

III. Covalent Compounds and Lewis Structures

- Covalent compounds form when the elements in a compound have smaller differences in electronegativity ($\Delta\chi = 0$ to 1.9 as a rough rule of thumb).
- Remember the ultimate criterion for the existence of a covalent compound: a substance that consists of discrete molecules.
- Lewis' theory of covalent compounds:
 - Give each atom an octet (H a duet) of valence electrons.
 - Molecules will usually maximize the number of paired electrons (pairing penalty notwithstanding—we'll see why later).
 - "Shared pair" (*i.e.* a covalent bond) between atoms or "lone pair" on one atom.
 - Shared pairs are "double-counted" when checking the octet/duet rule (the essence of the concept of covalency).
- We will see that Lewis' theory allow us to predict the three-dimensional shapes of molecules, which largely determines their physical properties and chemical reactivity!

Rules for Drawing Lewis Structures

Goal: Depict the location of all the valence electrons of a covalent "species" (neutral or charged)

- (1) Count the total number of valence electrons in the species.
 - (a) The periodic table group number tells us how many valence electrons an element has.
 - (b) For anions, add the magnitude of the overall charge to the total number of valence electrons.
 - (c) For cations, subtract the magnitude of the overall charge from the total number of valence electrons.
 - (d) A valid Lewis structure must show all valence electrons.
- (2) Make reasonable connections between atoms
 - (a) Know the common "valences" (that is, the number of connections atoms make):

Valence:	1	2	3	4
Groups:	17 (and H)	2 and 16	13 and 15	14

 - (i) Second-period atoms can make no more than 4 connections.
 - (ii) Valence s electrons on an atom sometimes unpair to form covalent bonds with other atoms. This allows the atom both to achieve an octet (or something close) and get rid of a destabilizing pairing penalty.
 - (b) Put the atom(s) with the highest valence at the center of the structure.
 - (c) Arrange the "left-over" lone pairs symmetrically around the structure.
 - (d) Check all octets/duets!
- (3) Some octet rule exceptions are stable, especially for elements close to the periodic table's diagonal boundary between metals and non-metals.

(4) Bond Order (B.O.) = the number of bonds between a pair of atoms

Higher bond order results in shorter and stronger bonds (i.e. bonds with higher bond dissociation energies).

(5) **Always** label non-zero formal charge on each atom.

$$\text{formal charge} = (\# \text{ of valence electrons}) - (\# \text{ of unshared electrons}) \\ - (\# \text{ of shared electron pairs})$$

➤ Sum of formal charges must equal the overall (real) charge on species.

(6) Valence expansion (also known as hypervalency) is allowed for atoms in the 3rd period and below of the periodic table. (Why?)

(7) Maximize bonding (that is, the number of shared electron pairs in the compound) and minimize the separation of opposite formal charge without violating the octet/valence expansion rules.

(8) Species with an odd number of electrons will have one unpaired electron.

(a) Species is called a radical (or a monoradical).

(b) Location of unpaired electron directs reactivity.

Resonance Structures

(1) A set of Lewis structures one draws when there is an ambiguity in the location of multiple bonds--e.g. is a pair of atoms connected by a single or a double bond?

(2) A “movement” or “pushing” of electrons, not of nuclei. That is, you should maintain the same sequence of atoms in all resonance structures.

(3) Sometimes, the symmetry of the species requires that you draw a set of resonance structures. These structures will be equivalent or degenerate (equal in energy).

(4) Other times, you may draw multiple, non-equivalent resonance structures. The best (lowest-energy) structure (the “major resonance contributor”) will...

a. Minimize the separation of opposite formal charge.

b. Maximize the separation of like formal charge.

c. If possible, put negative formal charge on the most electronegative atom.

d. If possible, put positive formal charge on the least electronegative atom.

(5) Next year in Organic Chemistry, you will see that a higher energy resonance structure (a “minor resonance contributor”) may provide the best rationale for a reaction!