Chapter 15

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

REPRESENTING MOLECULES

Lewis dot diagrams work well to show the bonding of electrons between atoms, but they are two-dimensional (2-D) and do not show the arrangement of atoms in a three-dimensional (3-D) space. That 3-D arrangement illustrates the **MOLECULAR GEOMETRY** of the molecule.

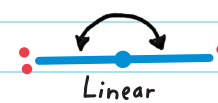
> Molecular geometry is the 3-D arrangement of atoms within a molecule.

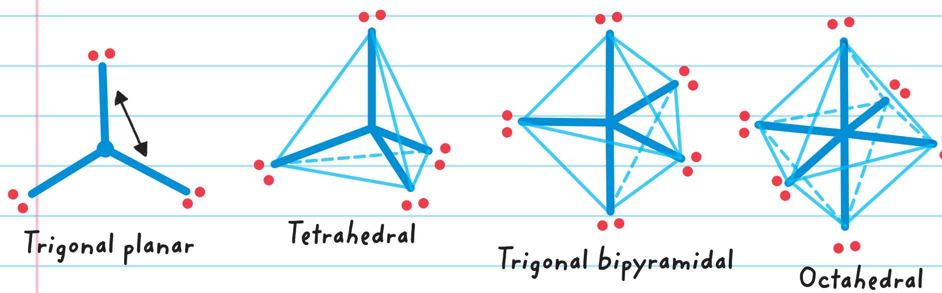
VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR) allows scientists to predict the 3-D shape of a molecule that is centered around a central atom. VSEPR shows a molecule's appearance in three dimensions. Electrons don't like to be next to each other; they repel, because they are all negative. But there are several electrons, so they have to find the positions with the smallest repulsion.

VSEPR uses the following rules:

- Electron pairs in the valence shell of an atom will repel or move away from each other.
- Nonbonded electron pairs are found closer to the atom and exhibit more repulsion than bonded pairs.

VSEPR molecules have five basic shapes:

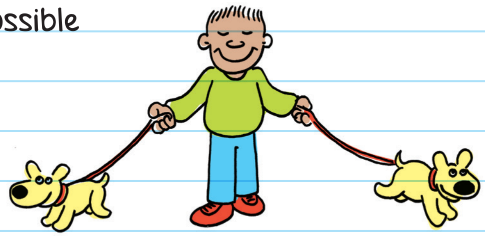


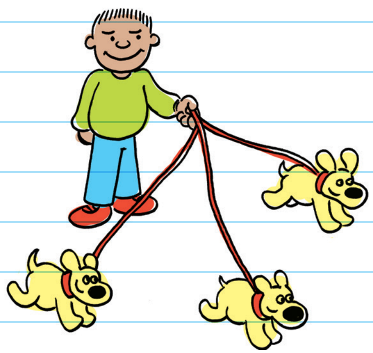


> Double or triple covalent bonds are treated just like single bonds in a VSEPR diagram: They are represented with a single bar.

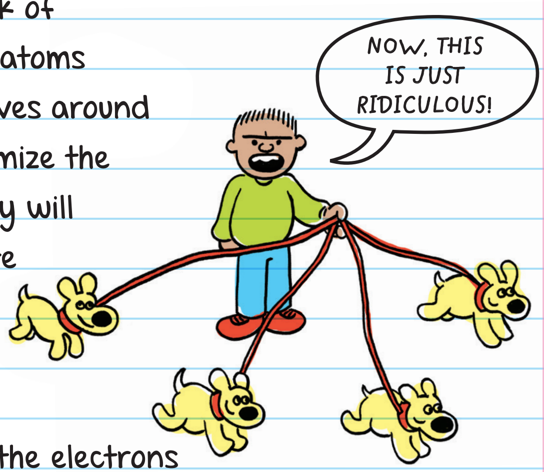
How the Structures Are Formed

Atoms arrange themselves to be as far away from each other as possible. For example, beryllium fluoride (BeF_2) has two bonds. The fluorine (F) atoms want to be as far away from each other as possible (otherwise, their electrons will repel), so they occupy positions at a 180-degree angle to make a linear (straight) structure. Imagine having to walk two dogs who didn't like each other. They would want to be as far away from each other as possible.





BF_3 has three bonds, so being linear doesn't work. Think of geometry class. If the F atoms need to arrange themselves around a boron (B) atom to maximize the space between them, they will occupy positions to create 120-degree angles between them.



As you add more bonds, the electrons repel each other to maximize the distance between them.

POLAR VS NONPOLAR BONDS

Covalent bonds are classified as being either **polar** or **nonpolar**. **POLARITY**, a physical property of the compound, is important because it determines other physical properties of the compound, such as boiling point, melting point, solubility, and intermolecular interactions.

Atoms using **NONPOLAR BONDS** equally share the electrons between them, due to the similar electronegativity values of the atoms in the molecule.

POLAR BONDS have unequal sharing of electrons between atoms, due to the different electronegativity values of the atoms in the molecule.

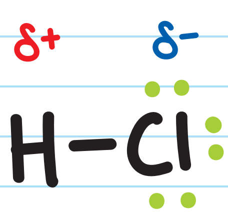
All ionic bonds are polar bonds.

In a polar covalent bond, the electrons are shared, but they can be found more on one side. It's like sharing a blanket where you have two-thirds of it and the other person has one-third.

In a polar covalent bond, the side that is closer to the bonded pair of electrons is slightly more negative. This means that the other side of the bond is slightly more positive. This small difference in charge is called a **DIPOLE**.

Because the charges are partial (less than 1), they are written as δ+ and δ-.

> δ (read as delta) means slightly
>
> δ+ means slightly positive
>
> δ- means slightly negative



The notation shows that the H side is slightly more positive and the Cl side slightly negative, because hydrogen tends to give up an electron and chlorine tends to gain one.

How can you tell whether the sharing is equal?

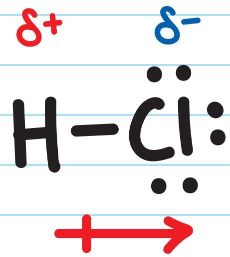
Electronegativity values can be used to classify a bond as polar covalent, nonpolar covalent, or ionic. Below is a list of the electronegativity values for each element. You can use the values to compare element electronegativities.

H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.00	Ar
K 0.2	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 166	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.8	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.2	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.5
Cs 0.9	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.8	Po 2.0	At 2.2	Rn 2.4
Fr 0.7	Ra 0.7	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						

Lanthanides	Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.1	Lu 1.2
Actinides	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cr 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.8

Electronegativity data is not available for the elements not shown.

This drawing of hydrogen chloride (HCl) shows the **DIPOLE MOMENT** of the molecule, which is indicated by an arrow with a line across one end. The vertical bar at the left end of the arrow shows the element that is donating the electron. The arrowhead end shows the direction in which the electrons are moving, toward the element that is accepting the electron. Because no arrow is heading in the opposite direction, HCl is considered to be a polar molecule.



The arrow also points to the more electronegative atom, indicating where the electrons are most likely to be found.

Diatomic molecules such as O_2, H_2, and N_2 have no difference in electronegativity values because the electronegativity of each atom is the same. These molecules are nonpolar, but the atoms do not need to be the same for the bond to be labeled nonpolar.

Carbon's electronegativity is 2.5 and hydrogen's value is 2.1.

Nonpolar covalent bonds form between atoms with an electronegativity difference of between 0 and 0.4.

$2.5 - 2.1 = 0.4$

0.4 rounds down to zero. Therefore, a bond between carbon and hydrogen is nonpolar.

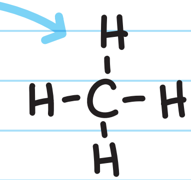
Polar covalent bonds form between atoms with an electronegativity difference of between 0.5 and 1.7.

MOLECULAR POLARITY IN BONDS

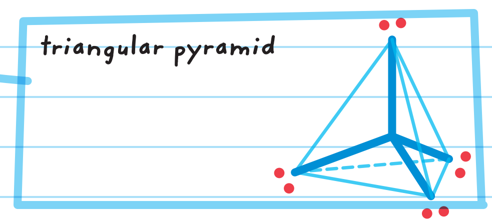
Molecular polarity depends on the shape of the molecule and how the electron pairs occupy space.

Bonds are polar if the atoms have an electronegativity difference greater than 0.5. The entire molecular is polar if the shape is asymmetric.

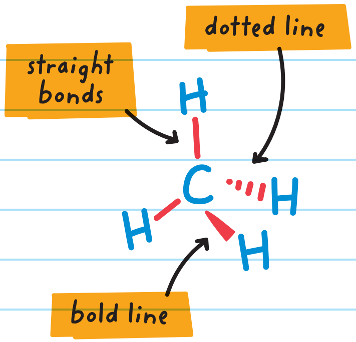
For example, if you write CH_4 with the structural formula, it looks like this, which appears to be linear. But if you apply VSEPR, it looks more like a tetrahedron, showing electron pairs that are far apart from one another in a 3-D model.



Lewis dot structure



In the model, the straight bonds are in a 2-D plane. The dotted line represents the atom away from you, and the bold line represents the H closest to you.



VSEPR structure

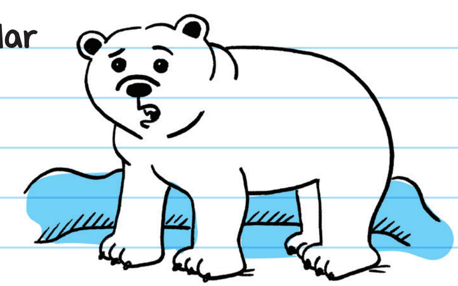
Because of its geometry, the molecule is nonpolar overall.

SNAP
Symmetrical molecules are **N**onpolar and **A**symmetric molecules are **P**olar.

Nonpolar molecules include:

- CO_2
- Any of the noble gases
- Any diatomic molecules, such as H_2 and Cl_2
- Many carbon compounds, such as CCl_4, CH_4, and C_6H_6

Can a molecule be nonpolar but the bonds are polar at the same time?

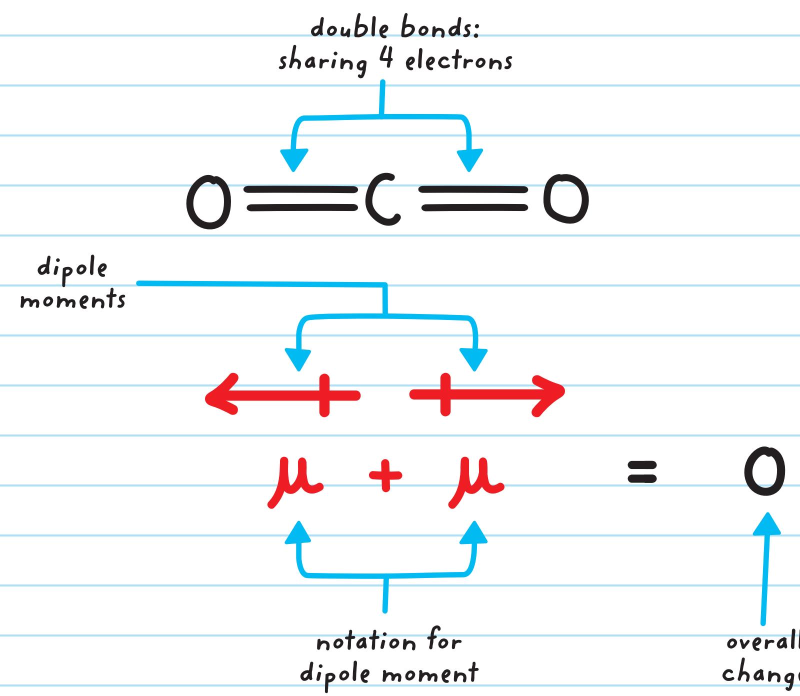


YES

It is possible for the individual bonds in a molecule to be polar while the overall molecule is nonpolar. That means some of the bonds within the molecule have slight dipoles, but overall, the molecule itself distributes the dipoles equally in space.

For example, in carbon dioxide (CO_2), carbon forms a double bond with each oxygen. But each oxygen has six lone electrons. These are very electronegative and pull the electrons in the covalent bond toward them, causing a dipole to form.

This does not mean that it's a polar molecule.



The geometric shape, which is linear, cancels out the dipole moment, making the overall charge 0. Therefore, it is a nonpolar molecule.

Characteristics of ionic, polar, and nonpolar bonds.

Comparison of Ionic, Polar, and Nonpolar Bonding

IONIC	COVALENT	
Ions (metal + nonmetal)	**Polar** (two different nonmetals)	**Nonpolar** (two identical nonmetals)
Complete transfer of electrons	Unequal sharing of electrons	Equal sharing of electrons
Full ionic charges	Partial ionic charges	No charges
$Na^{+}Cl^{-}$	$H \longrightarrow Cl$	H – H

CHECK YOUR KNOWLEDGE

1. What is molecular geometry and why is it so important in chemistry?
2. How do nonbonded pairs behave differently from bonded pairs of electrons?
3. What are the five basic VSEPR arrangements?
4. Draw the Lewis dot diagram and VSEPR diagram of CH_4.
5. What is the difference between a polar and a nonpolar bond?
6. Define a dipole. What symbols are used to show that a dipole is present?
7. How does electronegativity difference determine bond polarity?

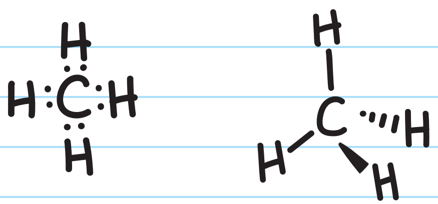
ANSWERS

CHECK YOUR ANSWERS

1. Molecular geometry is the three-dimensional arrangement of atoms within a molecule. It helps to determine the structure of a molecule, which determines its properties.

2. Nonbonded electron pairs are found closer to the atom and exhibit more repulsion than bonded pairs.

3. The five basic VSEPR arrangements are linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral.

4. 

5. Nonpolar bonds have an equal sharing of the electrons between the atoms. Polar bonds have an unequal sharing of electrons between atoms.

6. A dipole occurs when the side that has elements with more electronegativity is slightly more negative. That means the other side of the bond is slightly more positive. This small difference in charge is called a dipole. Because the charges are less than 1, they are written as delta plus (δ+) and delta minus (δ−).

7. Polar covalent bonds form between atoms with an electronegativity difference of between 0.5 and 1.7. Nonpolar bonds do not have a large difference in electronegativity.