative charge (δ^-) and one end has a partial positive charge (δ^+). This idea is illustrated in Figure 4.10, which shows a diagram of the covalent bond in hydrogen fluoride (HF).

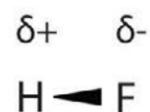


Figure 4.10 Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ^- in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ^+ in the diagram). Such a bond is called a **polar covalent bond**.

The fluorine atom attracts the electrons in the bond more than the hydrogen atom does. The result is an unequal distribution of electrons in the bond, favoring the fluorine side of the covalent bond. Because of this unequal distribution, the fluorine side of the covalent bond actually takes on a partial negative charge (indicated by the δ^- in Figure 4.10), while the hydrogen side of the bond, being electron deficient, takes on a partial positive charge (indicated by the δ^+ in Figure 4.10). A covalent bond that has an unequal sharing of electrons

is called a polar covalent bond. (A covalent bond that has an equal sharing of electrons, as in a covalent bond with the same atom on each side, is called a nonpolar covalent bond.) A molecule with a net unequal distribution of electrons in its covalent bonds is a polar molecule. HF is an example of a polar molecule.

The charge separation in a polar covalent bond is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a **dipole-dipole interaction**. If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 4.11. These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 4.11, part c). Hence dipole-dipole interactions, such as those in part (b) in Figure 4.11, are attractive intermolecular interactions, whereas those in part (d) in Figure 4.11 are repulsive intermolecular

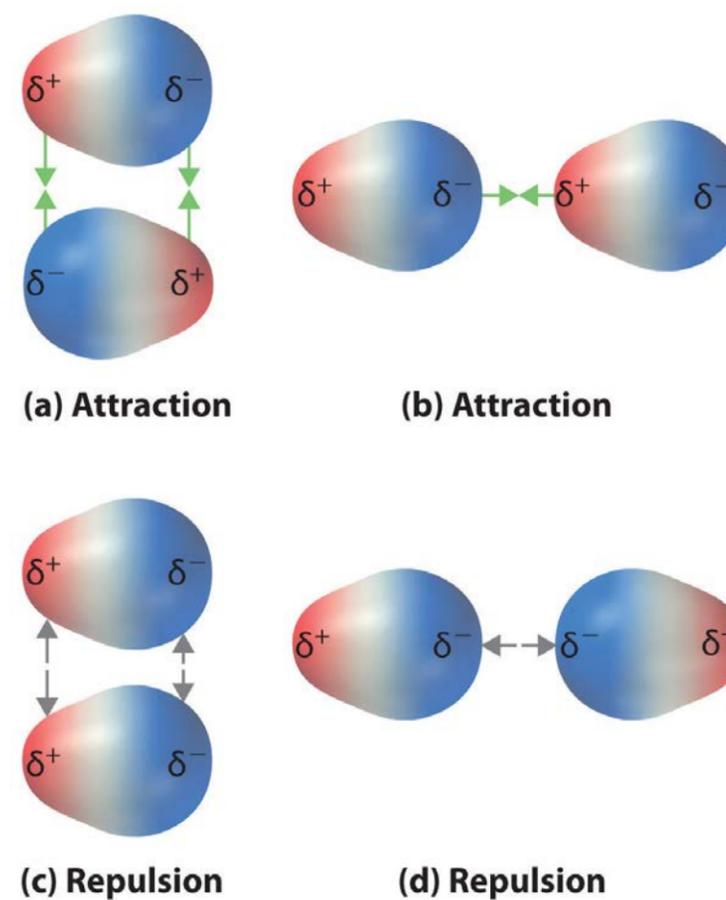


Figure 4.11 Attractive and Repulsive Dipole-Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

interactions. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 4.12. On average, however, the attractive interactions dominate.

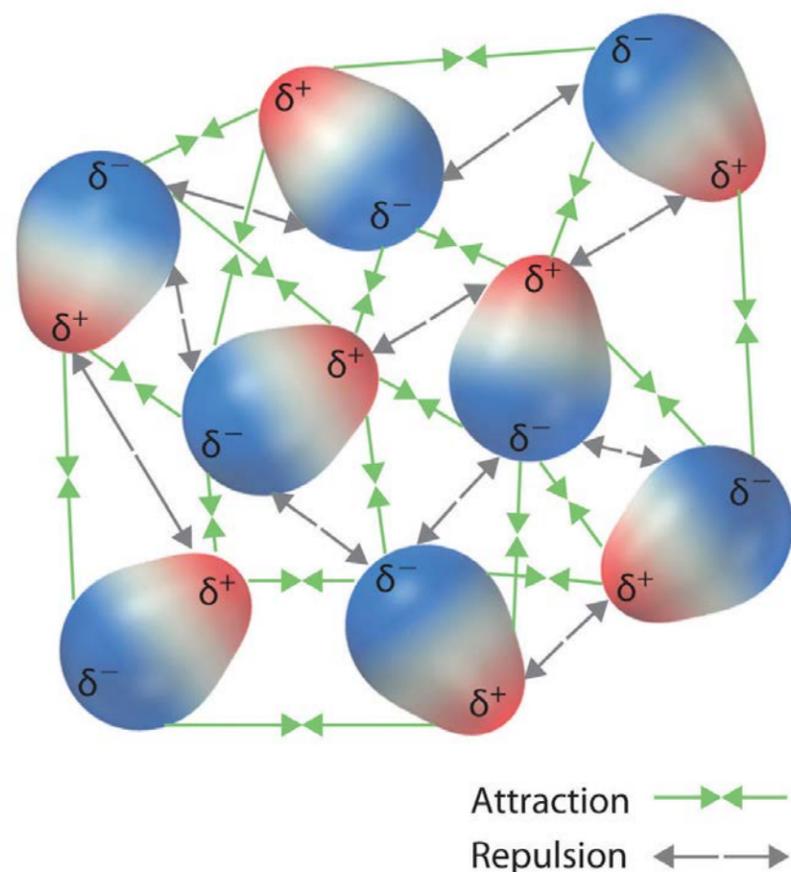
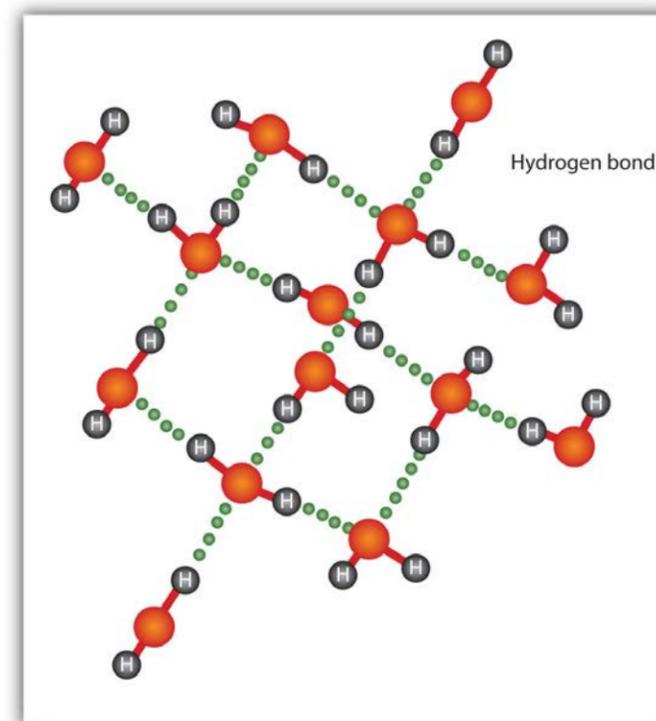


Figure 4.12 Both Attractive and Repulsive Dipole-Dipole Interactions Occur in a Liquid Sample with Many Molecules.

The H–F, O–H, and N–H bonds are strongly polar; in molecules that have these bonds, particularly strong dipole-dipole interactions (as strong as 10% of a true covalent bond) can occur. Because of this strong interaction, **hydrogen bonding** is used to describe this dipole-dipole interaction. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Figure 4.13 shows how molecules experiencing hydrogen bonding can interact in water.

Figure 4.13 Hydrogen Bonding between Water Molecules. The presence of hydrogen bonding in molecules like water can have a large impact on the physical properties of a substance.



Finally, there are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge that disappears almost as soon as it appears and sets up a momentary ‘induced dipole’. These are very weak intermolecular interactions and are called **London dispersion forces**. Since electrons naturally orbit the nucleus of the atom, there are momentary dipoles that are present in the atom as the electrons are shifting from one side to the other. If other atoms are in close proximity, the electrons of the other atoms will orbit in concert with the neighboring atom, i.e. the electrons of one atom are repulsive to the electrons of the neighboring atoms, such that when they are close to the neighboring atom, the neighboring electrons will shift away to the other side of the atom. Thus, the electron movements between atoms of different molecules will synchronize and orbit in a pattern that maximizes the distance between electrons of a neighboring atom. Note that all substances experience London dispersion forces. However, these are the only intermolecular forces that nonpolar covalent compounds experience. Nonpolar covalent molecules tend to be soft in the solid phase and have relatively low melting points. Butter fat would be a good example of a nonpolar covalent compound.

Because London dispersion forces are caused by the instantaneous distribution of electrons in a molecule, larger molecules with a large number of electrons can experience higher levels of London dispersion forces. Examples include waxes, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

The phase that a substance adopts depends on the type and magnitude of the intermolecular interactions the particles of a substance experience. If the intermolecular interactions are relatively strong, then a large amount of energy—in terms of temperature—is necessary for a substance to change phases. If the intermolecular interactions are weak, a low temperature is all that is necessary to move a substance out of the solid phase. Overall, ionic interactions are the strongest intermolecular forces followed by hydrogen bonding, other dipole-dipole interactions, and lastly, induced dipoles (London dispersion forces). Intermolecular force strength is indicated in Table 4.3 ‘Strength of Intermolecular Forces.

Table 4.3 Strength of Intermolecular Forces

Bond Type	Dissociation Energy (kcal/mol)
Ionic Bond Lattice	250-4000 kcal/mol
Hydrogen Bond	1-12 (water H-bonds are ~5)
Other Dipole-Dipole Interactions	0.5-2
London Dispersion Forces	< 1.0

Source: https://en.wikipedia.org/wiki/Intermolecular_force

Example 1: Intermolecular Forces

Question: What intermolecular forces besides London dispersion forces, if any, exist in each substance listed below? Do you think any of these substances solids at room temperature?

1. potassium chloride (KCl)
2. ethanol (C₂H₅OH)
3. bromine (Br₂)

Solution:

Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.

Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)

Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than London dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

Skill Building: Intermolecular Forces

Question: What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

1. methylamine (CH_3NH_2)
2. calcium sulfate (CaSO_4)
3. carbon monoxide (CO)

Exercises: Intermolecular Forces

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.
2. List the three common phases in the order they exist from lowest energy to highest energy.
3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.
4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.
5. What type of intermolecular interaction is predominate in each substance?
water
A. (H_2O)sodium sulfate
B. (Na_2SO_4)decane
C. ($\text{C}_{10}\text{H}_{22}$)
6. What type of intermolecular interaction is predominate in each substance?
A. diamond (C , crystal)
B. helium (He)
C. ammonia (NH_3)
7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?

Exercises: Intermolecular Forces – Odd Answers

1. solid, liquid, and gas
3. London forces, hydrogen bonding, and ionic interactions
5.
 - A. hydrogen bonding
 - B. ionic interactions
 - C. dispersion forces
7. The two covalent bonds are oriented in such a way that their dipoles cancel out.
9. very hard, high melting point

Chapter Summary

Chapter Summary: Molecular Shapes and Characteristics

The mass of an ionic molecule is called the **formula mass** and the mass of a covalent molecule is called its **molecular mass**. Both are the sum of the masses of the atoms in the molecule.

Electronegativity is the strength with which an atom can attract electrons. Electronegativity differences between atoms help to determine what type of bond will form. Electronegativity differences of 0.5 or below generally indicate a nonpolar covalent bond, whereas 0.5 to 1.8 indicate a polar covalent bond and above 1.8 indicates an ionic bond.

Within a molecule, the two electrons shared in a covalent bond are called a **bonding pair of electrons**. The electrons that do not participate in covalent bonds are called **nonbonding pairs** (or **lone pairs**) of electrons. They are useful in helping to predict the molecular shape of the molecule.

The shape of a molecule can be predicted using **valence shell electron pair repulsion (VSEPR)**, which uses the fact that the negative electrons in covalent bonds repel each other as much as possible.

The geometric shape of a central atom can be determined by calculating the **steric number** and determining the **AXE formula** for the central atom in question. In the AXE formula, 'A' is the central atom, 'X' is the number of bonding pairs of electrons and 'E' is the number of lone pair electrons. Steric number is the sum of the bonding and non-bonding pairs of electrons. Note that double and triple bonds only count as a single bond for the AXE formula and steric number determination.

Chapter Summary: Intermolecular Forces

A **phase** is a certain form of matter that has the same physical properties throughout. Three phases are common: the solid, the liquid, and the gas phase. What determines the phase of a substance? Generally, the strength of the **intermolecular interactions** determines whether a substance is a solid, liquid, or gas under any particular conditions.

Covalent network bonding is a very strong form of covalent bonding where all of the atoms in the structure are bonded together as one large molecule. Diamond is one example of a substance that has this type of interaction.

The four major intermolecular forces include:

1. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong.
2. **dipole-dipole interactions** occur between polar covalent molecules the unequal sharing of electrons can cause permanent dipoles in the molecule.
3. A strong type of dipole-dipole interaction is called **hydrogen bonding** and occurs when H is bonded to O, N, or F.
4. **London dispersion forces** are weak interactions caused by the formation of momentary, induced dipoles within a molecule. All substances have London dispersion forces. However, **Nonpolar covalent molecules** only have London dispersion forces.