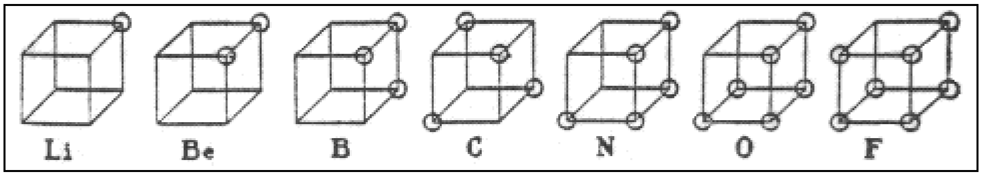
8.1 The Localized Bonding Model

LE: a molecule is composed of atoms that are bound together by sharing pairs of electrons using atomic orbitals of bound atoms. Electron pairs are localized between the nuclei of the two atoms.

8.2 Lewis Structures



G. N. Lewis; a molecule that shows how the valence electrons are arranged among the atoms in the molecule. Atoms achieve a stable noble gas configuration.

Ex. MgO [Mg]$^{2+}$ [:O:]$^{2-}$

Covalent Molecules:

Duet Rule: 1st period atoms fill their valence shell with 2 electrons. H becomes stable as the inert He atom.

Octet Rule: 2nd period elements achieve an octet of valence electrons to become stable. $2s^2 2p^6$

Rules for Writing these Lewis Structures:

1. Determine total number of electrons that each atom requires to have a stable valence shell; i.e. H=2 , second period require 8.
2. Sum all of the valence electrons. Remember the valence electrons belong to the molecule, not the atom. Roman Numerals above representative elements indicate number of valence electrons. Polyatomic ions charges are electrons added (or lost) from the molecule.
3. Subtract #1 from #2 and divide in half (2 e^-/bond). This gives number of bonds.
4. Place bonds between atoms and use remaining valence electrons to complete octets.

P.385 #67 (In class) or Example: N_2, NH_3, CO_2, N_3^-

8.3 Exceptions to the Octet Rule

Electron deficient (very reactive) B. Boron only has 3 valence electrons, 6 bonds, trivalent and Be has only 2 valence electrons, 2 bonds, bivalent.

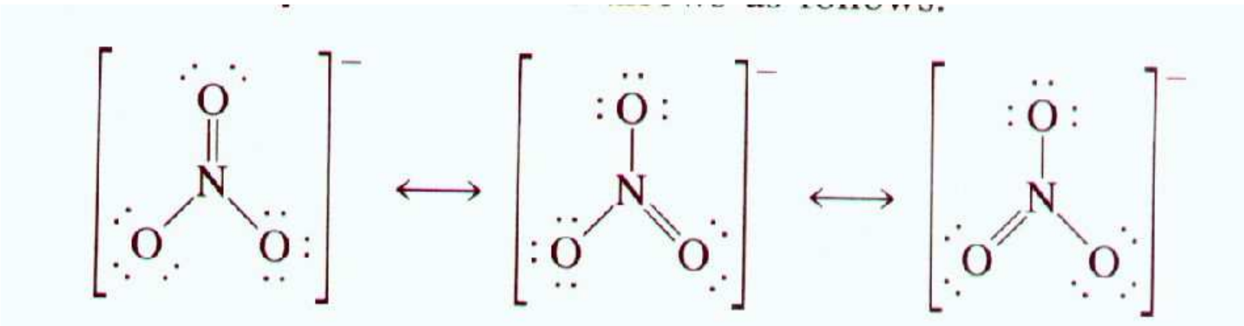
Expanded Octet: Period 3 and beyond (with empty d orbitals)

Rule 5: Satisfy the octet for each atom. If electrons remain place them on the central atom that has available d orbitals.

Example: ClF_3, PCl_5, XeO_3, $RnCl_2$, $BeCl_2$, ICl_4^-, BH_3

8.4 Resonance

NO_3^- has a Lewis structure as shown below.



Experiments indicate that although the N=O bond is shorter than the N-O bond all three of NO_3^-'s N-O bonds are of equal length. Somewhat between the (1/3) N=O and (2/3) N-O. It has three equivalent bonds. Resonance shows that the correct structure is an average of all three.

Resonance occurs when more than one valid Lewis structure can be drawn.

The arrangement about the nuclei is the same, only the placement of electrons is different.

Example: NO_2^-

Compare N_2O as NNO and NON (the latter is an isomer) such as C_2H_6O as alcohol or ether.

Explanation: The electrons are not localized, they are delocalized they can move around the entire molecule.

Odd electron models

Can not be adequately handled with the localized electron model.

Formal Charge

How do decide which is the more stable structure?

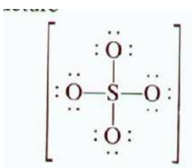
Formal Charge: difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atoms in the molecule.

How to for determine *Formal Charges*:

(different from oxidation states in redox because the shared electrons do not belong entirely to the more electronegative atom)

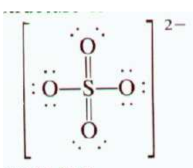
1. Total the number of assigned valence electrons in the free neutral atom.
2. Take the sum of the lone pair electrons and one half the shared electrons. This is the number of valence electrons assigned to the atom in the molecule.
3. Subtract step 1 – step 2.
4. The sum of all the formal charges of atoms in the molecule must equal the overall sum on the molecule.
5. If non-equivalent Lewis Structures (different number of single, double, triple bonds as can be drawn in different Lewis structures) exist, those with formal charges closest to zero and with any negative formal charges on the most electronegative atom are considered to be the best describing the bonding in the atom or ion.

Formal charge =[valence e-'s free atom] – [assigned valence electrons (see rule 1)]



Ex. SO_4^{2-} (with 4 single bonds)

Formal Charge on O = [6 valence electrons] - [6 lone e-'s + ½ 2 (single bond)] = -1
Formal Charge on S = [6 valence electrons] – [0 lone + 8 shared/2] = +2
Overall = -2

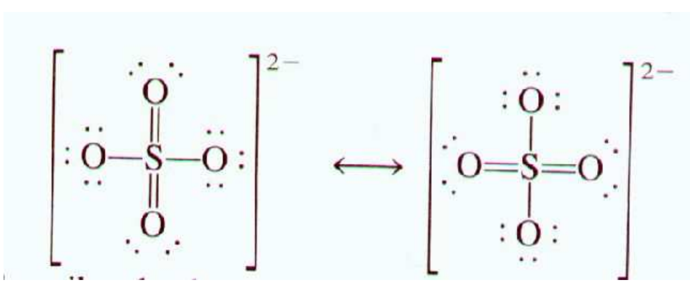


Ex. SO_4^{2-} (with 2 single bonds and 2 double bonds)

Formal charge on single bond O = 6 – 7 = -1
Formal charge on double bond O = 6 – 6 = 0
Formal charge on S = 6 – 6 = 0
Overall charge = -2

Evaluations:
Atoms in molecule try to achieve formal charge as close to zero as possible.
Any negative charge must be on the more electronegative atom.

SO_4^{2-} with 2 double bonds is more preferred with resonance structures.



Ex. XeO_3, P. 383, Sample Exercise 8.10.

Draw all possible resonance structures for XeO_3. We might expect that the one with the 3 double bonds that gives Xe a formal charge of zero to be most stable; however experiemental evidence reveals a rather weak bond, indicating that the weaker single bonds may actually exist.

Practice Problems for Study: P.385 #67, 69, 70, 71, 73, 78, 79, 80, 81, 83, 86, 109, 110, 112, 114, 128, 129, 130, 133