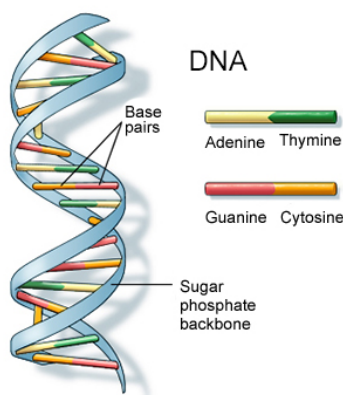


## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries



### Unit Overview

Molecules form when individual atoms create bonds by sharing electrons. Understanding how atoms combine to make molecules allows scientists to predict many of the physical and chemical properties of substances. Since the outermost eight electrons are key to forming compounds, this unit shows how the Octet Rule provides a basis for predicting how atoms may gain, lose, or share electrons to fill the slots in their outer shells. A fundamental understanding of how electrons form bonds leads to the three-dimensional shapes of molecules and has implications in all aspects of chemistry, including drug design.

by Adam Brunet

### Sections

1. Introduction
2. Valence Electron Patterns and Lewis Structures
3. Ionic Bonds
4. Covalent Bonds and the Octet Rule
5. Polarity and Basic Lewis Structures
6. Advanced Lewis Structures
7. VSEPR Theory
8. Hybrid Orbitals
9. Intermolecular Forces
10. Physical Properties of Molecules
11. Conclusion
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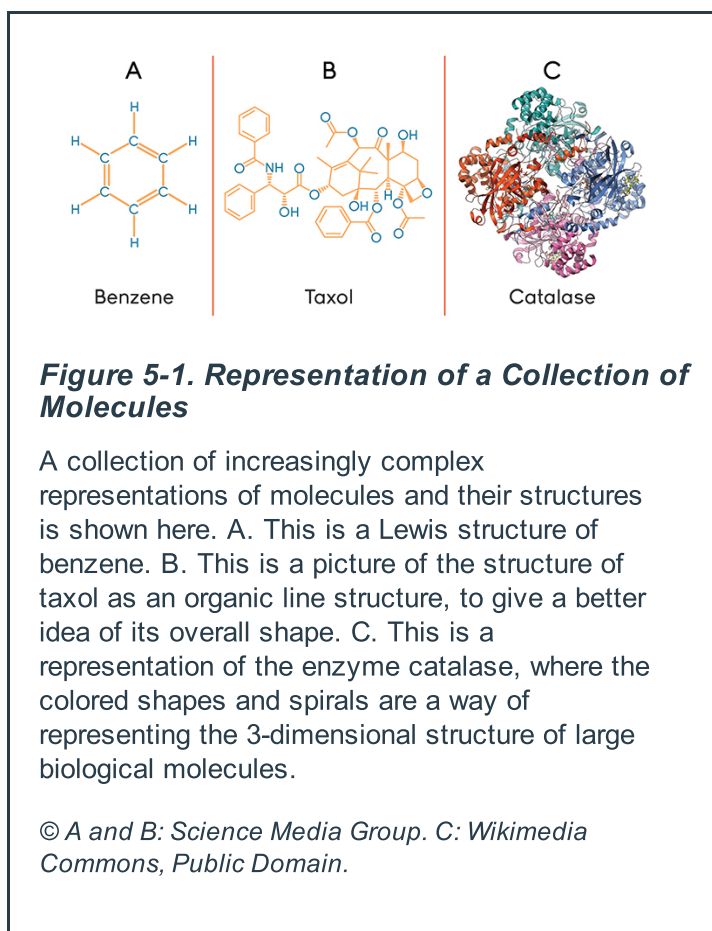
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## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 1: Introduction

While the universe is made up of over a hundred elements that can be organized into a helpful periodic table, what matters most for us to understand the chemical world is how these atoms organize together into the substances we see every day. It turns out that the electrons in the atoms, which were the focus of much of Units 3 and 4, are the stars of the show; these electrons are what will keep these atoms bound together in the substances that make up everything around us, including ourselves.

Over the course of this unit, we will see that by looking at some of the basic rules for how electrons behave and interact with each other will help us understand how atoms are held to each other. These interactions that hold two or more atoms together are called "**bonds**." Two specific types of bonding, ionic and covalent bonding will be the focus of this unit, and a third type of bonding, metallic bonding, will be addressed in Unit 13.



In addition to the forces holding atoms together in molecules, we'll also take a look at some **intermolecular forces**, that is, the forces that exist between different molecules. Intermolecular forces can cause molecules to stick together by mutual attraction, like water droplets.

To examine the question of molecules' physical structure—their geometry—we'll delve into the key methods for representing the structure of atoms and molecules: Lewis dot symbolism, VSEPR models, and hybrid orbitals. We'll then consider how, just like the pieces in a 3-D puzzle, a substance's geometry determines its macroscopic properties—how it will behave. In Figure 5-1, we can see how molecules range from what looks like a simple structure for benzene, a carcinogenic but common laboratory solvent, up to more complicated biological molecules. Figure 5-1A shows a Lewis structure of benzene and Figure 5-1B

shows the compound taxol, an anticancer drug that is isolated from the Pacific yew tree. Here, taxol is drawn as an organic line structure, a Lewis structure where the carbons and hydrogens are hidden to make the pictures less cluttered. Lastly, Figure 5-1C shows a representation of catalase, which is the enzyme found in our cells that protects us against dangerous peroxides. This enzyme is what causes the bubbling to happen when we put hydrogen peroxide on a cut to disinfect it. In this case, this molecule is so large, with thousands of atoms, that chemists use pictures that show the 3-dimensional shapes of the molecule, rather than displaying all of the individual atoms.

## Glossary

### ***Bond***

An association between two atoms in which they remain close together in space due to some type of electron-based interaction.

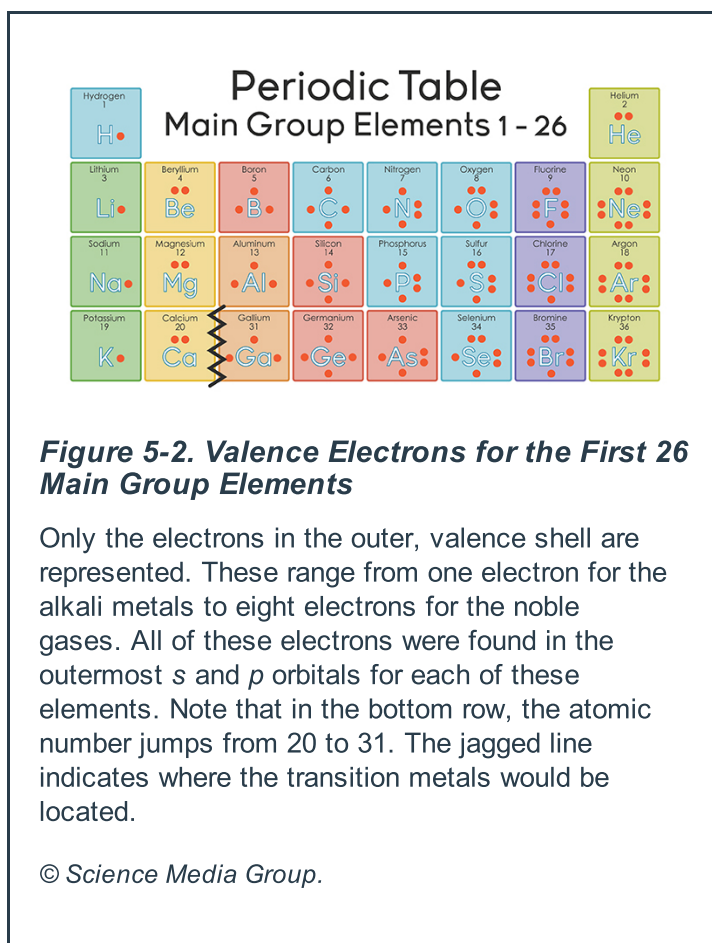
### ***Intermolecular forces***

Forces that exist between different molecules.

## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 2: Valence Electron Patterns and Lewis Structures

Valence electrons, first introduced in Unit 4, Section 5, are the electrons in the outermost shells of the atoms, and they are the most reactive and the most important for understanding how atoms come together to form compounds. Most of the elements that we will consider in forming compounds are the main group elements, and for these elements their valence electrons are always in their outermost *s* and *p* orbitals. In Figure 5-2, all of the valence electrons for the common main group elements are represented as dots around the symbol. For hydrogen and helium, they can only have two electrons in their valence shell in that first row, but for the elements after that, we can see that the number of valence electrons ranges from 1 to 8. There is also a great periodic pattern that the elements in the same column or family on the periodic table always have the same number of valence electrons.

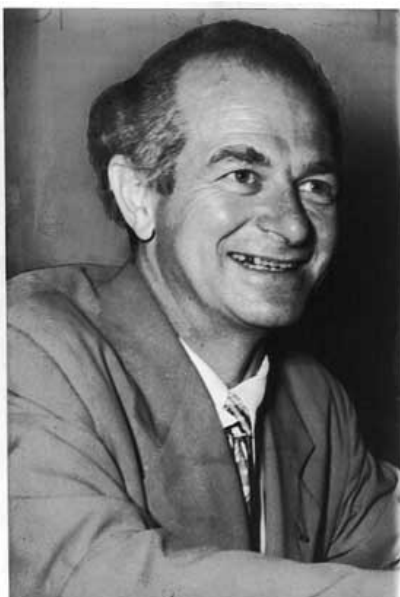


#### Lewis Dot Structures

This notion of representing valence electrons as dots is a shorthand created by American chemist Gilbert Newton Lewis (1875–1946). Accordingly, these are called "**Lewis dot structures**" for atoms. Lewis was investigating how atoms bond, and in particular, the role of the electrons in the outermost shell. He found he could explain many compounds of two or more atoms by assuming that they could share electrons to give each atom a total of eight electrons in their outermost shell. (Figure 5-3)



## Linus Pauling



*Portrait of Linus Pauling. © Library of Congress, LC-USZ62-76925.*

One of the most well-known chemists of the twentieth century was Linus Pauling. Among his many accomplishments, he is the man who first applied quantum mechanics to a description of orbital hybridization, critical to understanding chemical bonding (for which he received the Nobel Prize in Chemistry in 1954); he invented the concept of electronegativity and devised the original scale on which it was measured; he was the first to describe in detail what we now refer to as "resonance," an important topic in organic chemistry; using X-ray crystallography, he deduced the alpha-helical and beta-sheet structural patterns found in all proteins; and he was the first person to describe a genetic disease, sickle-cell anemia, in molecular detail, for which Francis Crick called him "the father of molecular biology." The breadth of his accomplishments has

rarely been matched by any other scientist.

In addition to his scientific achievements, Pauling was also a political activist and used his prestige to help get atmospheric testing of nuclear weapons banned, for which he was awarded the Nobel Peace Prize in 1962. This made him the only person besides Marie Curie to win the Nobel Prize in two different areas; he is also the only person to have won two unshared Nobel Prizes. In the 1950s, his controversial politics were not appreciated by the authorities, and the U.S. State Department rather arbitrarily declined to issue him a passport. At the time, Pauling was ahead of Watson and Crick in figuring out possible structures for DNA, but a key piece of the puzzle, the X-ray crystallography data of Rosalind Franklin was revealed at a conference in the UK he couldn't attend without a passport. Pauling's inability to travel abroad gave Watson and Crick the advantage they needed to figure out the structure of DNA first.

Lewis didn't simply figure out how to diagram molecules with dots, he was also the one who explained the covalent bond, coined the term "photon," figured out how electrons pair together, and, among other things, he inspired Linus Pauling (1901–1994), another extraordinary chemist, to study the nature of chemical bonding. He was nominated 35 times for the Nobel Prize but never won; however, two of his students, Harold Urey (1893–1981) and Glenn Seaborg (1912–1999), won Nobel Prizes for their work on the discoveries of new elements and new isotopes.



**Figure 5-3. Gilbert Newton Lewis**

The chemist who discovered the covalent bond and created the Lewis dot structure method of depicting molecules.

© Bancroft Library, University of California.

As shown in Figure 5-2, Lewis dot structures are drawn by using the chemical symbol from the periodic table to represent the nucleus of an atom, and placing dots around the outside to represent the electrons in the valence shell. Note how once there are more than four electrons in the atom's Lewis structure, the electrons get paired together on the side of the atom. This is one of the key insights of Lewis: He realized that because orbitals hold two electrons, electrons on atoms like to pair together, even when they make bonds. With only four orbitals in the valence shell of most main group elements, electrons have to be paired once there are enough to go around.

However, Lewis structures for individual atoms aren't particularly useful, but this pairing of electrons will be very important when we get to larger multi-atomic structures. When electrons pair together on one atom, they are called "lone pair electrons" or a "**lone pair**." Note how neon, the unreactive noble gas has eight electrons arranged into four lone pairs. This is a simple representation of how its eight electrons are held in its four valence *s* and *p* orbitals. This number, "eight", is special in chemistry because so many elements have eight spaces in valence orbitals. We saw in Unit 4, Section 8 that atoms form ions in ways to try to gain or lose electrons to achieve these eight electrons that fill that outermost shell and therefore create a stable atom or ion. In the next few sections, we will learn how the Octet Rule will use this magical number, eight, to help us build most of the molecules in nature.

## Glossary

### **Lewis dot structures**

A way of representing molecular structures in which atoms and their electrons are represented as two-electron bonds and lone pairs of electrons. Formal charges are assigned to each atom.

### **Lone pair**

A pair of valence electrons on an atom not involved in a bond.

## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 3: Ionic Bonds

Most of the elements in the periodic table are quite reactive, and this reactivity relates directly to the valence electrons of the elements. They have incomplete valence shells and thus are able to react with other substances to try to change the numbers of electrons in that outermost shell. As atoms react, they begin to form compounds, and the atoms of compounds are held together by bonds. A bond is an arrangement of *a pair of atoms in such a way that those atoms want to stay associated with each other rather than separate*. In all cases, the bonds between atoms—regardless of the type of bond—result from the electrons on the atoms that have come together.

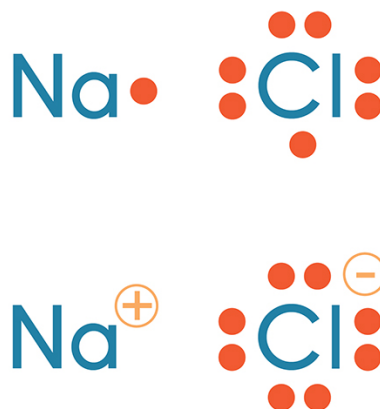


**Figure 5-4. Coulombic Forces Hold Ionic Bonds Together**

By rubbing this balloon on her head, some of the electrons from this young lady's hair get transferred to the balloon, making it negatively charged and her hair positively charged. Since opposite charges attract, her hair stays connected to the balloon even as it floats away.

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**Ionic bonds** are the simplest sort of bond. For ionic bonds to happen, atoms must have opposite charges. Because of the charges, they attract each other and so stay paired up due to **Coulombic forces**. Coulombic forces happen when negatively-charged things are attracted to positively-charged things, or when like charges repel each other (Figure 5-4). How did these ions form? Electrons jumped from the valence shell of one atom to another. The result is one atom with extra electrons creates a negatively charged anion, and one atom with a shortfall of electrons creates a positively charged cation.



**Figure 5-5. Formation of an Ionic Bond**

The electron configuration of sodium (Na,  $1s^2 2s^2 2p^6 3s^1$ ) and chlorine (Cl,  $1s^2 2s^2 2p^6 3s^2 3p^5$ ) makes it possible for them to form an ionic bond. After the transfer of an electron from the sodium to the chlorine, the compound sodium chloride (NaCl), common table salt, forms. Note that it is made up of Na<sup>+</sup> ( $1s^2 2s^2 2p^6$ ) and Cl<sup>-</sup> ( $1s^2 2s^2 2p^6 3s^2 3p^6$ ), each of which has 8 valence electrons between its outermost *s* and *p* orbitals. For each of these, the atoms and ions are written as Lewis dot formulas.

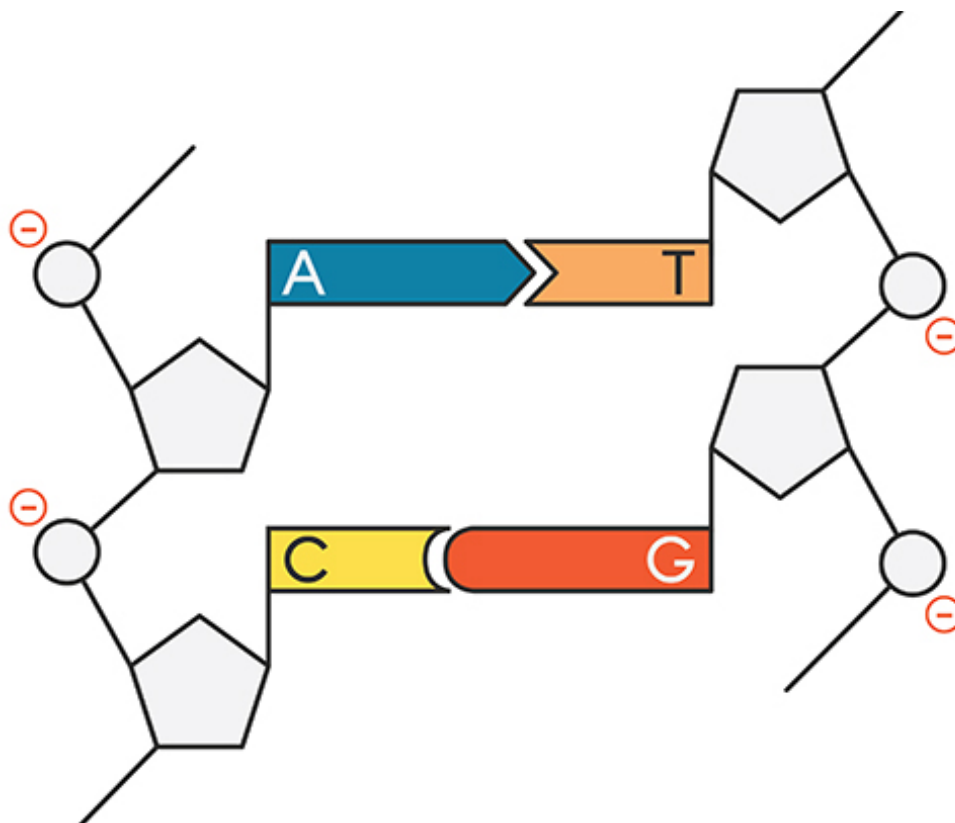
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Ionic bonds are common between atoms with large differences in electronegativity. Recall from the last unit that electronegativity is a measure of an atom's "love" for electrons, so if one atom has a high electronegativity it would like to gain electrons, and vice versa. This means that ionic compounds usually occur between atoms on opposite sides of the periodic table, such as sodium and chloride, which form sodium chloride, NaCl, or calcium and oxygen, which form calcium oxide, CaO. In both cases, the ionic compounds form from one non-metallic element and one main group metal.

To understand this more deeply, we need to return to this magic number eight that comes from the eight possible valence electrons that an atom can have. There is increased stability if an atom is able to completely fill its valence shell. Thus, there is always motivation for elements that are close to eight electrons to gain more in order to reach eight, and these elements are the ones with high electronegativities. On the other hand, some elements have only one or two electrons in their valence shell, and in that case it is easier for these elements to give up these electrons and have an empty shell. These elements are usually metals and have very low electronegativities. This actually still means that these elements have a full valence shell after losing electrons, it is just one level below the one that gave up those electrons.

## DNA and $Mg^{2+}$

As we know, like charges repel while opposites attract. Ions of a particular charge cannot exist in solution without other ions of the opposite charge. When we are talking about an ion in solution, there is always another ion, called the "counterion," which is present to make the total charge of the solution neutral. Suppose we want to add chloride ions ( $Cl^-$ ) to a solution. We can do this by adding sodium chloride, or potassium chloride, or some other molecule that includes chloride, but there *has* to be a positively charged counterion such as sodium ( $Na^+$ ) or potassium ( $K^+$ ) present. Often we are not really interested in the counterion, so we don't mention it or refer to it as a "spectator ion." But it is always there when ions exist in solution.



*Snippet of the DNA structure showing a negative phosphate charge with every base pair. © Wikimedia Commons, CC License 1.0. Author: Incnis Mersi, 02 March 2013.*

The DNA in our cells consists of a very long molecule formed by linking together a long chain of very similar molecules. It happens that at every link in the chain there is a negatively charged group. This means DNA contains many negatively-charged ions. Why don't all those negative charges repel each other and cause the genetic material to fall apart? The answer is Magnesium. Magnesium is an element that forms an ion with a positive two charge, and is represented  $Mg^{2+}$ . This ion acts as the counterion for the negative charges on DNA and makes it possible for it to adopt its famous double helix structure. When people discuss DNA they hardly ever mention the magnesium, but it is a critical component to have in our cells. Lots of people don't get enough magnesium in their diet, though this usually causes other severe problems long before its function as a counterion to DNA becomes an issue. Dietary sources rich in magnesium include spinach and squash—so eat vegetables!

Let's return to sodium chloride ( $NaCl$ ) which forms if sodium ( $Na$ ) and chlorine ( $Cl$ ) come together. If an electron departs from sodium and joins the chlorine, both resulting ions will have filled valence shells (Figure 5-5). The chlorine will have gained the one electron it needed to make a complete third shell. The

sodium, by losing the one electron in its third shell will now have the second shell as its valence shell, and this shell is already complete with eight electrons.

Sodium, then, has a positive charge because it is short one electron but the number of protons in the nucleus hasn't changed. Chlorine, meanwhile, is negative because it now has an extra electron, one more than the number of protons in the nucleus. The opposite charges on these atoms then hold them together in an ionic bond.

## **Glossary**

### ***Coulombic forces***

Attractive or repulsive forces exerted by particles that bear an electric charge on other particles that also bear an electric charge. Like charges repel each other, and opposite charges attract each other.

### ***Ionic bond***

A bond in which two atoms are held together by the fact that they possess opposite charges, as distinct from a covalent bond in which atoms are held together by the sharing of electrons.

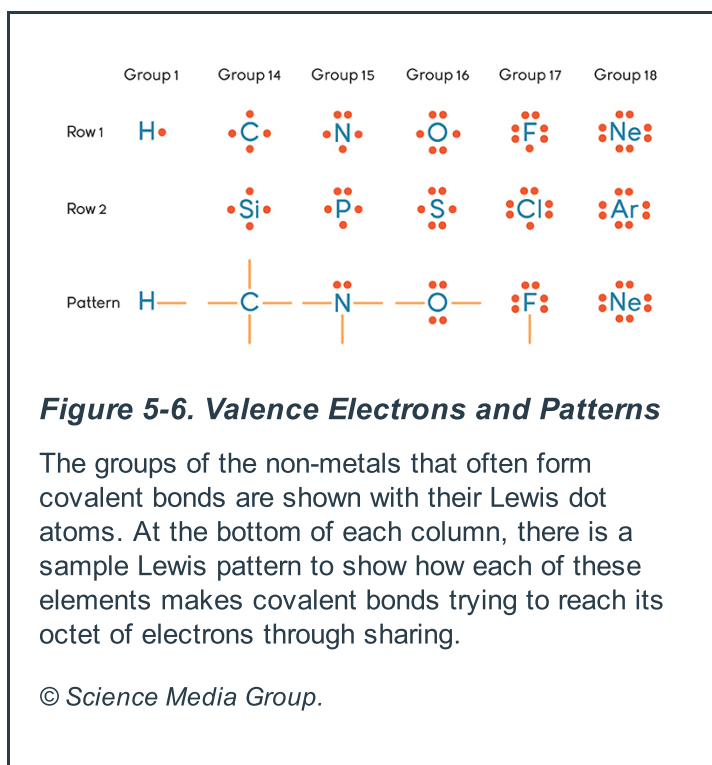


## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 4: Covalent Bonds and the Octet Rule

While ionic structures are very common, their Lewis structures are not very interesting or informative, because all that really matters are their charges. However, the second type of bonding, covalent bonding, relies heavily on Lewis structures to show the roles of the electrons in these bonds. These structures will then be able to help us understand more about the molecules, from their shapes to their physical properties.

What is a **covalent bond**? Unlike an ionic bond where atoms have very different electronegativities, and one atom gives up electrons to the other to form ions, covalent bonds usually form between two atoms that have similar electronegativities. These elements tend to be the non-metals, like those shown at the top of Figure 5-6. In a covalent bond, elements share pairs of electrons between them, trying to reach this magical number of eight valence electrons.



#### Octet Rule

For covalent bonding, elements try to follow the **octet rule**. The octet rule states that elements will work to get a total of eight valence electrons through a combination of lone pairs of electrons on the atom, and covalent bonds whereby two elements share a pair of electrons. A halogen, like chlorine, has seven valence electrons and needs one more to reach its octet; therefore, it can make one covalent bond along with its three lone pairs. In that covalent bond, two electrons are shared, one from each atom on either side of the bond. Whereas carbon, which has four valence electrons, needs to make four covalent bonds to get a total of eight electrons. Each time a covalent bond is formed between two atoms, each atom brings one electron—but through sharing, both atoms get to "feel" like they actually have two electrons from that bond. All of these patterns are summarized for the main group elements in Figure 5-6. The bottom row of the figure shows the patterns of covalent bonds and lone pairs each atom wants to reach its octet. Because the noble gases already have eight valence electrons, in general, they do not make covalent or ionic



compounds because they are already stable and have satisfied their octet. Note that hydrogen is special. Because it only has that lonely 1s orbital, it can only hold two electrons. Because of this, hydrogen atoms are said to have an "octet of two," for the octet rule.

To reiterate, in covalent bonds, both atomic nuclei are holding onto the same two electrons in the bond, so like the teams in a tug-of-war game holding onto the same rope they remain linked to each other. Figure 5-7 shows four covalent molecules, each of which is a diatomic molecule with two atoms of the same element sharing electrons. For each atom, you can count up its lone pair electrons and the electrons in the bonds attached to it. When you do this for the fluorine (F), oxygen (O), or nitrogen (N), you get a total of eight electrons around each atom, showing that these follow the octet rule. The hydrogen atoms have just the bond and no lone pairs, but that works out perfectly because that lone bond gets hydrogen the two electrons it needs for its octet of two.



**Figure 5-7. Diatomic Covalent Molecules**

The simplest covalently-bound molecules are diatomic molecules; these happen between only two atoms sharing at least two electrons. See how the patterns of Figure 5-6 are repeated here: Fluorines make one covalent bond, oxygens make two covalent bonds, and nitrogens make three covalent bonds. We can make more than one covalent bond to the same atom in order to share enough electrons to reach the octet. For example, the oxygen atom has two lone pairs and two bonds, each of which represents two electrons and four lone pair electrons. These, plus four covalently bonded electrons equals eight electrons to satisfy the octet rule.

© Science Media Group.

Additionally, each of the molecules in Figure 5-7 are two identical elements bound together, so they have identical electronegativities, which means they share the electrons evenly between them. This is referred to as a true or a **pure covalent bond**, and, as we will see in a later section, a symmetrical sharing of electrons leads to molecules that have a balanced electron cloud, also referred to as "non-polar" molecules.

For us, it is less important to be able at first to draw Lewis structures from scratch; however, it is very important for us to recognize a Lewis structure and then to use it to learn things about that molecule and its structure and properties. If we know the rules for making Lewis structures, we can tell if the ones we see are correct, which is the first important step in looking at molecules.

## Glossary

### ***Covalent bond***

A bond formed by the sharing of electrons between two atoms, as distinct from an ionic bond in which atoms are held together because they have opposite charges.

### ***Octet rule***

The principle that covalent bonds form such that the shared electrons complete the valence shell of each atom. For the common atoms other than hydrogen, this means eight valence electrons.

### ***Pure covalent bond***

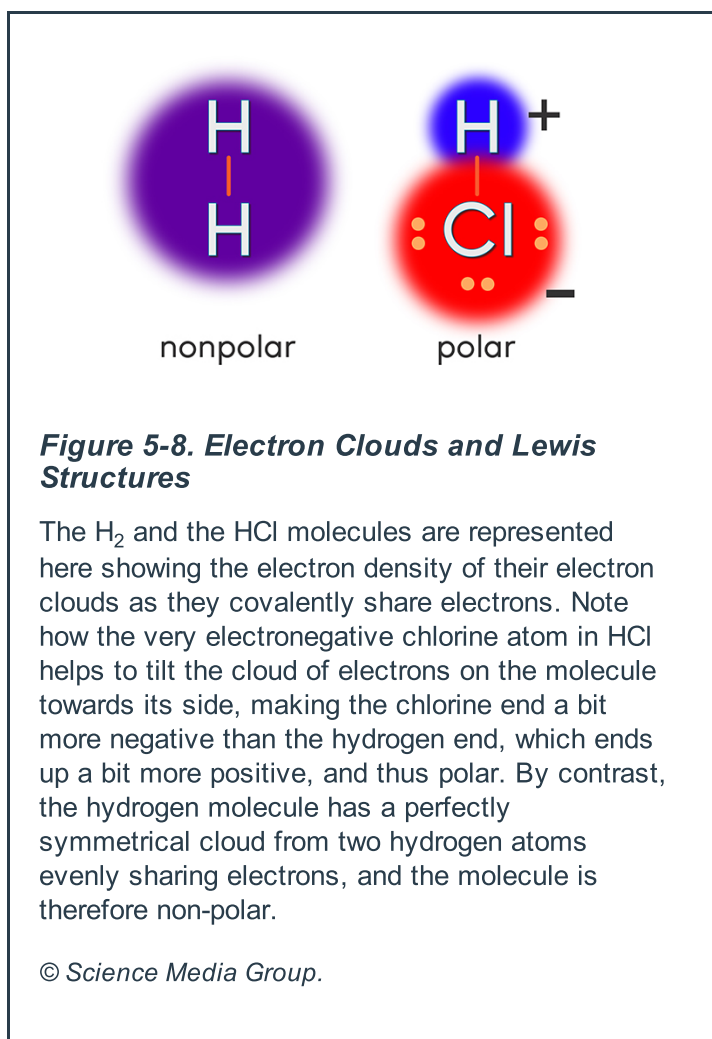
A covalent bond between two atoms of the same electronegativity that share the electrons in the bond equally.

## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 5: Polarity and Basic Lewis Structures

In the last section, we only saw simple diatomic Lewis structures where two of the same atom were bound together. However, most molecules are made up more than two atoms, and two atoms not of the same type of element will share electrons, too. Also, as the molecules and their Lewis structures get more complicated, the sharing of electrons between the atoms can become uneven, leading to "**polar covalent bonds.**"

In practice, electrons are shared *equally* only in covalent bonds between identical atoms, such as in diatomic molecules like  $\text{Cl}_2$ ,  $\text{O}_2$ , or  $\text{N}_2$ . In covalent bonds between two different atoms, the more electronegative atom pulls the **electron density** of the electron cloud toward itself more than the less electronegative atom. Electron density is just another way of describing areas of space where the electrons in bonds and lone pairs are likely to be. It is like when one of the teams in the tug-of-war is stronger than the other and ends up with more of the rope. For example, when a chlorine atom is bound to a hydrogen atom, as in hydrogen chloride or hydrochloric acid ( $\text{HCl}$ ), the electrons are a little more likely to be found near the chlorine than near the hydrogen, because chlorine is more electronegative. The chlorine portion of the molecule ends up with a slight negative charge as a result, and the hydrogen end is left with a slight positive charge. (Figure 5-8)



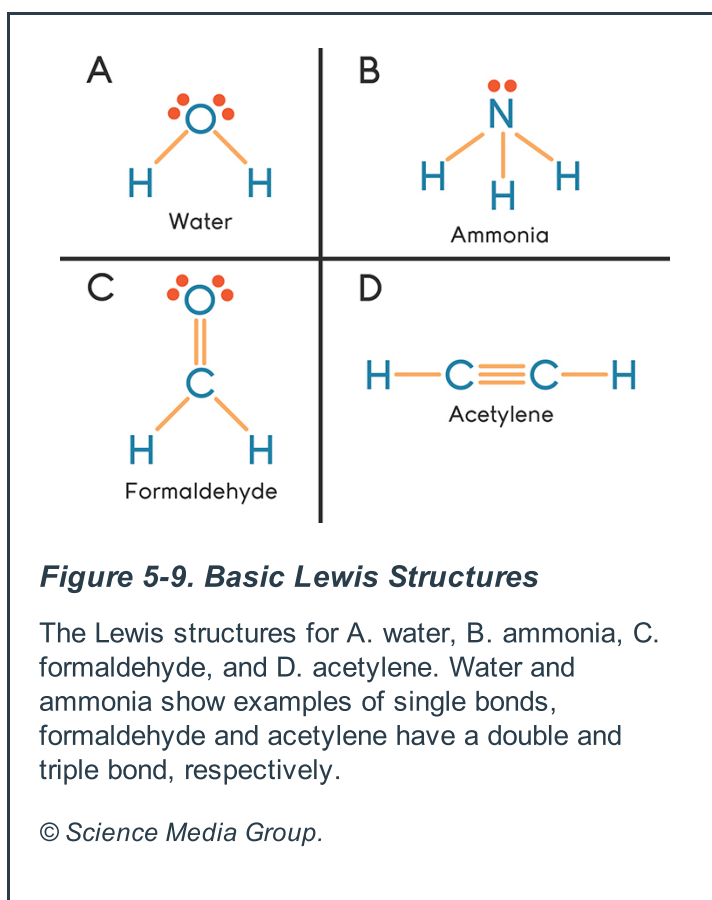
Because of this uneven electron cloud, and the partial positive and negative charges around an unsymmetrical molecule like hydrogen chloride, the molecule is said to be polar. Once again, polar refers to an uneven distribution of electrons and can apply to an individual bond or an entire molecule. So, the H-Cl bond is a polar covalent bond and the HCl molecule is polar. We will see later in this unit that the polarity of a molecule is one of the key factors in determining many of its properties.

Most bonds can therefore be said to lie on a continuum from pure covalent bonds (like fluorine ( $F_2$ )), in which both atoms have identical electronegativity and share the electrons equally, through polar covalent bonds (like hydrogen chloride (HCl)), in which the atoms' electronegativities are different and electrons are shared unequally between them, to ionic bonds (like sodium chloride (NaCl)), in which the difference in electronegativity is so great that electrons have been completely transferred from one of the atoms to the other; that is, one tug-of-war team is so much stronger they end up with all of the rope.

### Lewis Structures

We can describe molecules using the Lewis dot symbolism we saw above for individual atoms and diatomic molecules. However, we want to learn more about the bonds in larger molecules and how that will affect the three-dimensional shapes of these molecules. In order to do that, we need to look at Lewis structures for more complicated molecules. The four examples in Figure 5-9 are common molecules that will let us see the common patterns of Lewis structure and bonding.

Let's start with the most common molecule on planet Earth: water (Figure 5-9A). With a formula of  $H_2O$ , three atoms need to share electrons to reach their octets. The hydrogen atoms are always limited to at most one bond, since they can only hold at most two electrons, and one bond represents two electrons. The oxygen makes one covalent bond to each hydrogen atom, and it has two lone pairs as well. These two covalent bonds give four electrons towards the octet, and the two lone pairs give the other four for a total of eight. This matches perfectly with the pattern that was in the table in the last section, where it showed that oxygen likes to make two bonds and have two lone pairs to reach an octet. Each of these bonds between two atoms where just two electrons are being shared is called a **"single bond."**



Another molecule that is closely related to water is ammonia ( $NH_3$ , Figure 5-9B). Ammonia is a common household cleaner and a compound produced in small quantities in the kidneys to control the level of acidity in urine before being excreted by the body. Nitrogen follows its pattern here again to reach an octet:

It likes to make three single bonds and have one lone pair for a total of eight electrons.

It can also happen that two atoms share more than one pair of electrons, a situation referred to as a "multiple bond." For example, let's consider the molecule formaldehyde ( $\text{CH}_2\text{O}$ ), which was used historically to preserve biological samples in jars (Figure 5-9C). For carbon to reach an octet, it wants to make four covalent bonds, but with only three atoms present, it is going to have to make more than one covalent bond to one of the other atoms. Specifically, two pairs of electrons are being shared between the carbon and oxygen. When two pairs of electrons are shared in this way, it is called a "**double bond**."

It is also possible for atoms to share three pairs of electrons, a situation called a "**triple bond**." An example of this is the molecule acetylene, used in oxy-acetylene welding torches (Figure 5-9D). Again, note that the octet rule is satisfied. The carbon in acetylene has eight electrons just as it did in formaldehyde, but this time it accomplishes this by making a single bond to the hydrogen and a triple bond to the other carbon, for the same total of four covalent bonds.

## Glossary

### ***Double bond***

A bond between two atoms when two pairs of electrons are shared.

### ***Electron density***

In an electron cloud, the chance of finding that electron per volume in a given region of space.

### ***Polar covalent bonds***

Covalent bonds between two atoms of different electronegativity in which the electrons are shared unequally. The bond will be polarized toward the more electronegative atom.

### ***Single bond***

A covalent bond between two atoms where just two electrons are being shared.

### ***Triple bond***

A covalent bond between two atoms when they share three pairs of electrons.

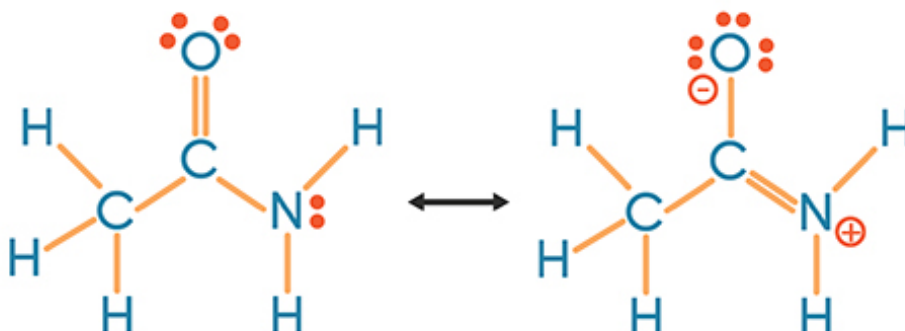
## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 6: Advanced Lewis Structures

#### Resonance

When a molecule is connected together with bonds, sometimes there is more than one way to arrange the atoms, that is, which atoms are attached to which ones. These different structural possibilities are called "isomers." However, there are times, without changing which atoms are connected to which, we can draw more than one Lewis structure. In that case, some of the multiple bonds and lone pairs are in different locations in the molecule, but all the atoms are attached to the same atoms.

When it is possible to draw more than one acceptable Lewis structure for a given molecule, where all the connections are the same in both structures but the *location of the electrons* is different, we call these structures "resonance structures." For example, the two resonance structures of the molecule acetamide,  $C_2H_5NO$ , can be seen in the figure below.



*Resonance and Acetamide.* © Science Media Group.

Note that all the atoms are still present, the net charge on the molecule is the same, and the connections are all the same. The only change is that we've arranged the electrons differently. In the first structure, which is actually the more stable one because it has no formal charges, there is a double bond between the C and the O. In the second resonance structure, that double bond is between the C and the N. Which one represents the actual molecule? We find that molecules behave as though they were composed of *all the resonance structures* at once. It seems that a molecule is a kind of average over all its legitimate Lewis structures, a phenomenon called the "superposition of states." For example, in one structure, the C-N bond is a single bond and in the other structure it is a double bond, which means in reality that C-N bond is somewhere between a single and a double bond.

Acetamide is one of the simplest molecules in nature that has an amide bond or peptide bond. This is the bond that occurs over and over again between the amino acids that make up all of the proteins in nature. This has powerful implications, because double bonds are more rigid in nature, which means that

peptide bonds are better at helping molecules form stable 3-D shapes than regular single bonds. This is a major factor in maintaining the shapes of protein molecules in nature.

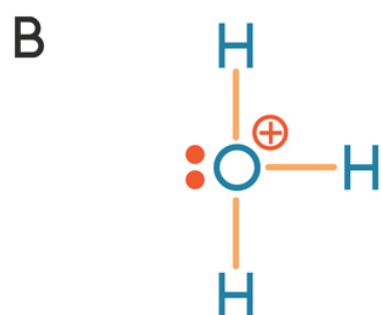
It turns out that the more resonance structures we can draw for a molecule or molecular ion, the more stable it is. This stability is called "resonance" or "resonance stabilization." Many of the patterns in chemistry, both in terms of acid-base chemistry and organic chemistry, can be explained by looking at all of the resonance structures for a molecule.

### Formal Charges

Sometimes, when molecules form where the normal patterns of bonding are not followed, or if the molecules are actually charged molecular ions, the atoms themselves can have a **formal charge** on them. This is because any atom brought some number of valence electrons into the molecule, and it wants to keep that same number of electrons close to it, to balance the charge of the positive protons in its nucleus. So, if the atom ends up with more or fewer electrons around it, it can end up with a negative or positive formal charge, respectively. The other thing about formal charges, is that if a molecule has formal charges, they all must add up to the total charge on a molecule. Therefore, any Lewis structure of a cation or an anion must have at least one formal charge on it.



Cyanide Ion



Hydronium Ion



Nitrogen Dioxide

**Figure 5-10. Advanced Lewis Structures**

Three examples of Lewis structures containing formal charges: A. cyanide ion, B. hydronium ion, C. nitrous oxide.

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In order to talk about formal charges, we have to first talk about what it means to "own" an electron. First of all, an atom owns all of the electrons in their lone pairs, because it isn't sharing any of those electrons. Secondly, an atom owns half of the electrons in each of its covalent bonds, because it is sharing those electrons with an atom that owns the other half. Let's look at a valid Lewis structure for the cyanide ion ( $\text{CN}^-$ ), a highly poisonous anion that is used in gold mining (Figure 5-10A). The carbon has a minus charge on it; that's the formal charge. Why does carbon have a negative formal charge on it? Well, the carbon owns the two electrons in its lone pair, and half of each of its three bonds, for a total of five electrons. But how many valence electrons did carbon bring to the molecule? Just four electrons. So, by owning one more electron than it normally has in its valence, it gets a -1 charge. Also, see that carbon is not making its typical four covalent bonds: When atoms break their normal octet rule patterns, they end up with formal charges.

### Radicals

When a molecule or atom has an odd number of electrons, one of those electrons cannot be paired off with another electron. As a matter of fact, there is no way to share an odd number of electrons and satisfy the octet rule by having eight electrons, so some atoms have to settle for having only seven electrons. This makes radicals, with their unpaired electron, very reactive. Radicals play important roles in many chemical reactions, including polymer formation, the formation and destruction of the ozone layer that protects us from radiation, and in numerous biological systems. Below are two Lewis structures for radicals. The first is nitrogen dioxide, which is a byproduct of many industrial processes and is present in car exhaust. If this radical reaches the upper atmosphere, it can begin to destroy the ozone molecules in the ozone layer. The other radical, the hydroxyl radical, forms sometimes in biological systems, and it is believed to be one of the major contributors to cell damage and aging as it reacts with molecules that are important in cell metabolism.



Nitrogen Dioxide

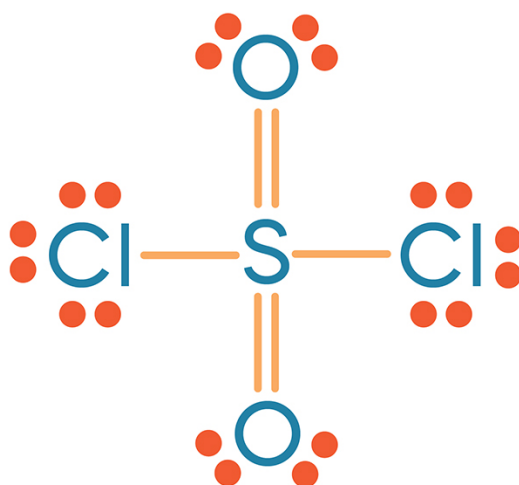


Hydroxyl Radical

*Nitrogen dioxide and hydroxyl radical. © Science Media Group.*

For comparison, let's look at the hydronium ion ( $\text{H}_3\text{O}^+$ ), which is the molecule responsible for acidity in water solutions (Figure 5-10B). Here, the oxygen atom owns the two electrons in its lone pair and half of the three covalent bonds, for a total of 5 electrons. However, oxygen normally has six valence electrons so it has an overall formal charge of plus one. Also, this charge correctly matches the total charge on the overall ion, and note that once again oxygen is breaking its normal pattern of two bonds and two lone pairs. Sometimes, a neutral molecule can have formal charges, such as nitrous oxide ( $\text{N}_2\text{O}$ ), which is also known as "laughing gas" and is used in as an anesthetic in dental surgeries. Note how both the nitrogen and the oxygen have formal charges, but their charges add up to zero, which is always the net charge on a neutral molecule. It is actually possible to draw another Lewis structure for nitrous oxide, where there is a double bond between both sets of atoms, rather than a triple bond and a single bond (Figure 5-10C). This pair of Lewis structures is called a pair of "resonance structures," which are discussed in the *Resonance* sidebar.

### Expanded Octets



**Figure 5-11. Sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ )**

The sulfur in the center of the molecule is actually making six covalent bonds, but that is allowed for sulfur, which is a third-row element. Notice that the oxygen, which is a second row element, and the chlorine still obey the octet rule. One of the other ways that Lewis structures for real molecules can bend the octet rule is when they are molecules called "radicals" (See the *Radicals* sidebar).

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For second row elements, their valence electrons are in their 2s and 2p orbitals, which can hold the eight electrons for the octet rule. However, when constructing the periodic table in Unit 4, we saw that the third shell has one s orbital, three p orbitals, and five d orbitals. However, since the 3s and 3p orbitals are lower energy than the 3d orbitals, electrons tend to occupy the s and p orbitals first. Hence, atoms in the third row of the periodic table can follow the octet rule. However, they don't have to. Sometimes, though, third and higher row elements will adopt an **expanded octet**. When this happens, an atom can have more than eight electrons in its valence shell, meaning that, unlike second-row atoms, these elements can form more than four bonds. Because of the 5d orbitals, elements that expand their octet can have up to 18 electrons. For example, the compound sulfur dioxide (SO<sub>2</sub>), which is used as a source of chlorine in chemical reactions, has an expanded octet. (Figure 5-11)

## Glossary

### **Expanded octet**

The situation in which a third row or higher element violates the octet rule, by having more than eight valence electrons and usually forming more than four bonds.

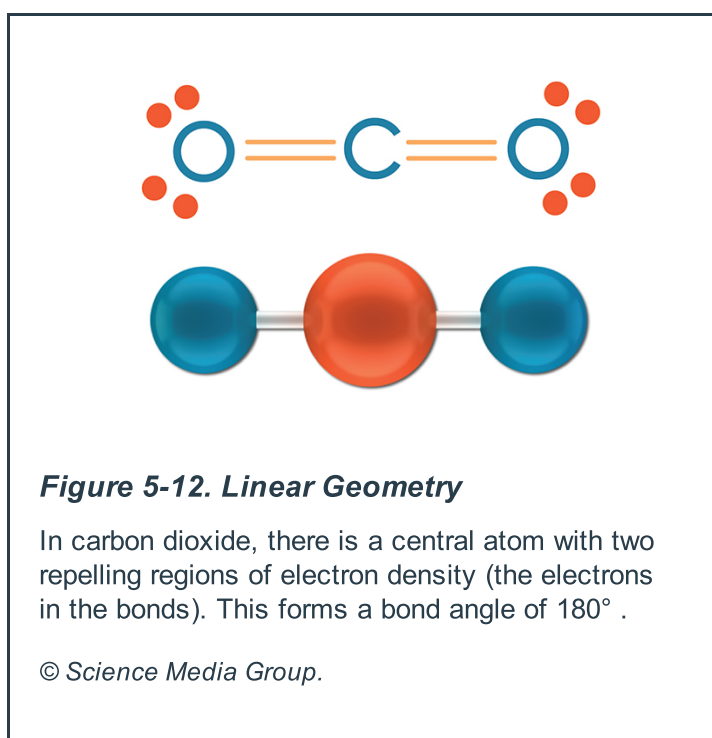
### **Formal charge**

An assignment of charge to each of the atoms in a molecule, based on the difference between their valence electrons and the electrons they control.

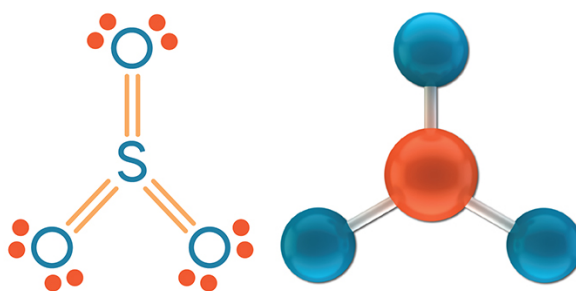
## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 7: VSEPR Theory

When we look at Lewis structures, we are only seeing a two-dimensional picture. To get the full picture of molecules, we need to find ways to represent those atoms in three dimensions. Why? Because the shape, or geometry, of a molecule helps us understand how that molecule will behave. In fact, a molecule's geometry affects its physical interaction with other molecules, determines which region of the molecule is likely to undergo chemical changes, influences properties like melting point and density, and influences the products that will form when it reacts with different substances. So let's take a look at how we can determine the shapes of molecules.



There is a simple model that allows us to predict, based on the Lewis structure, a molecule's three-dimensional geometry. It is called the "**Valence Shell Electron Pair Repulsion theory**," or VSEPR (pronounced "vesper"). In this model, we look at the arrangement of atoms and lone pairs around each atom individually. We call the atom under consideration the "**central atom**" and the other atoms or lone pairs attached to it the **substituents** of that atom. We consider each atom one at a time and then combine them to get the full picture.



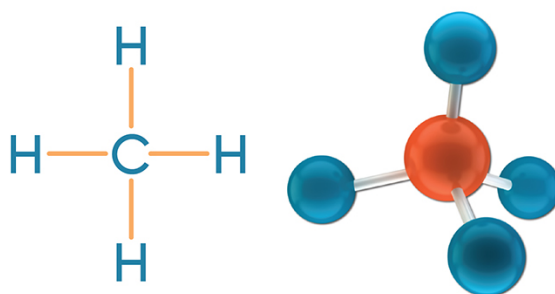
**Figure 5-13. Trigonal Planar Geometry**

In sulfur trioxide,  $\text{SO}_3$ , three repelling substituents form an equilateral triangle in a plane around the central atom. Each bond angle is  $120^\circ$ .

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The way VSEPR theory works is that we imagine that the electrons in the bonds or lone pairs desperately want to get as far away from each other as they can since all are negatively charged. But, since they are bound to the central atom, the best they can do is distribute themselves around the central atom with the angles between the atoms or lone pairs as large as possible. Imagine a central atom with bonds to two other things, for example the carbon in carbon dioxide, which is bound to two oxygens (Figure 5-12). The repelling electrons in the bonds will move to opposite sides of the central atom until they are  $180^\circ$  away from each other. We define the bond angle as the angle between the bonds to the central atom. When atoms arrange themselves in a straight line like this, we call it "linear geometry."

If there are three substituents around the central atom, as in sulfur trioxide ( $\text{SO}_3$ ), the farthest they can get from each other while still remaining bound to the central atom is to form a triangle in a plane around it, a geometry called "trigonal planar." The bond angles here are all  $120^\circ$ , as expected for an equilateral triangle. (Figure 5-13)

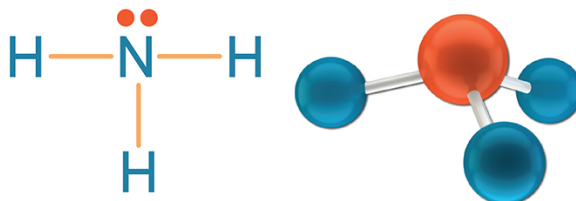


**Figure 5-14. Tetrahedral Geometry**

In methane,  $\text{CH}_4$ , the four mutually repelling bonds adopt a symmetric distribution around the central carbon, a geometry known as tetrahedral. The angle that separates each of the bonds is  $109.5^\circ$ .

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If there are four substituents repelling each other, the resulting geometry is called "tetrahedral," as shown below in Figure 5-14, and each of the bond angles is approximately  $109.5^\circ$ . Even though the Lewis structure makes any molecule seem flat, by combining the Lewis structure with VSEPR theory, we can understand and determine the 3-D structures of molecules.



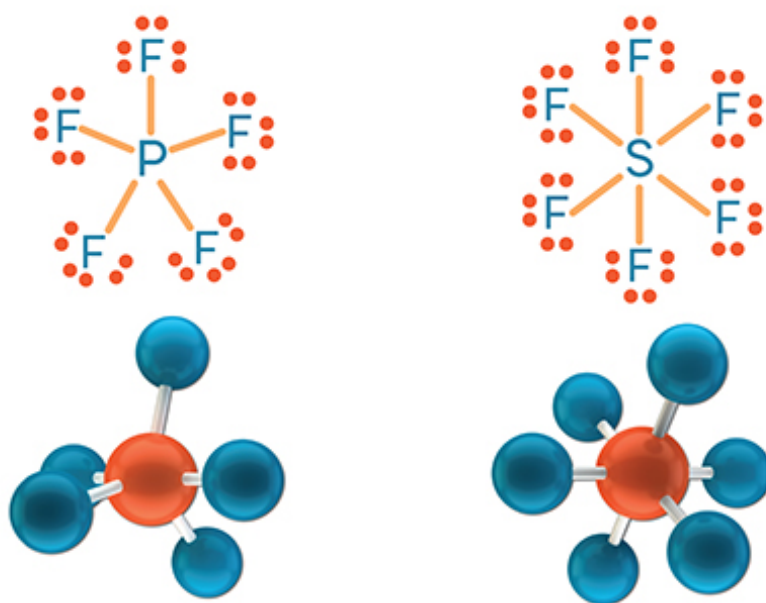
**Figure 5-15. Trigonal Pyramidal Geometry**

In ammonia (NH<sub>3</sub>), the three hydrogens and one lone pair adopt a tetrahedral arrangement to avoid electron-electron repulsion. Since we cannot see the lone pair, the geometry gets called "trigonal pyramidal."

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### Expanded Octet Geometries

While the organic molecules that make up nearly all of the biological molecules on our planet feature carbon bound to at most four other atoms, there are whole classes of compounds that the terms "linear," "trigonal planar," and "tetrahedral" aren't enough to describe. This happens when we have compounds that can expand their octets like  $\text{PF}_5$  or  $\text{SF}_6$ , two molecules that have a central atom bound to five or six atoms. In the case of six substituents, they will arrange themselves on the corners of a regular octahedron, which will make each pair of substituents have a  $90^\circ$  bond angle. However, for five substituents, there is no highly symmetrical geometry possible. What ends up happening is that two of the substituents are  $180^\circ$  from each other, and the other three substituents form a trigonal planar arrangement with  $120^\circ$  to each other in between the other two. This means that there are actually two types of positions in this geometry, which are called "equatorial" and "axial" positions. The two axial substituents are the pair that are  $180^\circ$  to each other, while the equatorial ones are in that trigonal plane with  $120^\circ$  bond angles to each other.



*Trigonal Bipyramidal and Octahedral Geometries. © Science Media Group.*

When describing molecular geometry, we deduce the shape by looking at the distribution of electrons around the central atom, including not just atoms but also lone electron pairs. But our description of the molecule depends only on the position of atomic nuclei. This means a molecule like ammonia, which has four repulsive regions of electron density (three bonds and the lone pair), has the geometry shown in Figure 5-15. The substituents arrange themselves tetrahedrally, just as we saw with methane. But when naming the molecular shape, we consider only the positions of the atoms, not the lone pairs; so rather than being tetrahedral, we would refer to this molecule as being trigonal pyramidal.

## Glossary

### ***Central atom***

The atom for which we are determining the geometry when applying VSEPR theory.

### ***Substituents***

The lone pairs and atoms of a molecule attached to the central atom when applying VSEPR theory.

### ***VSEPR Theory***

A theory that describes the shapes of molecules based on the mutual repulsion of the electron clouds surrounding the nucleus.



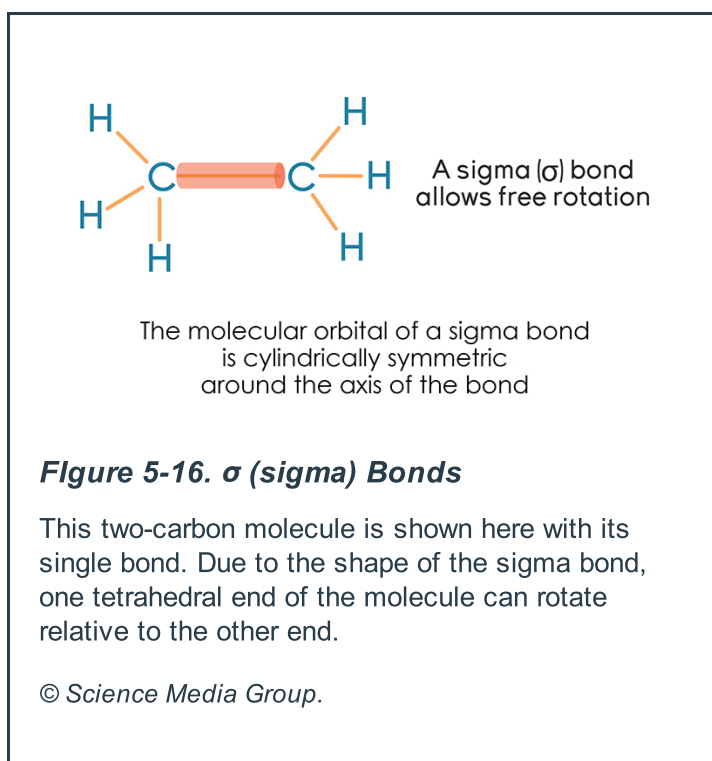
## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries

### Section 8: Hybrid Orbitals

So far, we've talked about sharing electrons in valence shells and we've seen pictures illustrating the bonds connecting the various components of molecules. But there is a more precise and fundamental way to discuss the manner in which atoms combine to form molecules: We can describe the combining of the "electron clouds" that surround the atomic nuclei. It is possible to determine the shapes and charges of these combined clouds, which tells us a lot about the behavior of the molecule. To describe these clouds we have to mathematically merge the atomic orbitals together to create new orbitals. When an electron is shared between two different atoms in a covalent bond, the two electron clouds that correspond to each of the atomic orbitals merge to become a larger cloud. This combination of atomic orbitals is called a **"molecular orbital."**

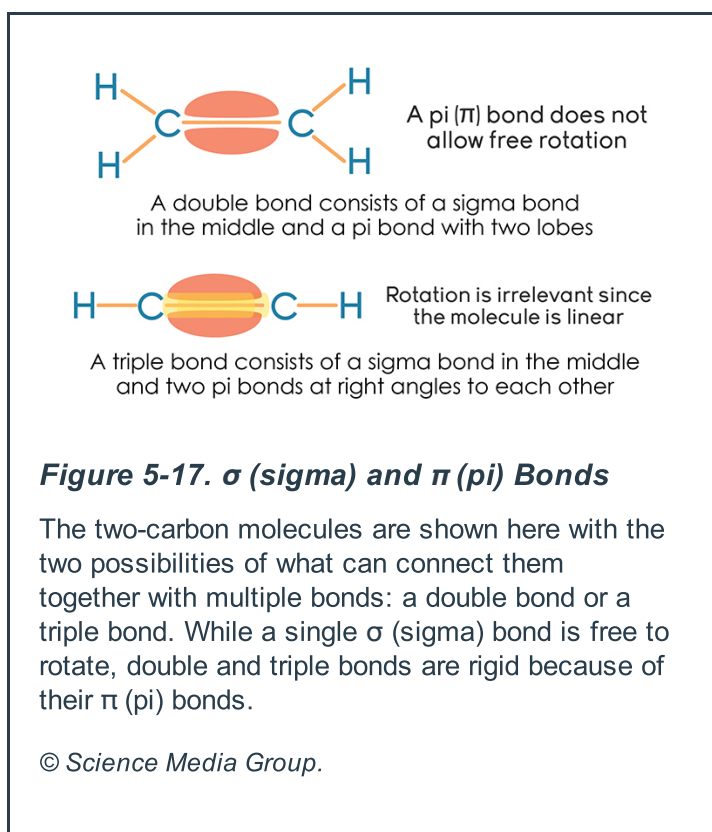
#### $\sigma$ (sigma) and $\pi$ (pi) Bonds

Between any two atoms, there is at least a single covalent bond, and there need to be molecular orbitals to make this connection. The molecular orbitals that form these single covalent bonds are called **" $\sigma$  (sigma) bonds"**; this comes from the fact that they are derived from the valence s orbitals and s in Greek is a sigma ( $\sigma$ ). Single covalent bonds have a cylindrically symmetric molecular orbital; the electrons move at identical distances around the axis between the two atomic nuclei (Figure 5-16). Sigma bonds are flexible in that the atoms in them can spin relative to one another while maintaining their strength. So, if a sigma bond is holding two atoms together, the molecule can rotate freely about that bond.



A double bond consists of a sigma bond and a second bond whose molecular orbital is not symmetric around the nuclear axis (Figure 5-17 (top)). This second bond is called a **" $\pi$  (pi) bond"** and it is shaped like a hot dog bun; a pi bond is called a pi bond because it is derived from *p* orbitals, which in Greek would be the letter  $\pi$  (pi). Recall that *p* orbitals have two portions on opposite sides of the nucleus, which is why a pi bond has two parts. Unlike sigma bonds, pi bonds are rigid; they cannot twist, because if the molecule were

to twist, the pi bond would break. Molecules that are held together by pi bonds are unable to rotate and create a rigid planar section of a molecule. A double bond is stronger than a single bond, but it is not twice as strong because pi bonds are not as strong as sigma bonds.



Accordingly, a triple bond consists of a sigma bond and two pi bonds (Figure 5-17 (bottom)). A triple bond will always be found in a geometrically linear portion of the molecule. While a triple bond is the strongest type of bond, it is not three times stronger than a single bond because pi bonds are weaker than sigma bonds.

## Glossary

### **Molecular orbital**

A region where atomic orbitals from different atoms overlap, creating a new orbital where electrons may be shared in a covalent bond.

### **Pi ( $\pi$ ) bond**

A covalent sharing of electrons formed by the side-to-side overlap of two p orbitals; found in double and triple bonds.

### **Sigma ( $\sigma$ ) bonds**

A covalent sharing of electrons that is formed by head-to-head overlap between two atomic orbitals and is cylindrically symmetrical about the axis between the nuclei.

## Unit 5: *The Structure of Molecules—Lewis Structures and Molecular Geometries*

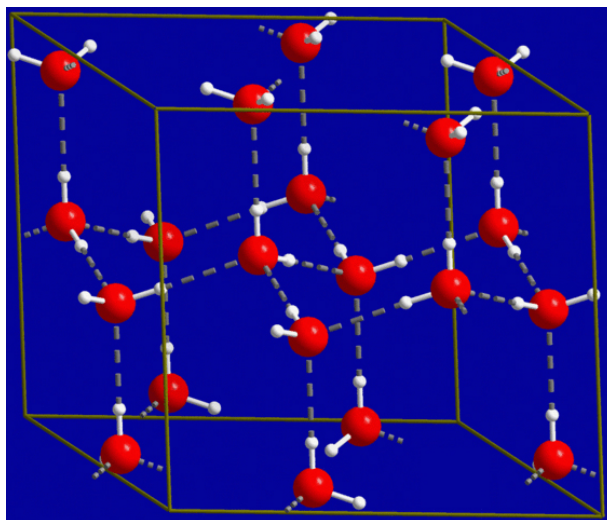
### Section 9: Intermolecular Forces

Ionic and covalent bonds hold atoms together in molecules. There are also forces of attraction that exist between molecules themselves. These intermolecular forces, while much weaker than ionic and covalent bonds, have important effects on the way molecules, once formed, interact with one another. We'll look at three of these forces, listed here from strongest to weakest:

- Hydrogen bonding
- Dipole-dipole forces
- London dispersion forces

#### ***Hydrogen Bonding***

The strongest form of intermolecular force is called "**hydrogen bonding**." There are two things that are required for a hydrogen bond to form. First, there must be a hydrogen atom that is attached to one of the most electronegative atoms: nitrogen, oxygen, or fluorine. This makes the hydrogen very electron deficient, as the electronegative atom is pulling electron density away from the hydrogen. The second thing that is required is a lone pair on another very electronegative atom, a fluorine, oxygen, or nitrogen. The electron deficient hydrogen shares electrons weakly with this lone pair, almost like the sharing in a covalent bond. The difference is that a hydrogen bond is about a hundred times weaker than a normal covalent bond. Because organic molecules have so many molecules with nitrogens and oxygens in them, hydrogen bonding is a common motif in biochemistry.



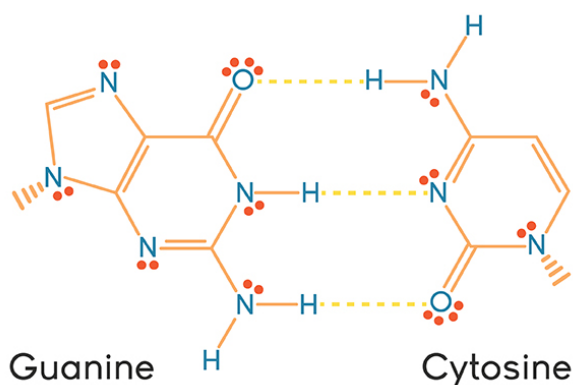
**Figure 5-18. The Structure of Ice**

This is a representation of the water molecules in an ice crystal. In the picture, red balls are oxygen atoms and white balls are hydrogen atoms. Hydrogen bonds are represented by the dotted lines. Note how each water molecule has both hydrogen atoms making hydrogen bonds, and both lone pairs on the oxygen are hydrogen bonding to nearby waters.

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Water is a very special compound in terms of hydrogen bonding. It has two hydrogens on an oxygen atom and two lone pairs on an oxygen atom. This means that, on average, every water molecule in a glass of water can make two hydrogen bonds. So, even though water is a three-atom molecule with a molecular weight of only 18 atomic mass units, it is a liquid that boils at the high temperature of  $100^{\circ}\text{C}$ . All other molecules of that size and weight are gases, because they don't have those strong additional intermolecular forces. This affects many of the properties of water. This is why there is surface tension that keeps water just over the rim of a glass or capillary action that draws water up thin tubes, like in the xylem tubes in plants that bring water up the stems. Water molecules work very hard to make sure they can make as many hydrogen bonds as possible, and this becomes very apparent when water begins to freeze into ice. In the solid state, in order to maximize each water molecule making its hydrogen bonds, it adopts the structure seen in Figure 5-18. This structure is very open, and has large hexagonal spaces in it. This open hexagonal pattern caused by the hydrogen bonding explains why snowflakes are six-sided and why ice is less dense than liquid water and it floats.

While many of water's properties are directly related to its ability to make hydrogen bonds, any molecule with hydrogens bound to nitrogen or oxygen, with lone pairs on a nitrogen or oxygen atom, can make hydrogen bonds. Proteins in the body are often held to their shape by the hydrogen bonding between the different amino acids. But, on an even grander scale, the two strands of DNA are held together by hydrogen bonds (Figure 5-19). While a hydrogen bond isn't very strong, with thousands of base pairs in DNA—each making two or three hydrogen bonds to each other—those intermolecular forces add up quickly, and therefore the DNA double helix is very stable.



**Figure 5-19. Hydrogen Bonding in DNA**

In the double helix of DNA, there are strands of molecules called "nucleoside phosphates" that are covalently bound together. However, each strand is held to the other strand by only weak hydrogen bonds. This diagram shows how the guanine and cytosine bases are perfectly designed by nature to hydrogen bond to each other. The hydrogen bonds are represented by the yellow dotted lines. Note how the molecules perfectly placed so that each hydrogen on an N or O lines up with a lone pair on another N or O.

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### **Dipole-Dipole Forces**

Earlier in this unit, we saw that molecules with an unsymmetrical cloud of electrons are called "polar molecules." A molecule that is polar can also be called a "dipole." The more uneven the cloud of electrons is, the more polar a molecule is, and the larger its dipole is. All of the molecules that can hydrogen bond are polar; this is because of all the lone pairs, such as the ones on water that make one side of the water molecule much more negative than the other. However, not all molecules that are polar can hydrogen bond.

The next strongest intermolecular force is that which occurs between polar molecules, called "dipole-dipole interactions" or "**dipole forces**." This type of force is also generally called a "**van der Waals force**." Van der Waals forces is a collective term for all non-covalent attractions between molecules, which will also include the London forces discussed at the end of this section. The strength of these dipole forces is related to how polar the molecules are or how big their dipoles are. Essentially, molecules are like little miniature magnets with a more negative end (usually with more lone pairs) and a more positive end. These molecules line themselves up so that their positive ends are near the negative ends of the next molecules. Then, a very weak coulombic force attracts them together. These are the types of intermolecular forces that hold molecules like chloroform ( $\text{CHCl}_3$ ) and hydrogen chloride ( $\text{HCl}$ ) to each other.

### **London Dispersion Forces**

**London dispersion forces** are the weakest intermolecular force. These forces are also under the category of van der Waals forces and are sometimes called "London forces" or "dispersion forces." These are the only type of forces available to nonpolar molecules, which have perfectly symmetrical magnetic clouds. Since these clouds aren't imbalanced, they don't have a very negative end and a very positive end like the polar molecules, which experience the dipole forces. However, a big cloud of electrons, just due to probability, is likely to have more electrons on one side compared to the other at any particular point in time. This creates a very small or temporary dipole in the molecule, which can then cause a nearby molecule to shift its cloud of electrons to balance it, making an induced dipole next to it. This pair of induced dipoles are very weakly attracted together, and they cause the molecules to stick together. These

forces of attraction are called London forces after the physicist Fritz London, who first characterized them in the 1930s. For non-polar molecules, like carbon dioxide ( $\text{CO}_2$ ) in the form of dry ice or the xenon molecules in liquid xenon, the forces holding these atoms and molecules together are the London forces.

London forces are extremely weak, but if a molecule is large, they can add up to a noticeable effect. For example, the stronger the force of attraction between molecules, the more energy has to be used to separate them. When one heats a liquid, at a certain temperature the molecules separate and become a gas. We call the temperature at which this happens the boiling point; molecules with stronger intermolecular forces have higher boiling points. Larger molecules tend to have higher boiling points than smaller molecules because the London forces between them make the molecules stick together more. Table 5-1 shows a group of non-polar molecules of increasing size. As molecular size increases, the boiling points increase as a result of increasing London forces.

**Table 5-1. London Dispersion Forces**

Molecule (from smallest to largest)	Boiling Point
methane, $\text{CH}_4$	-160°C
ethane, $\text{C}_2\text{H}_6$	-89°C
propane, $\text{C}_3\text{H}_8$	-42°C
butane, $\text{C}_4\text{H}_{10}$	-1°C
pentane, $\text{C}_5\text{H}_{12}$	36°C
hexane, $\text{C}_6\text{H}_{14}$	69°C
heptane, $\text{C}_8\text{H}_{18}$	99°C

In summary, while only certain molecules that have the proper sets of atoms present can hydrogen bond, ALL molecules have London dispersion forces. Also, all polar molecules, whether they can hydrogen bond or not, have dipole-dipole forces. In most molecular compounds, their liquid and solid forms are held together by combinations of all three of these intermolecular forces.

## Glossary

### **Dipole forces**

The intermolecular forces of attraction between molecules that are polar.

### **Hydrogen bonding**

A type of intermolecular attraction in which a hydrogen is shared between two very electronegative atoms. This commonly happens when a hydrogen is attached to a nitrogen or an oxygen atom, and the hydrogen reaches out to a nearby lone pair to make a weak bonding interaction.

### **London dispersion forces**

A type of intermolecular force that arises from brief, temporary dipoles in the electron cloud surrounding a molecule.

### **Van der Waals force**

A collective term for intermolecular forces including London dispersion forces and dipole forces.



## Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries



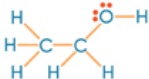

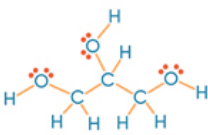
### Section 10: Physical Properties of Molecules

Molecules have properties that can be directly measured in the laboratory, which are the results of their molecular structure. This is because molecular structure determines the types of intermolecular forces that hold molecules together. The stronger these forces, the harder it becomes—and the more energy it takes—to move the molecules apart from each other. Some of the properties of molecules that are dependent on these forces are the temperatures at which phase transitions take place, such as the boiling point and the melting point. It also affects how dense compounds will be or how viscous they will be. Viscosity is a resistance to flow, and molecules with strong intermolecular forces will be more viscous, that is, pour like maple syrup. In addition, solubility, the ability for molecules to form solutions with other molecules, is one of these types of properties. We will focus on two of them here, specifically, boiling point and solubility.

#### Boiling Point

When we bring enough molecules of a substance together in the form of a liquid, we can heat it up and measure the temperature at which it turns into a gas, that is, its boiling point. The strength of intermolecular forces and the amount of them in the collection of molecules determine boiling point. More or stronger intermolecular forces result in a higher boiling point because the molecules want to stay closer together, in the liquid phase, rather than spread out into the gas phase (see Table 5-2). Thus, compounds that form hydrogen bonds boil at higher temperatures than compounds that have only the weaker London forces or dipole-dipole attractions.

**Table 5-2: Boiling points of Common Substances**

Substance	Lewis Structure	Boiling Point	
		°C	°F
Oxygen (O <sub>2</sub> )		-183	-297
Ammonia (NH <sub>3</sub> )		-35.5	-28.1
Ethanol (C <sub>2</sub> H <sub>5</sub> OH)		79	172.4
Water (H <sub>2</sub> O)		100	212
Glycerin (C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> )		290	554

The oxygen molecule, the one molecule that cannot make hydrogen bonds, has the lowest boiling point in the table. While both the ammonia and ethanol can make a hydrogen bond, the ethanol is a much heavier molecule and thus has additional, stronger van der Waals forces. Water, which has the ability to make two



hydrogen bonds, boils at an even higher temperature. And lastly, glycerin, which has the ability to form up to three hydrogen bonds and has a much higher molecular weight, boils at the highest temperature of them all.

### Solubility

Molecules are attracted to other molecules when there are strong intermolecular forces between them. Therefore, a polar molecule would like to find another polar molecule with which to make dipole forces. Water, which is one of the most polar molecules, therefore, is very good at dissolving other polar molecules; a solution with water as the solvent is called an "**aqueous solution**." For example, acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ) dissolved in water makes an aqueous solution known as vinegar.



**Figure 5-20. Polar and Non-polar Liquids**

Left: Diesel fuel, which is a nonpolar hydrocarbon floats on a puddle of water without mixing. Right: A separatory funnel is a common piece of glassware used in a chemistry lab. It allows for liquids that will not mix together, to separate into layers so that the more dense one can be drained out from the bottom of the funnel. In this funnel, oil floats on top of colored water.

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Nonpolar molecules, like those found in vegetable oil, lack any intermolecular forces except London forces. As such, they interact much less strongly with water. In fact, the water molecules attract each other more than they do the nonpolar compounds; this means the nonpolar molecules are pushed to the side and excluded from the water, and therefore they are not soluble in aqueous solvent. Water's attraction for itself pushes nonpolar compounds off to the side. This is why the oil and vinegar in salad dressing separate, similar to the examples in shown in Figure 5-20.

## Oil Spills and Tar Balls

Crude oil consists of a mixture of molecules called "hydrocarbons." All hydrocarbons are made of just two elements, hydrogen and carbon, so they have very similar chemical properties. These molecules have only London forces between them, so the rate at which they evaporate is very closely related to their size. When a crude oil spill occurs, a mixture of hydrocarbons of all different sizes is released to the environment. If the spill occurs at sea, the hydrocarbons float at the surface, since they are all less dense than water, and begin to evaporate.

The smaller molecules evaporate first because they are held together less strongly. The remainder of the oil spill gradually becomes more and more concentrated with the larger hydrocarbons from the crude oil. These large molecules lump together to form balls of goopy hydrocarbon, or "tar balls." This form of pollution can persist long after the oil spill, although tar balls may break down eventually from the action of waves and microorganisms.



*Oceanic Tarballs. © Wikimedia Commons, Public Domain.*

Nonpolar molecules will dissolve only in solvents composed of other nonpolar molecules, that is, in nonpolar solvents such as turpentine (mostly  $C_{10}H_{16}$ ), hexane ( $C_6H_{14}$ ) or benzene ( $C_6H_6$ ). Nonpolar solvents are also often called "organic solvents," because the most common ones are made of carbon, just like the common molecules that make up living things. Saying that a molecule is **hydrophobic** is another way of saying it doesn't dissolve in water (from the Greek *hydros* meaning "water," and *phobos* meaning "a fear of"); **hydrophilic** is another way of saying it will dissolve in aqueous solution (*philia* meaning "love of").

## Glossary

### **Aqueous solution**

A solution where the solvent (primary component) is water.

### **Hydrophilic**

Description of a molecule that dissolves easily in an aqueous or other polar solvent.

### **Hydrophobic**

Description of a molecule that dissolves readily in a nonpolar solvent.

## **Unit 5: *The Structure of Molecules—Lewis Structures and Molecular Geometries***

### **Section 11: Conclusion**

Atoms come together to form compounds in ways that range from ionic solids held together by Coulombic forces to covalently-bound molecules sharing electrons to stabilize each other. With a Lewis structure to keep track of where and how the electrons are shared in a molecule, a chemist can figure out the structure of a molecule in three dimensions, and from there, can determine how molecules will fit together and interact with one another. These interactions take the form of intermolecular forces, which though quite weak, have huge implications for life, from keeping water as a liquid on our planet to holding together the strands of our DNA. In the next unit, we will explore how molecules come together and react with each other to form new molecules.

## **Unit 5: The Structure of Molecules—Lewis Structures and Molecular Geometries**

### **Section 12: Further Reading**

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