

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:	7A (and H)	2A and 6A	3A and 5A	4A

- (i) Second-period atoms can make no more than 4 connections.
 - (ii) Valence s electrons on an atom sometimes unpair to form covalent bonds. 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) Bond Order (B.O.) = the number of bonds between a pair of atoms

Higher bond order results in shorter and stronger bonds

- (4) Some octet rule exceptions are stable, especially for elements close to the periodic table's diagonal boundary between metals and non-metals.
- (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.
- Species is called a radical (or a monoradical).
 - Location of unpaired electron directs reactivity.

Resonance Structures

- 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?
- A "movement" or "pushing" of electrons, not of nuclei. That is, you should maintain the same sequence of atoms in all resonance structures.
- 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).
- Other times, you may draw multiple, non-equivalent resonance structures. The best (lowest-energy) structure (the "major resonance contributor") will...
 - Minimize the separation of opposite formal charge.
 - Maximize the separation of like formal charge.
 - If possible, put negative formal charge on the most electronegative atom.
 - If possible, put positive formal charge on the least electronegative atom.
- 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!