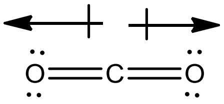
# Molecular Models:

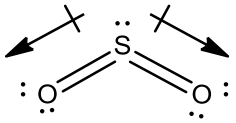
## The shape of simple molecules and ions

### Background

The shape of a molecule is very important when investigating its properties and reactivity. For example, compare $CO_2$ and $SO_2$. Carbon dioxide is a linear molecule while sulfur dioxide is a bent molecule. Both molecules contain polar bonds (see bond dipoles on the Lewis structures below), but carbon dioxide is a nonpolar molecule while sulfur dioxide is a polar molecule.

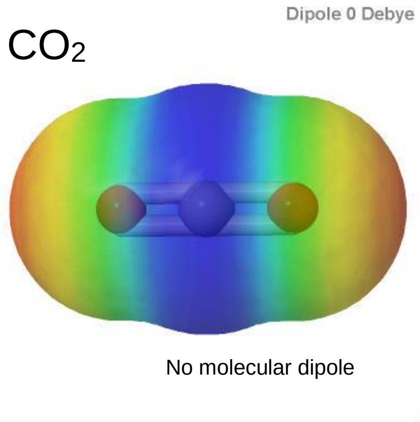


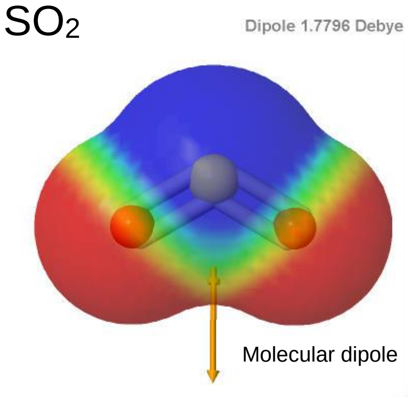
carbon dioxide
a **nonpolar** molecule
molecular dipole: 0 Debye



sulfur dioxide
a **polar** molecule
molecular dipole: 1.78 Debye

Electrostatic potential diagrams (below) show areas of lower to higher electron density as a continuum of colors, from blue (lower electron density) to red (higher electron density). $SO_2$ (on the right) has an asymmetric charge distribution, resulting in a net dipole moment (yellow arrow) compared to $CO_2$ (on the left).





Polarity determines many physical and chemical properties of molecules, and how molecules interact with other molecules. Therefore, you can see why chemists are extremely interested in predicting the shape of the molecules they are working on based on Lewis structures.

In this lab activity, we will use Lewis dot structures and the Valence-Shell Electron-Pair Repulsion (VSEPR) theory to predict the shape of small molecules and polyatomic ions. We will use the molecular kits to build 3-D models of these compounds.

### Molecular Models

You will use a model set that consists of balls representing the nucleus and the core electrons of an atom and sticks representing the bonds between the atoms. (Real atoms are nothing like this but we need simplified models to aid in our understanding of chemical bonding.) In order to predict and build the model of a molecule or an ion, it is convenient to proceed in a systematic way.

## The procedural overview for this lab activity on molecular models:

1. Calculate the number of valence electrons (ve) of the molecule. Remember to adjust the number of valence electrons if the molecule is an anion (add ve) or a cation (subtract ve).
2. Draw the corresponding Lewis structure. (See directions/examples below.)
3. Use your knowledge of the VSEPR theory to determine the electron geometry and the molecular geometry of the molecule (ion). (See directions/examples below.)
4. **Build a model of the molecule (ion)** using the balls that correspond to the different atoms. In cases involving double bonds don't forget to use the longer, flexible sticks in your model.
5. Determine whether the molecule (ion) is polar or nonpolar and indicate the approximate location of the dipole moment on the 3D sketch of the molecule (ion) in the last column of the table. (See directions/examples below.)
6. Predict whether the structure has resonance forms. (See directions/examples below.)

What follows is a very brief reminder of how to draw Lewis structures and how to determine VSEPR geometries and resonance structures. If you need a more detailed explanation, check the supplemental document on the Chem 161 webpage or your textbook.

## 5 simple steps to draw a Lewis structure:

1. Determine the total number of valence electrons based on the chemical formula.

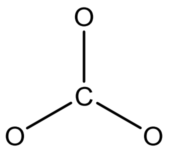
NOTE: For a polyatomic ion, add valence electrons (for anions) and subtract valence electrons (for cations).

2. Determine how atoms are connected. Identify the central atom(s) and terminal atoms.
3. Draw a skeletal structure by joining atoms with single bonds.
4. Distribute the remaining electrons in pairs by completing the octets around the terminal atoms and then assigning the remaining electrons (if any) to the central atoms.
5. If there are too few electrons, convert lone pairs from terminal atoms to form multiple bonds with central atoms.*

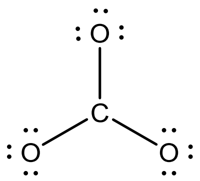
*Some exceptions: 3rd period or heavier elements may have 10 or 12 electrons around them (expanded valence shells). Atoms such as Be, B and Al may have 6 electrons around them. In species with an odd number of electrons the least electronegative atom carries the odd electron.

*Example*: Using the steps above, draw the Lewis structure for carbonate ion, $CO_3^{2-}$.

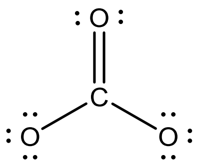
Step 1 – Total number of valence electrons = 4 + (3 x 6) + 2 = 24 valence electrons
Step 2 – Central atom is carbon with three oxygens bonded to it.
Step 3 – Skeletal structure with single bonds only (see below).
Step 4 – Distribute remaining valence electrons around terminal atoms (oxygen in this case) and remaining electrons go to the central atom (in this case there aren't any extras for the central atom).
Step 5 – There are too few electrons, so one double bond is required to fulfill the octet rule for carbon.



step 3



step 4



step 5

Now we need formal charges!

## To determine formal charges:

We can calculate the formal charge (FC) on the different atoms as follows:

**FC = (# of valence electrons in an atom) – (½ # of bonding $e^-$) – (# of non-bonding $e^-$)**

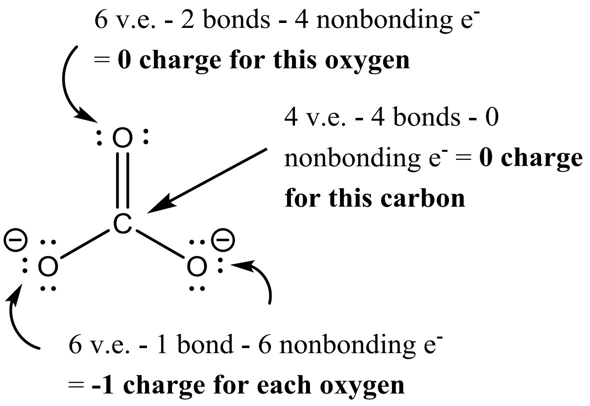
Note: The formal charge is the charge a bonded atom would have if its bonding electrons were shared equally. It is a computed value and completely ignores the effect of electronegativity. A simple mnemonic rule to remember how to calculate formal charge is the following one:

**FC = (# of valence e- in an atom) – (# of sticks) – (# of stones)**

Double check: Sum of formal charges on all atoms of an ion is equal to the charge on the ion. The most important resonance structures have complete octets and low or no formal charges.

- Sum of formal charges on all atoms of a molecule is zero.
- When charges are unavoidable, then the more important resonance structures have like charges separated, unlike charges close and negative charges on the more electronegative atoms (positive charges on more electropositive atoms).

*Example*: Go back to the previous example of carbonate (on the previous page). Determine the formal charges on all atoms in carbonate, $CO_3^{2-}$.



6 v.e. - 2 bonds - 4 nonbonding $e^-$
= **0 charge for this oxygen**

4 v.e. - 4 bonds - 0
nonbonding $e^-$ = **0 charge**
**for this carbon**

6 v.e. - 1 bond - 6 nonbonding $e^-$
= **-1 charge for each oxygen**

## To draw resonance structures:

When more than one Lewis dot structure can be written for a molecule or a polyatomic ion, the phenomenon of resonance occurs. Take the example of the carbonate ion, $CO_3^{2-}$. We can write the following three Lewis dot structures for it. (This is the answer to the examples above for practice – did you get it right?)

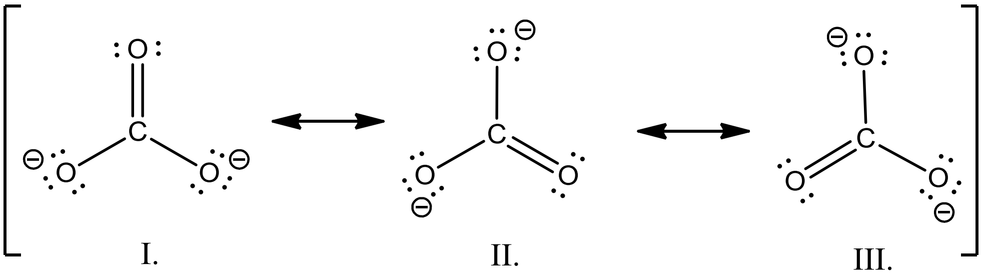


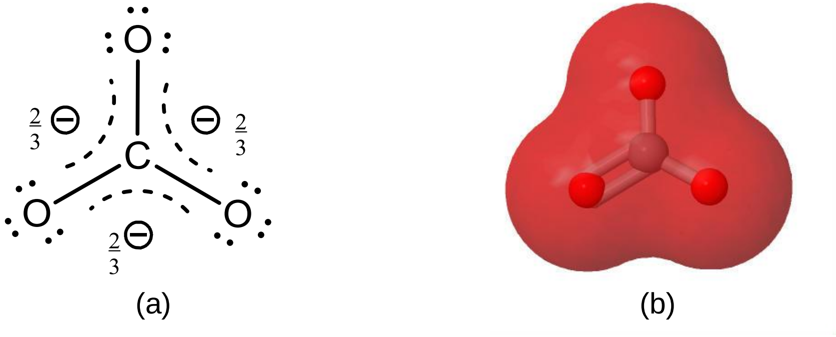
Figure 1. Three equivalent, but different, resonance structures of the carbonate ion.

Structures I, II, and III are equivalent. All are correct Lewis dot structures, i.e. they obey the octet rule if they are second period elements. But each structure is different from the other in terms of which oxygens are charged, or where the double bond is located. (These are not derived by simply rotating the molecule.)

When drawing resonance structures keep in mind:

- Resonance structures may exist for molecules with multiple bonds (double or triple bonds)
- The position of atoms stays fixed, and only the unshared electrons or electrons in a multiple bond or lone pair are moved. (This is in contrast to isomers, in which atoms may be in a different arrangement.)
- The more the number of resonance structures you can write for a species, the more stable it is.
- Electrons or molecules are not “flipping”. These structures are snapshots of the electron distribution in a molecule.

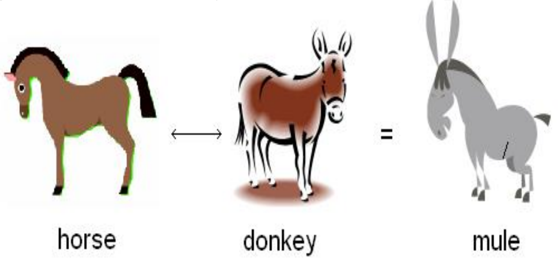
In reality, the true nature of a molecule or ion is a hybrid of all contributing resonance structures. For example, carbonate is best described as a resonance hybrid of I, II, and III. It is often difficult to represent the resonance hybrid, but one can imagine the resonance structures to “merge” together. For example, to merge I, II, and III in Figure 1 above, the two negative charges must be distributed over all oxygens .There is a partial double bond character to all bonds in between carbon atom and oxygen atom. One possible way to depict the resonance hybrid is as such:



(a) (b)

Figure 2. (a) This resonance hybrid of carbonate, $CO_3^{2-}$, shows the even distribution of electrons which is predicted by merging the three resonance structures in Figure 1. Each bond has some double bond character (1.33), and the distribution of electrons is symmetrical, unlike in each of the structures I, II or III. (b) The charge distribution is even (2/3 negative charge on each side), visually represented by the uniform color of the electrostatic potential map (red).

A good analogy for the resonance hybrid: How do we describe a mule, the cross between a female horse and a male donkey? Do we say that the mule is 50% of the time a donkey and 50% of the time a horse? NO! We can describe the mule with some of the characteristics of each parent. The mule has a thick short head and long ears like a donkey but its neck is shaped like a horse’s neck.



Thus, resonance structures show characteristics of a molecule (like the horse and the donkey in the example above), but the resonance hybrid is the “true molecule” which is the combination of all these characteristics simultaneously (the mule).

## Using VSEPR to determine electron geometry and molecular shape:

The central idea behind this method is that electron pairs in the valence shell try to get as far away from all other electron pairs in the valence shell (including non-bonding pairs)

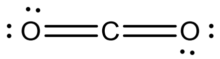
1. Determine which element is the central atom.
2. Determine how many surrounding substituents that central atom has.
By substituents we mean not only atoms but also non-bonding pairs of electrons.
3. Depending on the number of substituents (2, 3, 4, 5, or 6) we will have different 3D geometries so that the substituents are all as far apart as possible.
4. Based on the geometries and the number of lone pairs, you can determine the molecular shape.
5. Based on all the information above, hybridization of the central atom can be determined from the following table.

**Table 1. The number of electron groups on the central atom can be related to bond angles and electron geometry of molecules as given below:**

| No. of electron groups | *AXE class | Bond angle | Electron geometry / Molecular Shape | Hybridization |
|---|---|---|---|---|
| 2 | $AX_2E_0$ | 180° | Linear / linear | sp |
| 3 | $AX_3E_0$ | 120° | Trigonal planar / trigonal planar | $sp^2$ |
| 3 | $AX_2E_1$ | 120° | Trigonal planar / bent | $sp^2$ |
| 4 | $AX_4E_0$ | 109.5° | Tetrahedral / tetrahedral | $sp^3$ |
| 4 | $AX_3E_1$ | 109.5° | Tetrahedral / trigonal pyramidal | $sp^3$ |
| 4 | $AX_2E_2$ | 109.5° | Tetrahedral / bent | $sp^3$ |
| 5 | $AX_5E_0$ | 120°,<br>90 | Trigonal bipyramid / trigonal bipyramidal | $sp^3d$ |
| 5 | $AX_4E_1$ | 120°,<br>90° | Trigonal bipyramid / see-saw | $sp^3d$ |
| 5 | $AX_3E_2$ | 90° | Trigonal bipyramid / T-shape | $sp^3d$ |
| 5 | $AX_2E_3$ | 180° | Trigonal bipyramid / linear | $sp^3d$ |
| 6 | $AX_6E_0$ | 90° | Octahedral / octahedral | $sp^3d^2$ |
| 6 | $AX_5E_1$ | 90° | Octahedral / square pyramidal | $sp^3d^2$ |
| 6 | $AX_4E_2$ | 90° | Octahedral / square planar | $sp^3d^2$ |

**In AXE notation, A = central atom, X = atoms attached to A, and E is the number of lone pairs on A.*

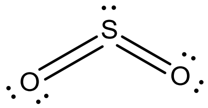
*Example: Determine the bond angle, geometry, shape and hybridization of* $CO_2$



carbon dioxide

There are two substituents (oxygens) attached to the central atom, carbon. The AXE class is $AX_2E_0$, since there are two oxygens and no lone pairs on the central atom. To be as far apart as possible, the oxygens will be 180° apart, which corresponds to a **linear** electron geometry and **linear** molecular shape. The carbon is sp hybridized (Table 1).

*Example: Determine the bond angle, geometry, shape and hybridization of* $SO_2$



sulfur dioxide

There are three substituents (two oxygens plus a lone pair) attached to the central atom. The AXE class is $AX_2E_1$ . Three groups are approx. 120° apart, which corresponds to a trigonal planar geometry. Since one of these substituents is a lone pair, the shape is bent. The sulfur is $sp^2$ hybridized. (Table 1).

## To determine the polarity of a molecule (ion):

Remember that polarity arises from:
1) Polar bonds = Differences in the electronegativities of atoms which share a covalent bond.
2) Shape = Molecules are polar if their dipole moments do not cancel. It is possible for a molecule with polar bonds to be a non-polar molecule if its shape is such that the dipoles cancel (usually highly symmetrical molecules).

**Differences between polar and nonpolar molecules**

| Polar Molecules | Non Polar Molecules |
|---|---|
| Bonds MUST be polar. | If bonds are non-polar, molecule is nonpolar. |
| If bond polarities do not cancel each other out, molecule is polar. | If bonds are polar and bond polarities cancel each other out, molecule is non polar. |
| There are one or more lone pairs on the central atom ($E \neq 0$).<br>In general $AX_2E_1$, $AX_3E_1$, $AX_2E_2$, $AX_4E_1$, $AX_3E_2$, $AX_5E_1$ are polar. | There is no lone pair on the central atom ($E=0$).<br>In general, $AX_2E_0$, $AX_3E_0$, $AX_4E_0$, $AX_5E_0$, $AX_6E_0$ are nonpolar. |

*Example: Determine the polarity of $CO_2$ and $SO_2$.*
Both molecules contain polar bonds (check the electronegativity values of C vs. O, and S vs. O). $CO_2$ is linear so its dipoles cancel. However, since $SO_2$ is bent, the dipoles do not cancel and the molecule is polar.

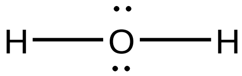
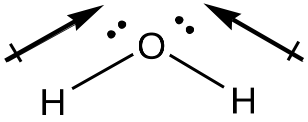
Polar compounds dissolve in polar solvents such as water; non-polar compounds dissolve in non-polar solvents like $CCl_4$. This idea will be emphasized more in the chapter on solutions.

Polar compounds have partial positive and negative charges so they attract one another strongly. This causes their melting points and boiling points to be higher than the nonpolar compounds. This idea will be emphasized more in the study of intermolecular forces.

Name_______________________________________ Date ___________
Lab Partner’s Name_________________________ Section __________

# REPORT SHEETS

For polar bonds, draw in the dipoles. See the example below.

| Molecule | # of Valence electrons | Lewis Structure | Electron geometry | Bond Angle | 3D structure and Molecular Geometry | Polar or Nonpolar | Hybridization (of the central atom) |
|---|---|---|---|---|---|---|---|
| $H_2O$ | 8 |  | Tetrahedral | 104.5° |  <br>Bent | Polar | $sp^3$ (O) |
| HF | | | | | | | |
| $N_2$ | | | | | | | |
| $NH_3$ | | | | | | | |

| Molecule | # of Valence electrons | Lewis Structure | Electron geometry | Bond Angle | 3D structure and Molecular Geometry | Polar or Nonpolar | Hybridization (of each central atom) |
|---|---|---|---|---|---|---|---|
| $CH_3OH$ (there is more than one central atom) | | | | | | | |
| $H_2O_2$ (there is more than one central atom) | | | | | | | |
| $C_2H_4$ (there is more than one central atom) | | | | | | | |
| $C_2H_2$ (there is more than one central atom) | | | | | | | |

| Molecule | # of Valence electrons | Lewis Structure | Electron geometry | Bond Angle | 3D structure and Molecular Geometry | Polar or Nonpolar | Hybridization |
|---|---|---|---|---|---|---|---|
| $PCl_5$ | | | | | | | |
| $BCl_3$ | | | | | | | |
| $SF_4$ | | | | | | | |
| $ICl_5$ | | | | | | | |

| Molecule | # of Valence electrons | Lewis Structure | Electron geometry | Bond Angle | 3D structure and Molecular Geometry | Polar or Nonpolar | Hybridization |
|---|---|---|---|---|---|---|---|
| $SF_6$ | | | | | | | |
| $ClF_3$ | | | | | | | |
| $NH_4^+$ | | | | | | | |
| $NO_2$ | | | | | | | |

<table>
<tr><th>Molecule</th><th># of Valence electrons</th><th>Lewis Structure</th><th>Electron geometry</th><th>Bond Angle</th><th>3D structure and Molecular Geometry</th><th>Polar or Nonpolar</th><th>Hybridization</th></tr>
<tr><td>$SeO_2$</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="8"><b>Draw at least three possible resonance structures for the molecule above. Assign formal charges!</b></td></tr>
<tr><td>$S\underline{C}N^{-1}$<br><b>(carbon is the central atom)</b></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="8"><b>Draw at least three possible resonance structures for the molecule above. Assign formal charges!</b></td></tr>
</table>

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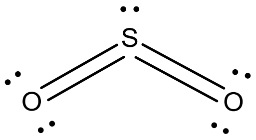
<tr><td>Molecule</td><td># of Valence electrons</td><td>Lewis Structure</td><td>Electron geometry</td><td>Bond Angle</td><td>3D structure and Molecular Geometry</td><td>Polar or Nonpolar</td><td>Hybridization</td></tr>
<tr><td>$NO_3^{-1}$</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="8"><b>Draw all possible resonance structures for the molecule above. Assign formal charges!</b></td></tr>
<tr><td>$HNO_3$</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="8"><b>Draw all possible resonance structures for the molecule above. Assign formal charges!</b></td></tr>
</table>

Name________________________________________ Section ___________

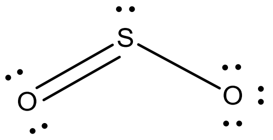
# Pre-lab Assignment—Complete BEFORE lab!
## Molecular Models

1. (a) State the *octet rule* in your own words. (b) Describe two exceptions to the octet rule.

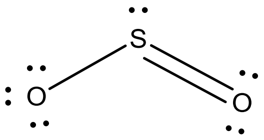
2. Verify the three possible resonance structures for sulfur dioxide, $SO_2$. Assign formal charges to all atoms in these structures.



I



II



III

The first page of this lab experiment shows the best structure, I. Explain why this is the best structure of the three.

________________________________________________________________________

________________________________________________________________________

3. For the pair that you chose above, circle the best resonance structure. **Explain** your choice:

________________________________________________________________________

________________________________________________________________________

4. Draw two resonance structures for **each** of the following polyatomic ions (for four total):

| **$SO_3^{2-}$** | **$CH_3COO^{1-}$** (both carbons are central atoms) |
|---|---|
|  |  |

5. Calculate and display the formal charge for all atoms in every structure drawn above. Verify that adding up the atomic formal charges within the ion results in its overall net charge.