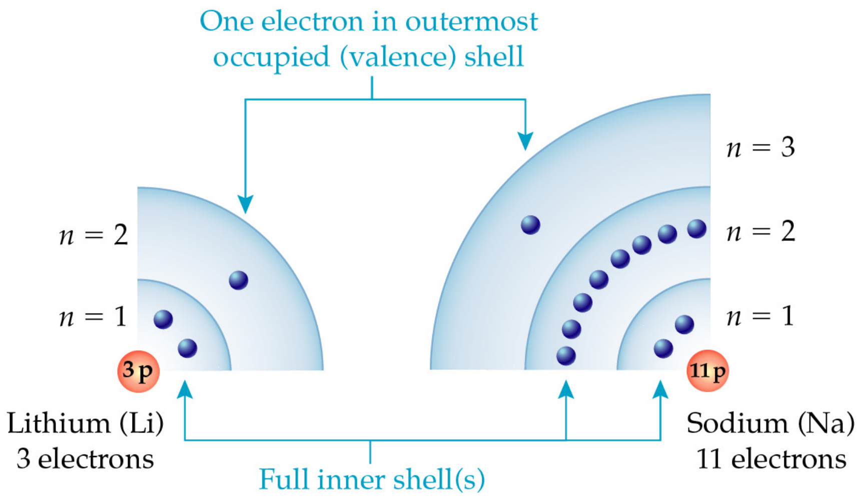
CHEMICAL BONDING

Chapter Ten

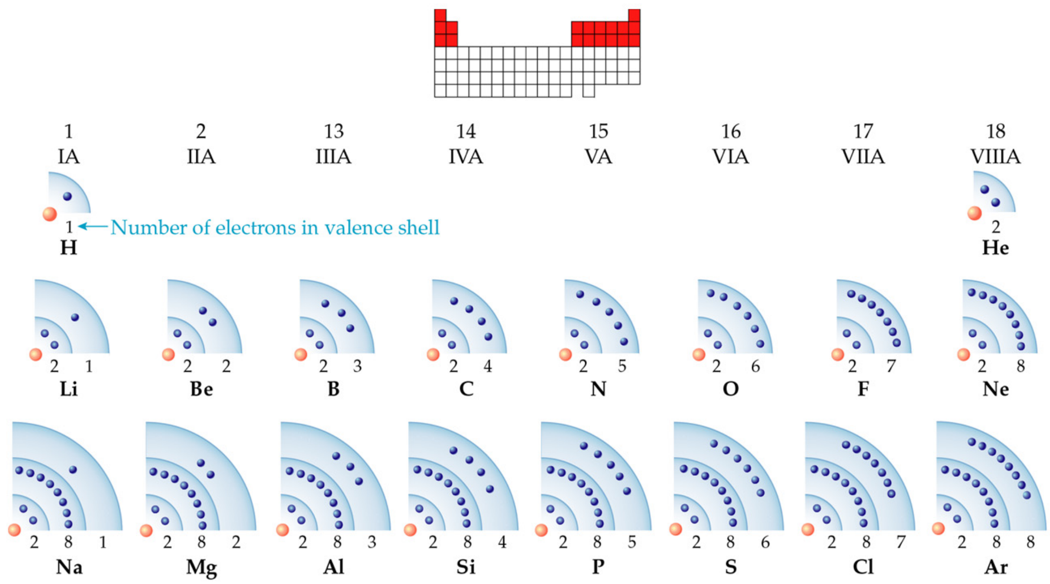
Valence Electrons

- The electrons occupying the outermost energy level of an atom are called the valence electrons; all other electrons are called the core electrons.
- The valence electrons, as we will see, are responsible for chemical bonding.
  - Knowing the number of valence electrons an atom has is the single most important information you can have in predicting how an atom will react chemically.
- Note that the valence electrons are not *always* the electrons with the highest energy, as we will see with the transition metals



Valence Electrons

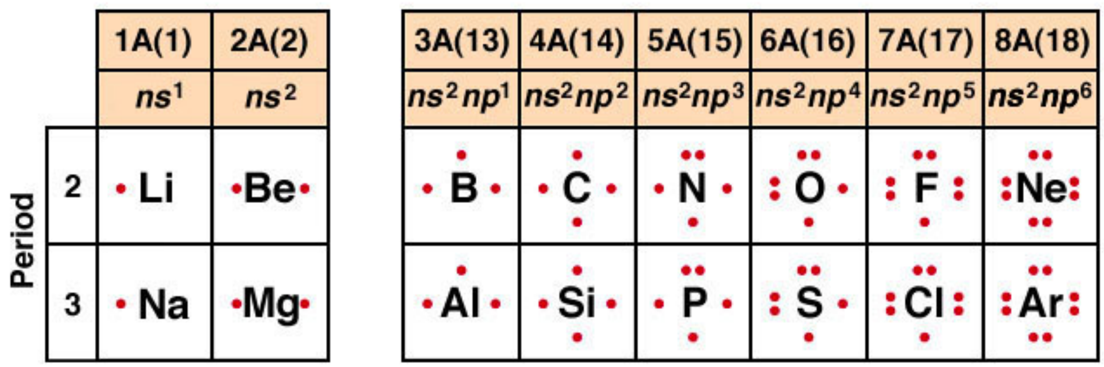
- For elements in group IA through VIIIA, the number of valence electrons an atom has is simply its group number.
  - So phosphorus, in group VA, has five valence electrons.
- Helium is the only significant exception; it has 2 valence electrons, even though it is in group VIIIA



Lewis Dot Diagrams

- Lewis dot diagrams are simple symbols which show the symbol of an element surrounded by as many dots as that atom has valence electrons.
- The first four electrons are drawn (in any order) on each of the four "sides" of the symbol.
- The next four electrons are "paired up" with the other four atoms (again, in any order).
- These symbols will be used to model chemical bonding.

Lewis Electron-Dot Symbols for Elements in Periods 2 and 3



Notice that the number of valence electrons matches the group number for these “main group” elements.

Examples

Draw the Lewis dot diagrams for selenium and rubidium atoms.

The Octet Rule

- The Octet Rule states that atoms react in such a way as to give them eight electrons in their outermost energy level (their valence shell).
- The Noble Gases, those elements in the period on the far right of the Periodic Table, generally do not react with other atoms, as their valence shell is filled with eight electrons (or two in the case of helium).
- By gaining or losing enough electrons to give an atom eight electrons in its valence shell, the atom gains the stable features of a noble gas.

Getting an Octet

- Atoms usually achieve an octet in the following way:
  - Metals lose their valence electrons, giving them an empty outer shell.
    - Note that the ion now has the electron configuration of a noble gas.
  - Nonmetals gain *or* share enough electrons to give themselves eight electrons in their outer shell.
    - Nonmetals generally share with other nonmetal atoms, or take electrons away from metal atoms.

Example

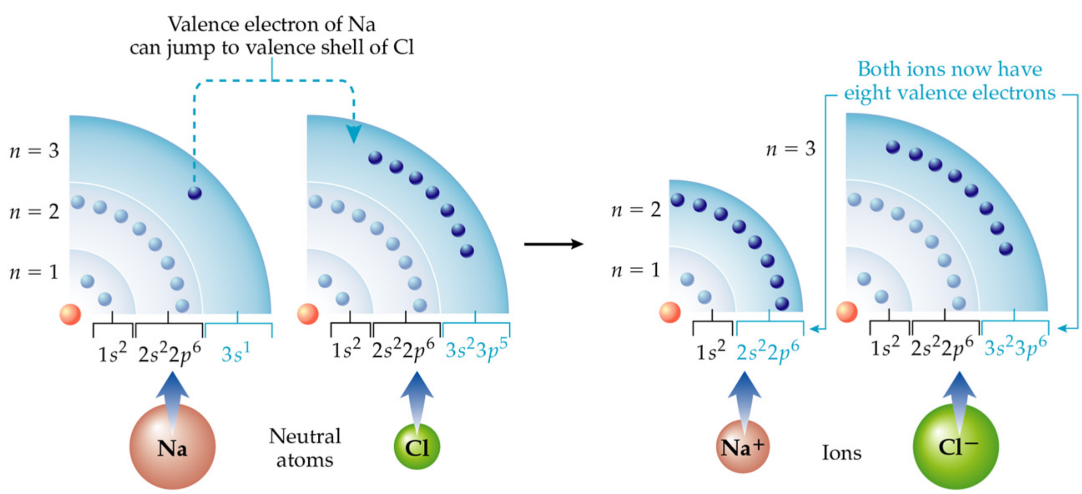
- How many electrons will usually be gained or lost by each of the following atoms?
  - Bromine
  - Barium
  - Potassium
  - Aluminum
  - Oxygen
  - Neon

The Duet Rule

- Hydrogen atoms attempt to pick up another electron, giving them the same electron configuration as the noble gas helium; this is called <u>The Duet Rule</u>.
- Likewise, when lithium loses an electron to become Li^+, it has the same electron configuration as helium.

A Cautionary Note

- Gaining and losing electrons does <u>not</u> occur unless there are other atoms around to encourage this.
  - A sodium atom cannot just toss its valence electron away; it must give it to another atom which wants to take it, like chlorine.
- Considering this, be sure that you do not confuse an atom of an element (which has its usual number of electrons) with an ion (which has gained or lost electrons).



What is Bonding?

- Bonding describes how atoms interact with each other in an *attractive* sense.
- There are three types of bonding:
  - Ionic bonding
  - Covalent bonding
  - Metallic bonding

Ionic Bonding

- We have already seen several examples of ionic compounds
- Ionic bonding results from the attractions between ions of opposite charge
- Ionic bonding is generally the strongest of the bonding types.
  - It requires a great amount of energy to separate the ions from each other, resulting in high melting points.
- Recall that ionic compounds do not form molecules
  - NaCl represents the formula unit, not the molecular formula

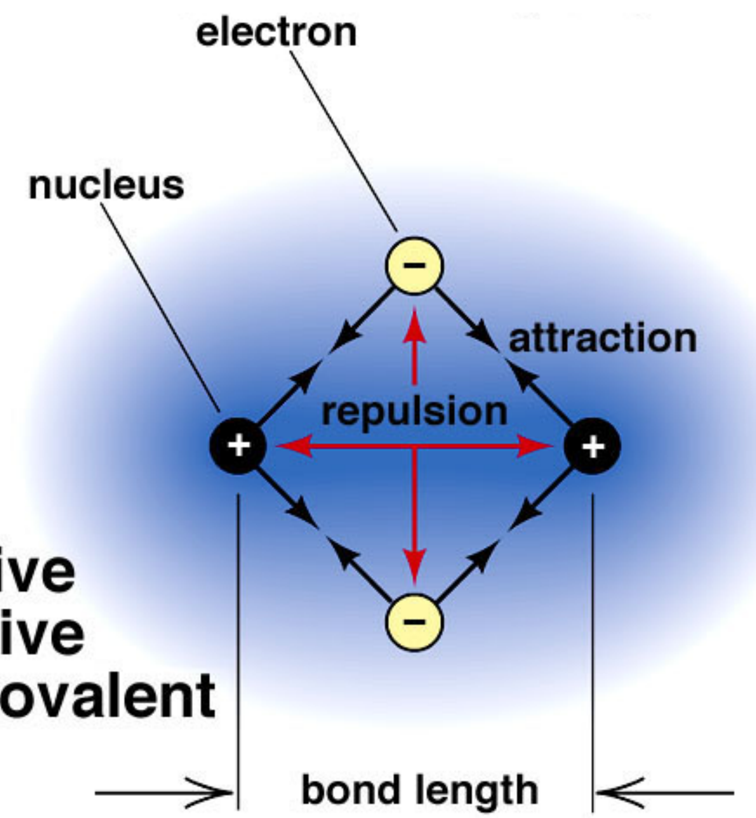
Covalent Bonding

- Covalent bonds result from the sharing of electrons between two atoms.
- Recall that covalent bonding is usually found between nonmetal atoms.
  - This is a bit oversimplified, but will work well for our purposes in this class.
- In following the octet rule, atoms share enough electrons with each other to give each eight valence electrons (or two in the case of hydrogen).
- Covalent bonds are generally not as strong as ionic bonds; still, many are relatively strong.
  - Example: Compare heating salt (ionic) and sugar (covalent).

Examples of Covalent Compounds

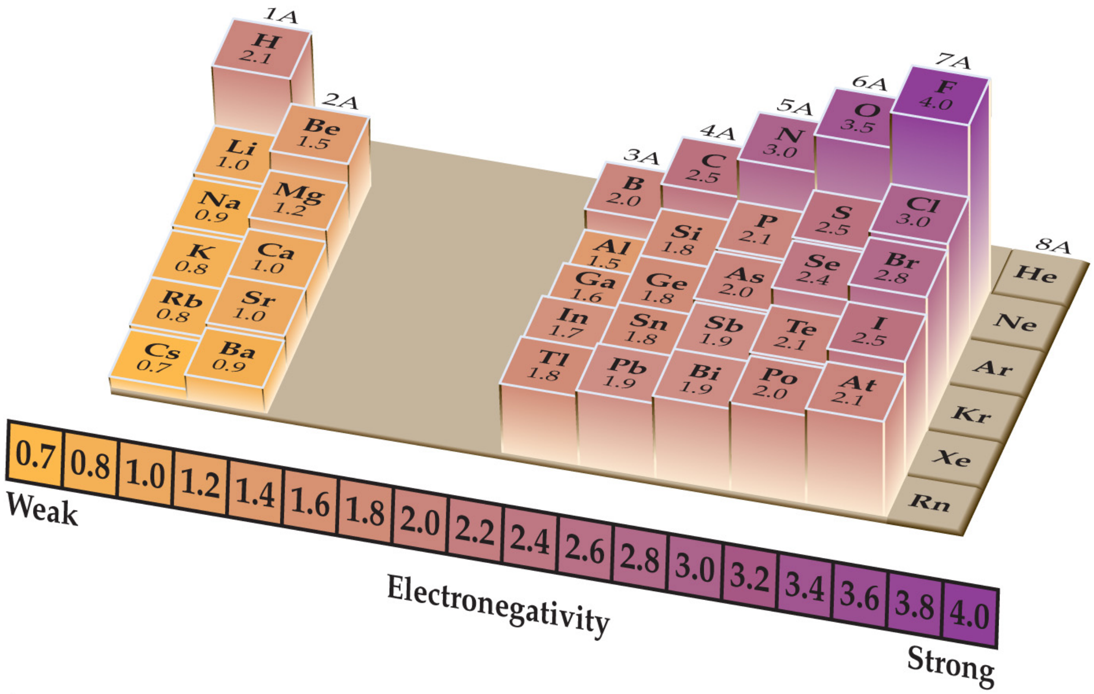
- H_2O
- $C_6H_{12}O_6$
- Cl_2 (an element)
- C_6H_6
- CO_2
- H_2S
- SO_3

The Attractive and Repulsive Forces in Covalent Bonding



Electronegativity

- The <u>electronegativity</u> of an atom indicates how strong its attraction for electrons is.
  - The greater an atom's electronegativity, the more strongly it pulls electrons toward it.
- Like the atomic radius and the ionization energy, electronegativity has a periodic trend:
  - Electronegativity increases up a group and from left to right across a period.
    - Fluorine is the most electronegative atom; in general, the closer a main group element is to fluorine on the periodic table, the more electronegative it is.
    - The noble gases have virtually no electronegativity.



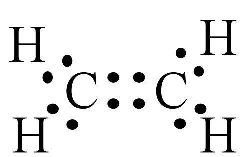
Lewis Structures

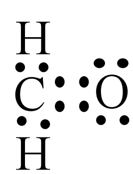
- <u>Lewis Structures</u> are simple drawings that show the covalent bonds between atoms.
- As in Lewis dot diagrams, electrons are represented by dots.
  - Since two electrons are required to make a bond, a pair of electrons between two atoms indicates a bond.

Multiple Bonds

- Remember, atoms bond in order to gain an octet (or duet for hydrogen).
- In order to do this, atoms can also share more than one pair of electrons, up to a maximum of three pairs.
  - Sharing one pair of electrons forms a <u>single bond</u>.
  - Sharing two pairs forms a <u>double bond</u>.
  - Sharing three pairs forms a <u>triple bond</u>.
  - There are not quadruple bonds!

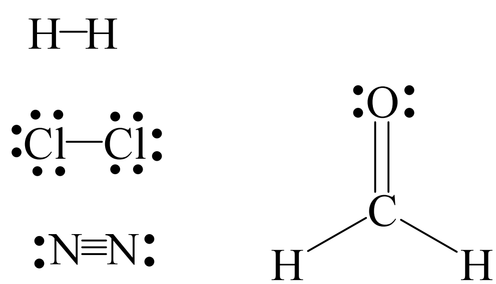
Examples of Multiple Bonds





More on Lewis Structures

- It is much simpler when drawing Lewis structures to represent electron pairs as lines rather than dots.
  - However, always keep in mind that the lines stand for electron pairs!

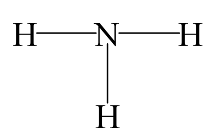


Drawing Lewis Structures

There are several steps involved in taking a formula and converting it to a Lewis structure; just keep in mind the goals set out by the octet and duet rules.

1. Draw a simple "skeleton" of the molecule, showing which atoms are connected to which. If there is one "central" atom (the one surrounded by the others) it is usually the least electronegative.

   <u>Note:</u> Hydrogen is never a central atom!



Drawing Lewis Structures

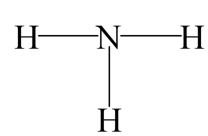
2. Add up the total number of valence electrons in the formula.
   Ex. NH_3 has $5 + (3\times1)=8$ v.e.

   Note that if the molecule is an ion, each negative charge adds one electron to this count, and each positive charge takes one away.

Drawing Lewis Structures

Figure out how many electrons you have left. Remember that each bond stands for two electrons, so subtract two from the total number of valence electrons for every bond you drew in the previous step.

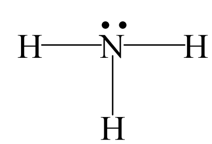
$8 - 6 = 2$ electrons left



Drawing Lewis Structures

3. Give enough electron pairs to each atom in the structure to give each atom (except hydrogen) an octet, using the following guidelines:
   -Electrons go to the most electronegative atoms first. (These are almost always the terminal atoms)
   -You must stop adding electron pairs when you run out of electrons (from the original number you started with in step 2).

Drawing Lewis Structures



2 – 2 = 0
No electrons left!

Drawing Lewis Structures

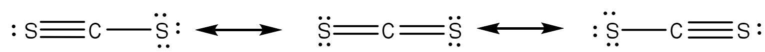
4. *This step is not always necessary:*
   If you have run out of electrons, and some atoms still need octets, change a lone pair on the *least electronegative adjacent atom* (except hydrogen) to a double bond between the two atoms. If necessary, you may need to make a triple bond by taking away another lone pair.
   Note that fluorine will not share its lone pairs.

Resonance

- Sometimes you will find that you can construct molecules with the same basic skeleton, but with electrons in different places
  - You are most likely to see this when determining double and triple bonds
- We call the different structures that can be produced <u>resonance structures</u>
- None of the resonance structures are entirely accurate representations of the molecule. The actual molecule is actually a *hybrid* of all possible structures

Resonance

- For example, consider the compound carbon disulfide
- There are three different ways of accomplishing step 4, each producing a resonance structure:



- It turns out that the middle structure is the "best" resonance structure, but the reasoning behind this is beyond the scope of this course
  - You will study this very important subject in depth in CHEM 130

Examples

Draw Lewis Structures for each of the following molecules:

CH_4

H_2O

HCN

NO_3^-

N_2H_2

C_2H_2

Exceptions to the Octet Rule

- Boron and beryllium often will not be able to gain a complete octet.
  - For example, consider BH_3 and BF_3
- Atoms in period 3 and below only may exceed the octet rule for reasons we will not consider here. You will often see this in cases where the central atom is P, S, Cl, Br, or I; others exist as well.
  - For example, consider PCl_5, SF_6,and SO_3.

Common Covalent Bonding Patterns

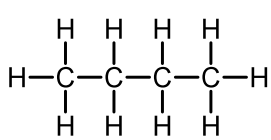
- Many elements tend to form covalent bonds in a predictable fashion
- For example,
  - hydrogen always makes a single bond
  - carbon almost always has a total of four bonds, and very rarely possesses lone pairs
  - halogen atoms frequently form only a single covalent bond and possess three lone pairs
- These results are summarized on the following table

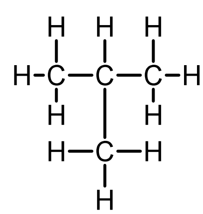
Common Covalent Bonding Patterns

Element	# Bonds	# lone pairs
H	1	0
C	4	0
N, P	3	1
O, S, Se	2	2
F, Cl, Br, I	1	3

Isomers

- It is often the case that more than one reasonable structure can be drawn for a given molecular formula
- Consider the formula C_4H_{10} :





- Isomers are compounds which share the same molecular formula, but which have different bonding connections in their atoms

Isomers

Example

Draw the three isomers which have formula C_5H_{12} . Follow the common bonding patterns.

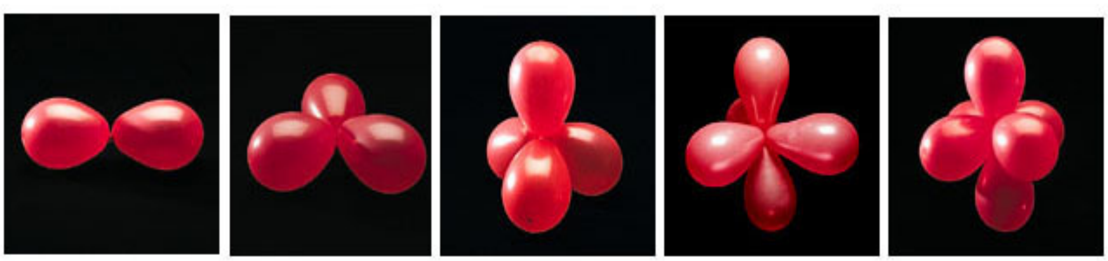
Shapes of Molecules

- From Lewis structures we can usually figure out the three-dimensional structure of simple molecules.
- VSEPR theory (stands for Valence Shell Electron Pair Repulsion) helps us to understand the shapes that molecules take.
- According to VSEPR, electron pairs move as far away from each other (in three dimensions) as possible.
  - Remember that electrons all have negative charge, so they repel one another.

The Electron Geometries of Molecules

- Depending on the number of attached atoms and lone pairs, an electron geometry – describing the position of bonded atoms and lone pairs about a given atom – can be assigned to an atom in a molecule.
  - Linear: 2 electron-pair (EP) groups
  - Trigonal Planar: 3 EP groups
  - Tetrahedral: 4 EP groups
  - Trigonal Bipyramidal: 5 EP groups
  - Octahedral: 6 EP groups

A Balloon Analogy for the Mutual Repulsion of Electron Groups



Assigning Shapes to Molecules

- A shape is assigned to each central atom in a molecule.
  - To be a central atom, an atom must have two or more atoms bonded to it.
- The number of atoms bonded to the central atom is added up. Call this *m*.
  - Careful! Add the number of *atoms*, not the number of bonds!
- The number of lone pairs on the central atoms is added up. Call this *n*.

Assigning Shapes to Molecules

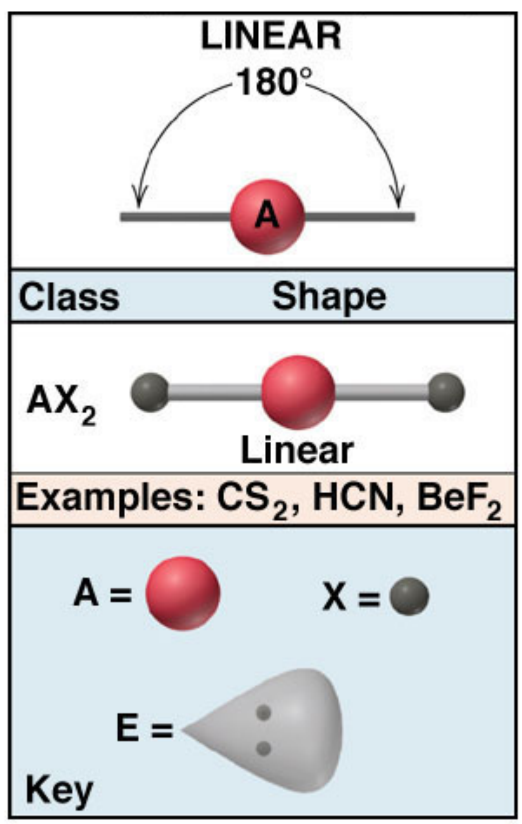
- Take these numbers and put them in the following formula:

  AX_mE_n
- The A in this formula stands for the central atom, the X for the attached atoms, and the E for the lone pairs.
- From this code we can name the shape of the molecule.

Linear

- AX_2 is called the *linear* shape.
- The bond angle (atoms between the three bonds) in this shape is 180°.

The Single Molecular Shape of the Linear Electron-Group Arrangement

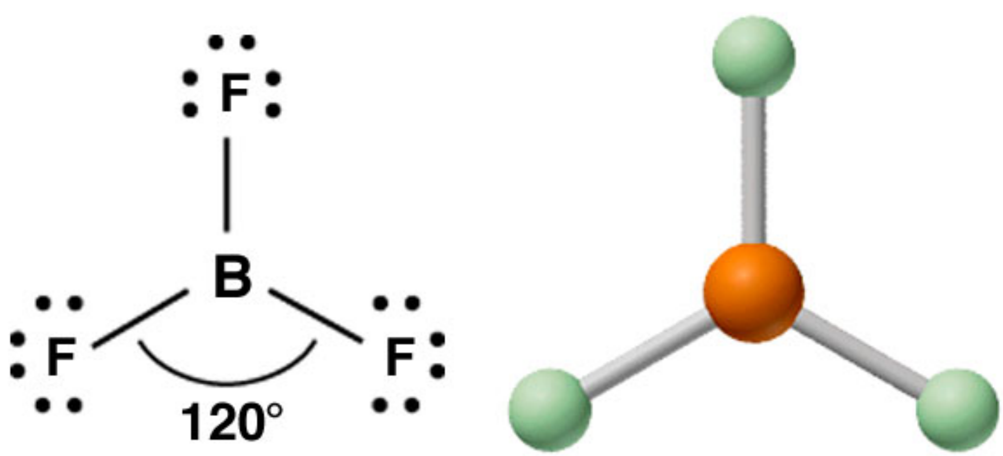


Trigonal Planar and Bent/V-Shaped

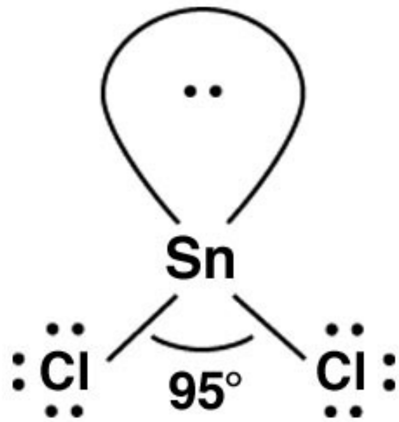
- The shape associated with AX_3 is *trigonal planar* because it resembles a flat triangle.
- The shape associated with AX_2E_1 is called *bent/V-shaped*.
  - When naming a shape we pretend to only "see" the atoms, not the lone pairs. That is why we have two different shape names for the same geometry.
- Both of these shapes have bond angles of approximately 120°, which may vary slightly in some molecules.

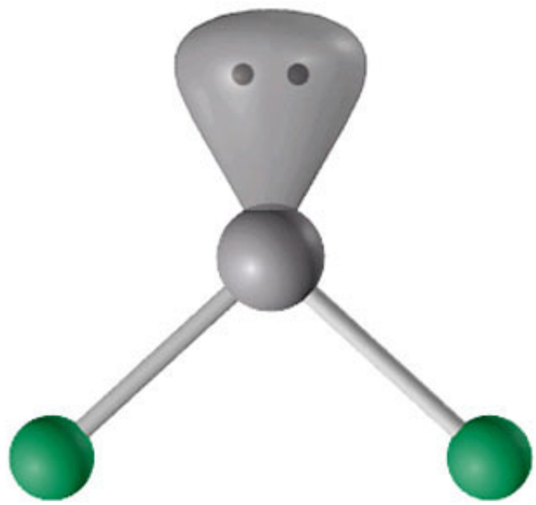
Trigonal Planar Arrangement of BF_3

F—B—F angle is 120°:



Bent (V shaped) Arrangement of $SnCl_2$

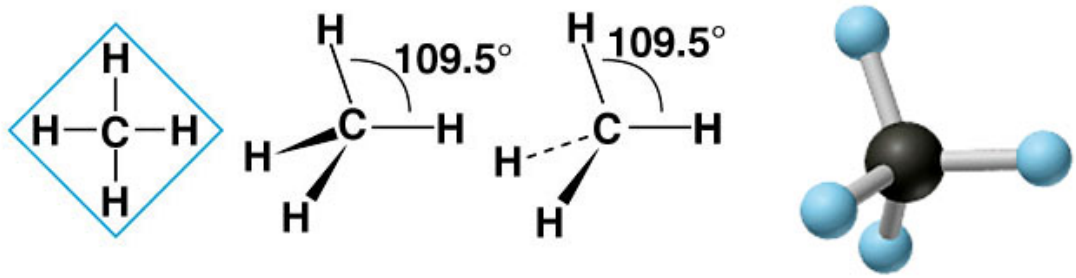




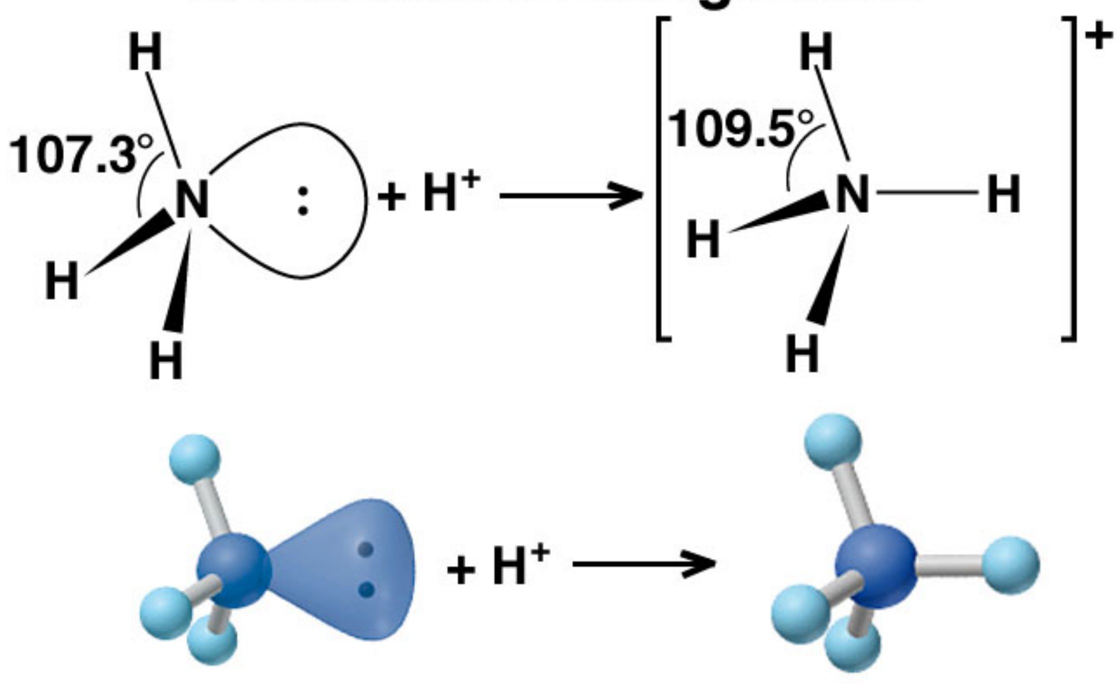
Tetrahedral Geometries

- The shape associated with AX_4 is called *tetrahedral*, with all atoms at the four points of a pyramid.
- Replacing an atom with an electron pair gives AX_3E_1, which is called *trigonal pyramidal*.
- Changing another atom to a lone pair gives the the AX_2E_2 code, which is called the *bent/V-shaped* shape.
  - This is the same shape name as we saw earlier, but it has a different geometry and different bond angles.
- The bond angles associated with these three are approximately 109.5°.

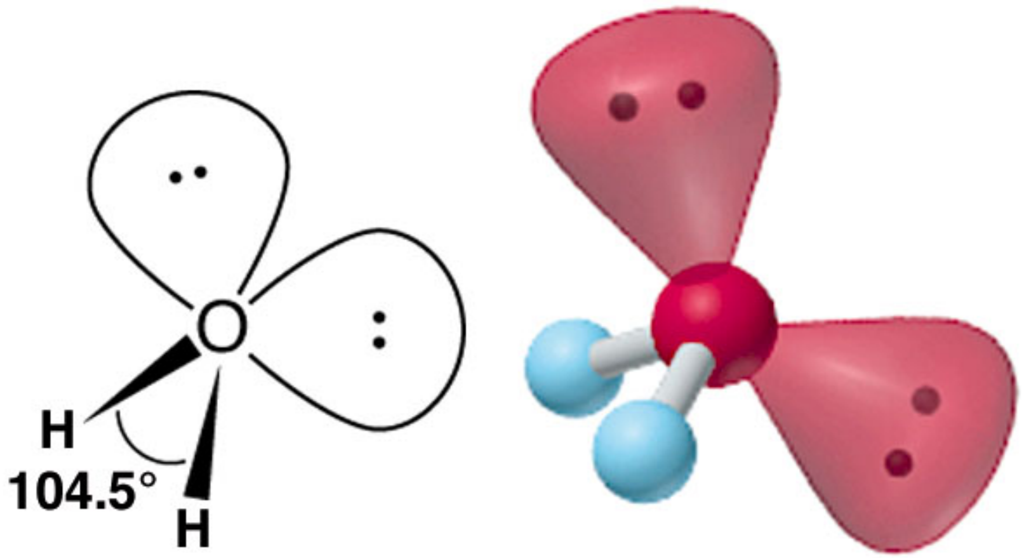
Tetrahedral Arrangement of Methane



Trigonal Pyramidal Shape of Tetrahedral Arrangement



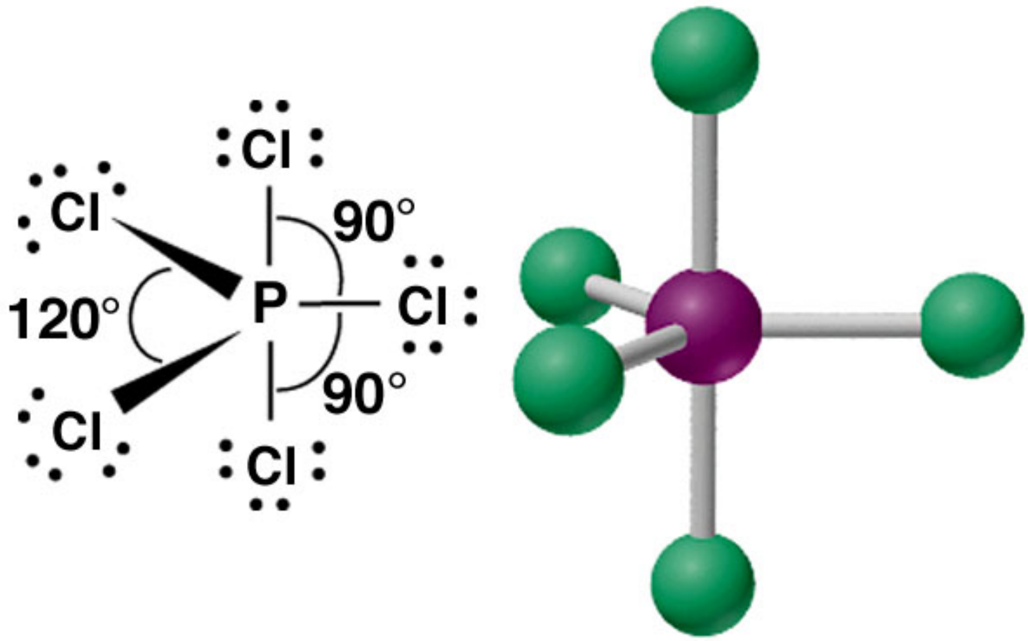
Bent or V Shaped Tetrahedral Arrangement



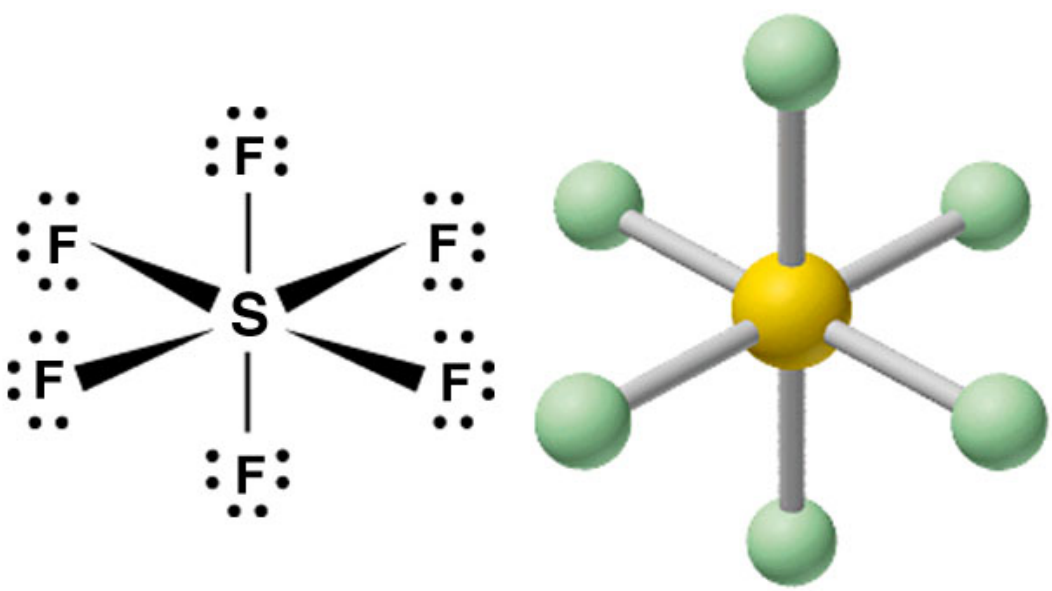
Trigonal Bipyramidal and Octahedral Shapes

- The AX_5 shape is called *trigonal bipyramidal*, and resembles two pyramids sharing a common face.
  - The bond angles associated with this shape are both 90° and 120°, depending on where you look.
- The AX_6 shape is called *octahedral*.
  - The bond angles for this shape are 90°.
- Other shapes within these geometries are not included in this course, but they do exist.

Trigonal Bipyramidal Arrangement of PCl_5



Octahedral Arrangement of SF_6



Polarity and Dipole Moment

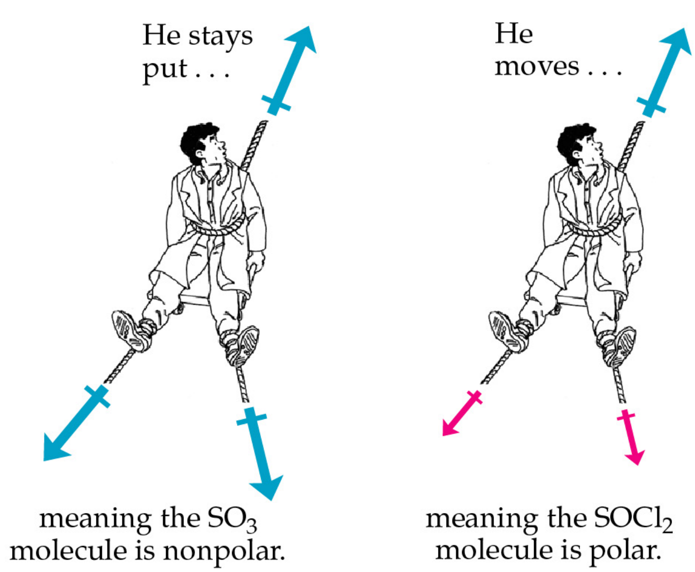
- If two atoms which are covalently bonded have substantially different electronegativity values, then the bond is said to be polar covalent.
  - The electrons are not shared equally in the bond.
  - The electrons will tend to stay closer to the more electronegative atom.
- The molecule *might* have a dipole moment, which is shown by drawing a special arrow pointing towards the more electronegative atom.

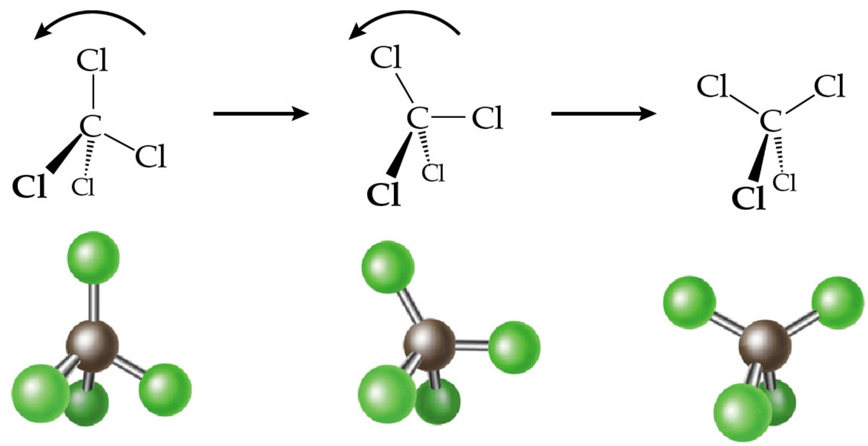
Dipole Moments

- Molecules which have fairly electronegative atoms may have a dipole moment.
- Since electrons are drawn towards more electronegative atoms, a "partial negative charge" (δ-) develops in this region of the molecule, and a partial positive charge (δ+) develops on the other side.
- Consider CH_3F.

Dipole Moments

- In thinking about dipole moments, we have to consider the three-dimensional structure of the molecule.
- Dipoles can cancel each other out, if the same type of bonds are oriented in opposite directions.

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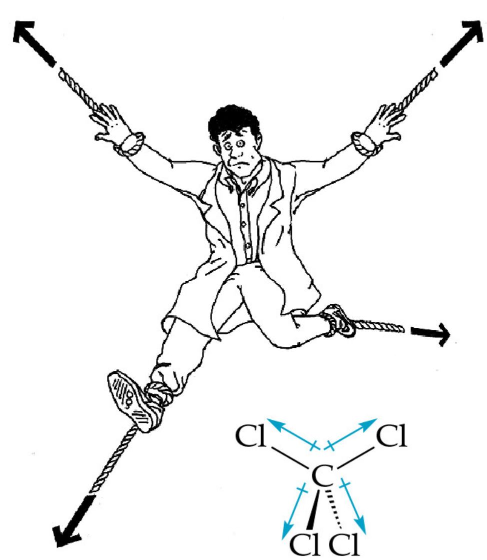
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Example

- Example: Which of these molecules have dipole moments? Which, if any, have *polar bonds* but no dipole moment?

CCl_4 NH_3 H_2O CO_2