LEWIS STRUCTURES

These rules apply to most materials covered in undergraduate chemistry courses. They do not necessarily apply to all materials, especially those held together by non-classical bonding (i.e., boron hydrides and metallocenes).

Initially you may wish to outline this procedure to make sure you follow each step (in order). Later much of this will become automatic and it will not be necessary for you to write down each step. Do not rush this until you are sure that you are ready, do not be afraid to revert to the outlined procedure should it become necessary.

1. The first step in deriving a Lewis structure is to determine the total number of electrons that are present. All of these electrons must be in the final structure. This process involves two steps:

   a. For a main group element, the number of valence electrons is equal to the group number (except He—which has two). For the other elements, the number of valence electrons is not readily determined.

      Note: The new system of numbering the Periodic Table uses 1-18 instead of I-VIII for the groups, when using this form remember that columns 1 and 2 have 1 and 2 valence electrons, respectively, and that columns 13-18 have 3-8 valence electrons, respectively.

   b. The total electrons in a molecule or ion is the sum of the valence electrons from the individual atoms plus those due to the charge on an anion or minus those due to the charge on a cation.

Examples:

   S       6 electrons
   B       3 electrons
   CH₄     8 electrons (C-4 electrons + 4 H-1 electron each)
   NO₃⁻    24 electrons (N-5 electrons + 3 O-6 electrons each + 1 (- charge)
   NO₂     17 electrons (N-5 electrons + 2 O-6 electrons each)
   NH₄⁺    8 electrons (N-5 electrons + 4 H-1 electron each - 1 (+ charge)
   SbF₅     40 electrons (Sb-5 electrons + 5 F-7 electrons each)
2. The second step in drawing a Lewis structure is the positioning of the atoms. The following guidelines may help with the original positioning (note: some of these may give conflicting predictions, so remember these are only guidelines). In addition, if you are given the arrangement, then it does not matter whether it follows these guidelines, or if it is an exception, use what is given to you.

a. The atom needing the most electrons will often be the central atom.

   HCN is more likely than HNC or CHN

   C needs 4 electrons, N needs 3 and H needs 1.

   If two atoms need the same number, the larger is usually the central atom.

b. The most electronegative atom is seldom the central atom.

   SCN\(^-\) is more likely than CSN\(^-\) or CNS\(^-\)

   N and S are both to the right of C on the Periodic Table, and, therefore should be more electronegative.

c. In oxyacids, attach the acidic hydrogens to oxygens (only one H per O).

   HOCl and not OClH

d. Identical atoms seldom bond to each other.

   HOH and not HHO

   Carbon is a common exception. Other exceptions occur when there is no alternative, e.g. O\(_3\)

e. Hydrogen will not be the central atom, or in any way attach to more than one other atom.

   HOCl but never OHCl
3. Electrons tend to occur in pairs – either as lone pairs on an atom or as bonding pairs between two atoms.

A few substances (free radicals) do contain unpaired electrons. Many of these are easily identified because the total electrons (step 1b) are an odd number. Even then, expect only one electron to be unpaired.

\[
\text{NO is an example (N-5 electrons + O-6 electrons = 11 electrons)} \\
\text{Thus 1 electron will be unpaired.} \\
\text{The unpaired electron will most likely be on the N (less electronegative)}
\]

4. The number of electron pairs between two atoms determines the number of bonds (1 pair = single bond, 2 pairs = double bond, 3 pairs = triple bond). For the main group elements, a triple bond seems to be the limit. The greater the number electron pairs the stronger and shorter the bond.

Examples:
\[
\begin{align*}
\text{H:}: & \text{H} \\
\text{O::C::O} & \\
\text{H:C::N} &
\end{align*}
\]

There are no electrons shared between ions. Each ion has its own individual Lewis structure. Thus, it is incorrect to place electrons between the ions in an ionic compound.

Thus \([\text{Na}^+] \quad [\text{H}^-]\) is correct, but \(\text{Na}:\text{H}\) is not.

5. Most atoms prefer to have an octet (8 electrons) surrounding them. There are exceptions, however in most cases only one atom (other than H) per molecule is an exception.

The most common exceptions to the octet rule are:

Hydrogen, which only needs two electrons, (and other elements adopting a helium configuration of two electrons) are exceptions.

Elements beginning with less than four valence electrons often end with less than an octet.

Example: \(\text{BF}_3\)

Elements in compounds/ions with an odd number of electrons (the element with the lowest electronegativity is the one that has the odd electron, and therefore less than an octet).

Example: \(\text{NO}_2\)
Elements with more than four bonds to them will exceed an octet.

**Example:** SbF$_5$

Compounds of the noble gases: Example: KrF$_2$

An atom where the number of valence electrons plus the number of atoms bonded to it exceeds 8.

**Example:** ClF$_3$

6. Only elements in the third period (Na-Ar) or lower on the Periodic Table have the option to exceed an octet. Usually only the central atom, if necessary, exceeds an octet.

**Examples:** SiF$_6^{2-}$, PCl$_5$, SeF$_6$, IF$_7$, and XeF$_6$

7. More than one structure may fulfill the requirements for a correct Lewis structure.

If the only difference is the positioning of the electrons then the different forms are resonance structures.

**Example:** [O:N::O]$^-$ and [O::N:O]$^-$

If atoms move then the different forms are isomers.

**Example:** NOBr and ONBr

These alternatives are not required unless the problem asks for all alternatives (isomers). Do not confuse isomers with resonance and vice versa.

8. The more electronegative atom **will** obtain an octet.

9. It is not very likely that two atoms in a simple molecule or ion will be exceptions (other than H).
10. Various equations will predict the number of covalent bonds present. Be careful when using these because most do not take into account the fact that there are exceptions to the octet rule. Below is one of these equations:

\[
\text{Total bonds} = \frac{\text{Number of Electrons Required} - \text{Electron Total}}{2\text{Electrons Per Bond}}
\]

The number of electrons required is simply eight times the number of non-hydrogen atoms plus two times the number of hydrogen atoms.

The electron total is the number determined in 1b.

Do not forget, equations such as this will give incorrect predictions for compounds that are exceptions to the octet rule (other than those where hydrogen is the only exception). The most obvious indication that you are dealing with an exception is when an equation such as this one predicts fewer bonds than would be necessary to connect all the atoms with single bonds.

**Example: NO$_3^-$**

\[
\text{Total bonds} = \frac{[(4\text{atoms})(8\text{electrons})] - (24\text{electrons})}{2} = 4
\]

Four bonds will be present (in this case 2 single and 1 double)

**Example: ClF$_3$**

\[
\text{Total bonds} = \frac{[(4\text{atoms})(8\text{electrons})] - (28\text{electrons})}{2} = 2
\]

This is not possible because a minimum of 3 bonds are needed.

The Cl is an exception to the octet rule.
11. Formal charges give an additional method of checking the probability of a Lewis structure being correct.

The formal charge on an atom is calculated as follows:

Formal Charge = Group Number - Electrons in - 1/2 Electrons in
of the atom          lone pairs                 bonds
(Number of
valence electrons)

Apply this procedure to each atom in the substance.

The total of all the formal charges should equal zero for a compound, or the charge for an ion.

Example: HOC\text{I}

\begin{align*}
\text{H:} & \quad 1 - 0 - (1/2)2 = 0 \\
\text{O:} & \quad 6 - 4 - (1/2)4 = 0 \\
\text{Cl:} & \quad 7 - 6 - (1/2)2 = 0
\end{align*}

The total is 0 (since this is not an ion).

Example: NO\text{2}\text{−}

(Draw either resonance form. Use O:N::O)

\begin{align*}
\text{O:} & \quad 6 - 6 - (1/2)2 = -1 \\
\text{N:} & \quad 5 - 2 - (1/2)6 = 0 \\
\text{O:} & \quad 6 - 4 - (1/2)4 = 0
\end{align*}

The total is -1 (the charge on the ion).
12. If formal charges are calculated, the following additional factors may be considered:

   a. Very high formal charges (i.e., +3, -3 or greater) are very unlikely, especially if there are more than one such within a single structure.

   b. Adjacent atoms should not have like charges (i.e., either both positive or both negative).

   c. Charges should agree with electronegativities (i.e., negative charges should only appear on the more electronegative atoms).

   d. Unlike charges should be close together (preferably on adjacent atoms) not widely separated.

13. When drawing a Lewis structure it is possible to begin with any atom, and work through the other atoms in any order.

   a. If hydrogen is present it is often convenient to begin with it, as it only has one electron and only needs one (stop at two total). Never connect two atoms to one hydrogen atom.

   b. It is often convenient to assign electrons to give the most electronegative atom(s) their octets.

   c. Do not expect any method to work in exactly the same way in every case. Do not try to make every example to work in exactly the same manner.

14. No matter what, the number of electrons indicated by the Lewis structure MUST be identical to the number calculated in step 1. There is no possible way to have a correct answer if these numbers do not agree exactly. Also, resist the temptation to just add or remove electrons to force the numbers to agree.