## 2.5 Lewis Diagrams

Essential knowledge statement from the AP Chemistry CED:

- Lewis diagrams can be constructed according to an established set of principles.

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Valence electrons were mentioned in Unit 1 (Atomic Structure and Properties) in Topic 1.8 (Valence Electrons and Ionic Compounds). Groups 1, 2, and 13–18 are known as the **main-group elements**. The number of valence electrons for a main-group element is based on the pattern of electron configurations.

The term **Lewis symbol** (or Lewis dot symbol) refers to a method used to represent the valence electrons of an atom. They are named after the American chemist Gilbert N. Lewis (1875-1946), who proposed that covalent bonds are formed when electron pairs are shared between atoms. Lewis symbols for the Period 2 elements are shown in the table below.

| Electron Configuration | $1s^2 2s^1$ | $1s^2 2s^2$ | $1s^2 2s^2 2p^1$ | $1s^2 2s^2 2p^2$ | $1s^2 2s^2 2p^3$ | $1s^2 2s^2 2p^4$ | $1s^2 2s^2 2p^5$ | $1s^2 2s^2 2p^6$ |
|---|---|---|---|---|---|---|---|---|
| Valence Electrons | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Lewis diagram | •Li | •Be• | •B• | •C• | •N• | •O: | •F: | :Ne: |

**Lewis diagrams** (or Lewis electron-dot diagrams) show how atoms are connected to each other in molecules and polyatomic ions. The **octet rule** states that an atom, usually a nonmetal in Groups 14–17, tends to form covalent bonds in such a way that it is surrounded by a total of eight valence electrons. *Hydrogen (H) does not obey the octet rule.* A hydrogen atom only forms one single bond, giving it access to a total of two valence electrons.

The single dots featured in the Lewis symbols for carbon (C), nitrogen (N), oxygen (O) and fluorine (F) represent the **bonding capacity**. This is the number of covalent bonds that the atom *typically* forms in order to complete its octet. Note that the concept of bonding capacity is merely a guideline. In certain molecules or polyatomic ions, an atom may form a number of bonds that is either less than or greater than its normal bonding capacity.

- A single bond is a pair of shared electrons, also known as a bonding pair of electrons.
- A single bond can be represented by two dots (X:X). It is usually represented by a dash (X–X).
- Two pairs of electrons are shared in a double bond (X=X).
- Three pairs of electrons are shared in a triple bond (X≡X).
- An unshared pair of electrons is also known as a lone pair or a nonbonding pair of electrons.
- Lewis diagrams may include both bonding electrons and nonbonding electrons.

1. Use a separate sheet of paper to draw the correct Lewis electron dot structures for each of the following.

   **For now, you can ignore the geometry (shapes) of these molecules and ions. That topic is important, but it will be covered in Topic 2.7 (VSEPR and Bond Hybridization)**

| | | | | | |
|---|---|---|---|---|---|
| $CH_4$ | $NH_3$ | $H_2O$ | $HF$ | $CH_2F_2$ | $H_2O_2$ |
| $CF_4$ | $NF_3$ | $OF_2$ | $F_2$ | $C_2H_5F$ | $C_2H_5OH$ |
| $H_3O^+$ | $NH_4^+$ | $ClO^-$ | $ClO_2^-$ | $SO_3^{2-}$ | $SO_4^{2-}$ |

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**Procedure for drawing a Lewis diagram**

**Step 1: Count the total number of valence electrons.**
- For a neutral molecule, add up the valence electrons for all of the atoms in the molecule.
- For a polyatomic ion, add up the valence electrons for all of the atoms and then add electrons (for negative charges) or subtract electrons (for positive charges), based on the overall charge of the ion.

**Step 2: Use single bonds to connect the atoms, forming a skeletal structure of the molecule or ion.**
- A general rule is that the central atom is the one that tends to form the most bonds or the one that has the lowest electronegativity value.
- If one atom A is different than the rest of the atoms in the formula (e.g., a compound with a formula such as $AX_2$, $AX_3$, $AX_4$, etc.), then atom A will be the central atom.
- On the AP Chemistry exam, students are often provided with the skeletal structure of the atoms. Then they are asked to complete the Lewis diagram by drawing all of the bonding and nonbonding electron pairs in the molecule or ion.
- Hydrogen (H) and fluorine (F) will never be the central atom. Each of these atoms only forms one bond. These atoms would be terminal atoms on the outer edge of the structure.
- When drawing the Lewis diagram for a polyatomic ion, draw brackets around the entire skeleton structure, and write the charge of the ion outside the brackets in the top right corner.

**Step 3: Add lone pairs of electrons around each terminal atom, in order to complete the octets for the terminal atoms.**
- Skip this step for a hydrogen atom, because a hydrogen atom only needs a single bond to complete its valence shell. A hydrogen atom will never have lone pairs on it.
- If any valence electrons (from the total determined in Step 1) remain unused, place lone pairs of electrons on the central atom until the Lewis structure contains the total number of valence electrons from Step 1.
- Some molecules and ions are hypervalent. Their Lewis structures represent exceptions to the octet rule. Adding lone pairs to the central atom of a hypervalent molecule or ion will cause it to have more than an octet.

**Step 4: If the central atom has an octet, the structure is complete. If the central atom has less than an octet, move one or more of the lone pairs from the terminal atoms toward the center, forming additional bonds until each atom has a complete octet.**

2. Use a separate sheet of paper to draw the correct Lewis electron dot structures for each of the following.

| | | | | | |
|---|---|---|---|---|---|
| $O_2$ | $N_2$ | $CO$ | $CO_2$ | $HCN$ | $CH_2O$ |
| $C_2H_4$ | $C_2H_2$ | $O_3$ | $SO_2$ | $SO_3$ | $C_3H_6$ *Do not draw a ring of C atoms. |
| $NO_3^-$ | $CO_3^{2-}$ | $CN^-$ | | | |

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**2.6 Resonance and Formal Charge**

Essential knowledge statements from the AP Chemistry CED:

- In cases where more than one equivalent Lewis structure can be constructed, resonance must be included as a refinement to the Lewis structure. In many such cases, this refinement is needed to provide qualitatively accurate predictions of molecular structure and properties.
- The octet rule and formal charge can be used as criteria for determining which of several possible valid Lewis diagrams provides the best model for predicting molecular structure and properties.
- As with any model, there are limitations to the use of the Lewis structure model, particularly in cases with an odd number of valence electrons.

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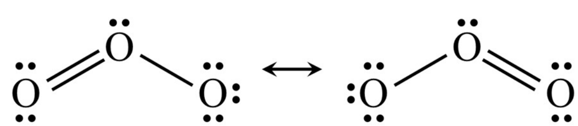

The two structures of the ozone ($O_3$) molecule shown above illustrate the concept of resonance. The bonding in the $O_3$ molecule cannot be represented with a single Lewis structure. Resonance structures exist when there is the same arrangement of atoms, but a different arrangement of the bonding and nonbonding electrons.

When you were studying Topic 2.2 (Intramolecular Force and Potential Energy), you learned that bonds with a higher order are shorter in length. Since each Lewis structure shown above contains a single bond and a double bond, you might assume that the two oxygen-oxygen bonds have different lengths, according to the information in the table below.

| Bond | Bond Length (pm) |
|---|---|
| O–O | 148 |
| O=O | 121 |

However, experimental evidence indicates that the two oxygen-oxygen bonds in $O_3$ have the same length (128 pm). Therefore neither of the two Lewis structures shown above is an accurate representation of the bonding in the $O_3$ molecule.

When more than one resonance structure can be drawn for a substance, the actual structure is considered to be a hybrid or an average of the resonance structures. The electrons are said to be **delocalized**, or spread out, instead of being localized in a particular bond.

Even though a double-headed arrow is drawn in between the resonance structures, the Lewis structures are NOT being interconverted back and forth. Instead, the actual structure is a hybrid or an average of the Lewis structures.

The bond order of the oxygen-oxygen bonds in $O_3$ is equal to 1.5. This value represents the average of a single bond (bond order = 1) and a double bond (bond order = 2).

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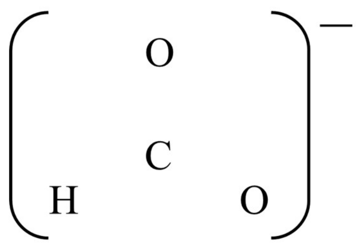
3. The skeleton structure of the methanoate ion, $HCO_2^-$ is shown below.

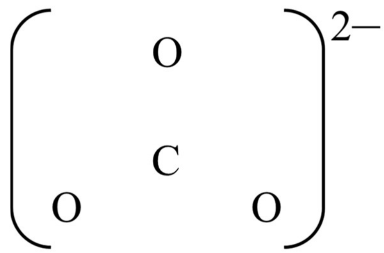



(a) In the space below, draw two equivalent resonance structures for the $HCO_2^-$ ion.

(b) Do you predict that the two carbon-oxygen bonds in the $HCO_2^-$ ion have the same length or have different lengths? Justify your answer.

(c) What is the best way to describe the bond order of the carbon-oxygen bonds in the $HCO_2^-$ ion?

4. The skeleton structure of the carbonate ion, $CO_3^{2-}$, is shown below.




(a) In the space below, draw three equivalent resonance structures for the $CO_3^{2-}$ ion.

(b) Do you predict that the three carbon-oxygen bonds in the $CO_3^{2-}$ ion have the same length or have different lengths? Justify your answer.

(c) What is the best way to describe the bond order of the carbon-oxygen bonds in the $CO_3^{2-}$ ion?

5. The skeleton structure of dinitrogen monoxide, $N_2O$, is shown below.

N N O

In the space below, draw three different resonance structures for the $N_2O$ molecule.

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**Formal charge** is a bookkeeping system used to analyze Lewis structures. Formal charges are not actual charges in a molecule or ion. Instead they are formally assigned to each atom in a Lewis structure according to the following equation.

formal charge = (valence electrons) – (electrons assigned to the atom in the structure)

The number of electrons assigned to an atom in a Lewis structure is equal to the sum of the covalent bonds drawn to the atom plus the number of nonbonding electrons on that atom. You can think of formal charge like this:

formal charge = (valence electrons) – ("dots" + "bonds")

If we can draw at least two different Lewis structures for a molecule or polyatomic ion, we can use formal charge to determine which Lewis structure is more dominant or preferred.

- The dominant Lewis structure is usually the one in which the atoms have formal charges that are closest to zero.
- If a Lewis structure contains a negative formal charge, the dominant Lewis structure is the one in which the negative formal charge is assigned to the more electronegative atom.

Formal charges can be assigned to each atom in a Lewis structure. Then the experimental data for that substance can be examined. The actual structure of a substance is often an intermediate between two or more contributing resonance structures.

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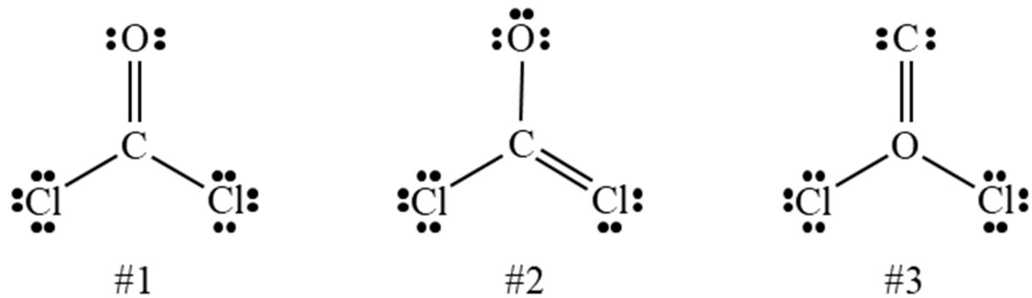
6. Review the three resonance structures for $N_2O$ that were drawn in Question #5.

(a) Use the information above to assign formal charges to each atom in each Lewis structure.

(b) Use the information above to decide which Lewis structure is the <u>least</u> likely to represent the bonding in $N_2O$.

(c) Use the information above to decide which Lewis structure is the <u>most</u> likely to represent the bonding in $N_2O$.



7. Each atom in each Lewis structure shown above obeys the octet rule. Assign formal charges to each atom in each structure. Based on formal charges, which Lewis structure is most dominant or preferred? Justify your answer.

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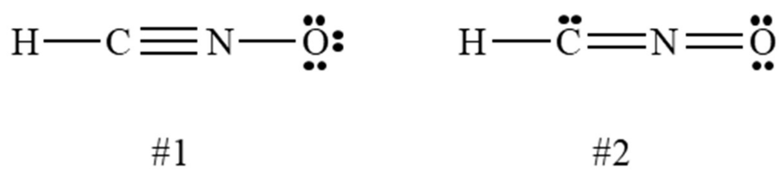

8. Each atom in each Lewis structure shown above obeys the octet rule. Assign formal charges to each atom in each structure. Based on formal charges, which Lewis structure is more dominant or preferred? Justify your answer.

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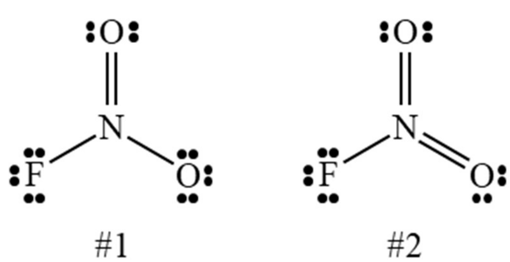
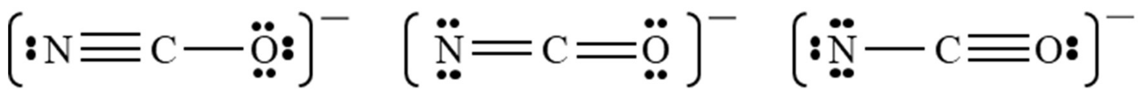


9. Which Lewis structure shown above is more preferred? Justify your answer.



#1 #2 #3

10. Each atom in each Lewis structure shown above obeys the octet rule. Assign formal charges to each atom in each structure. Based on formal charges, which Lewis structure is most dominant or preferred? Justify your answer.

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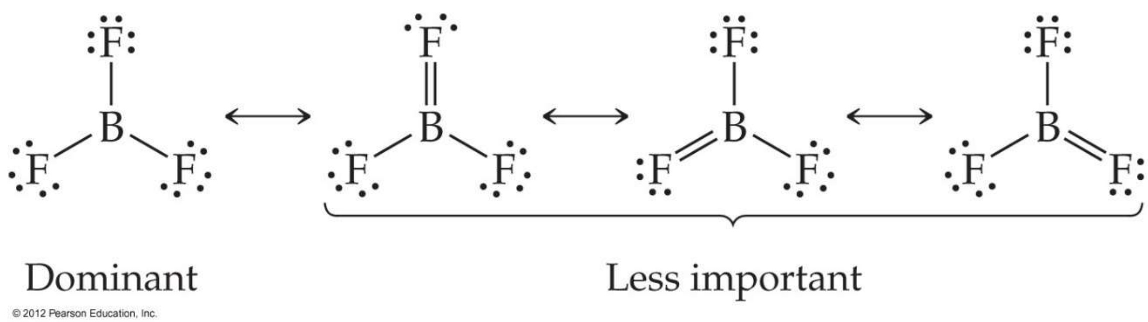
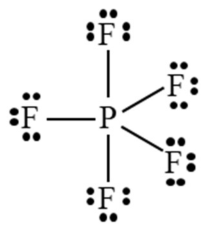
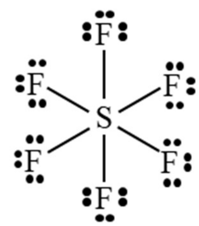



11. The molecule $BF_3$ is usually represented with a Lewis structure that shows three single B–F bonds. The Lewis structure on the far left is an exception to the octet rule, because it has only six valence electrons around the boron atom. It might seem appropriate to draw a Lewis structure with a B=F double bond in order to complete the octet for boron. However, this creates Lewis structures that are unfavorable. Considering the fact that fluorine (F) is the most electronegative element on the periodic table, explain why the Lewis structures on the right are unfavorable or less important than the Lewis structure on the far left.

Another example of a molecule whose Lewis structure includes an atom with fewer than eight electrons around it is the molecule $BeF_2$ (shown below).

There are many examples of hypervalent molecules and polyatomic ions whose Lewis structures contain a central atom with more than eight electrons around it. Two examples are shown below.

| phosphorus pentafluoride, $PF_5$ | sulfur hexafluoride, $SF_6$ |
|---|---|
|  |  |

The elements located in period 3 and below in the periodic table are capable of forming structures with expanded octets. The elements located in period 2 do not form expanded octets. The reason for this is because of the size of the central atom. The atoms in period 3 and below are large enough in size to accommodate the extra electrons around the central atom. The atoms in period 2 are too small to accommodate these extra electrons. Therefore molecules such as nitrogen pentafluoride ($NF_5$) and oxygen hexafluoride ($OF_6$) <u>do not exist</u>.

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12. Draw the correct Lewis electron dot structures for each of the following.

$SF_4$ $ClF_3$ $XeF_2$ $BrF_5$ $XeF_4$ $Br_3^-$