Arrangement of Valence Electrons in Molecules

Assumptions:

(A) Only valence electrons are involved in the bonding of atoms to form molecules.
- Only the electrons on the very outside of atoms interact with other atoms.
- The inner core electrons are too tightly bound by the nucleus to interact.

(B) Atoms react to form molecules so to achieve the stable noble gas electrons configuration.
- Atoms in molecules follow the octet rule, hydrogen follows the duet rule.

(C) In covalent compounds, atoms share electrons to form bonds in order to achieve stable noble gas configuration.
- In ionic compounds electrons are transferred from one atom to another in order to achieve stable noble gas configuration.

General Procedure for Drawing Lewis Structures*

* For the most part, drawing Lewis Structures is trial and error. However, if you attack each structure with the same procedure, you can become very adept at drawing Lewis Structures. DO NOT worry about formal charge! Ignore formal charge in the reading assignment. For our purposes, the best Lewis structure is the one that satisfies the octet rule when possible.

The general procedure is:

1. Count the number of valence electrons.
2. Identify the central atom and place all terminal atoms around the central atom attached with single bonds (called the skeletal structure). The central atom is generally the first atom listed in a chemical formula (except H₂O, H₂S etc.) For molecules with more than one central atom, we will always give the skeletal structure, e.g., organic compounds. Hydrogen atoms are always attached with just one single bond so hydrogen is always on the outside, i.e., H is never a central atom.

* Courtesy of Tom Hummel’s Handouts for Chemistry 102
3. Complete the octet for all atoms in the Lewis structure using lone pairs of electrons. Hydrogen will always be satisfied with the single bond (duet rule).

4. Count the number of valence electrons used in this structure. If you have used the correct number of valence electrons, then this structure is the correct Lewis structure. If you haven’t used the correct number of valence electrons, then this structure cannot be the correct Lewis structure. However, one of the following four scenarios will apply that will allow to amend this original structure to converge on the correct Lewis structure.

a) If you have used too many electrons in this initial structure, then start over but this time form one double bond an again complete the octet with one pair of electrons. Count valence electrons used in the new structure. If the correct number of valence electrons have been used then you are done. If not, continue adding multiple bonds and subtracting lone pairs until you converge on the correct Lewis structure, i.e., the one that satisfies the octet rule for all atoms (other than H) and uses the correct number of valence electrons available. Note that resonance structures may exist when multiple bonds are used in a Lewis structure, so check for resonance possibilities. Also note that hydrogen will never form multiple bonds with other atoms since this would require sharing more than two electrons (would violate the duet rule for H).

b) If too few electrons are used (exceptions to octet) always put the extra electrons on the central atom.

c) If you only have 4 or 6 valence electrons to use in the Lewis structure, then the octet rule can’t be satisfied, e.g. BeH₂ or BH₃. Just attach the hydrogen atoms with single bonds and you are done.

d) If you have an odd number of electrons, complete the octet for all the atoms except for the least electronegative atom. Put 7 electrons around the least electronegative atom (generally the central atom). Of course there will be resonance structures, but the structures with the 7 electrons around the least electronegative atom will be the most stable. This is a minor point.

Covalency Rules for Organic Compounds

Drawing Lewis Structures for organic compounds (compounds composed of a carbon backbone with atoms of N, O and H bonded to the carbons). Organic compounds will generally follow the “covalency rules” which are derived from trying to achieve a formal charge of zero for each atom in
the structure. The covalency rules predict the number of bonds atoms like to form in order to complete the octet. These rules only work consistently for organic compounds and should NOT be applied to other compounds where they do not work consistently. The covalency rules are:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bonds Formed in Lewis Structure</th>
<th>Lone Pairs on Atom in Lewis Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Halogens (F, Cl, Br, I)</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

For organic compounds, just add bonds and lone pairs to atoms so the above covalency rules are followed. This will give you, the correct structure about 99% of the time. Remember, these covalency rules only work consistently for organic compounds: do not apply these rules to nonorganic compounds.

**Ionic:**

**Covalent:**

(i) HF  
(ii) O₂  
(iii) CO  
(iv) SiH₄  
(v) CF₄  
(vi) SCl₃⁺  
(vii) OF₂  
(viii) SO₃

**Resonance:** Experiment shows that all S-O bonds are identical in length and strength, with a bond length between that of a single and double bond. Therefore, just one structure is not accurate, the actual structure is an average of the three.

- You can recognize resonance when you can draw more than one valid Lewis structure for a molecule – usually involves placement of a multiple bond.
- You **must** draw all Lewis resonance structures to show that the actual structures is actually an average of all the resonance structures.
- The localized electron model assumes electrons are fixed but in molecules that exhibit resonance the electrons are delocalized, or free to move about the molecule.
- **NOTE:** The molecule is not jumping from one structure to the next.

Other examples:

(a) NO₂⁻
(b) CO₂

**Lewis Structures of Organic Compounds – See Above**

**Molecules that are exceptions to the octet rule:**

**A) Molecules with fewer than 8 valence electrons**

(i) BeH₂
(ii) BH₃
(iii) BF₃

**B) Molecules/Ions with an odd number of valence electrons**

(i) NO₂

**(C) Species that have more than 8 valence electrons around the central atom**

- Rationalized by the availability of low energy d orbitals.
- Row 2 elements (C, O, N, F) do not have 2 orbitals available and therefore can never have more than 8 electrons around them.

(i) SF₆
(ii) PCl₅
(iii) SF₄
(iv) KrF₂