Electron Dot Structures

& Chemical Bonding

Chapters 9-10

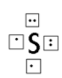
Electron Dot Structures & Valence Electrons

- **Electron Dot Structures** – also known as **Lewis dot structures** – represent the valence electrons of atoms and show how they bond.
- **Valence electrons** are the outermost electrons of an atom that participate in chemical reactions.
- The outermost ***s*** and ***p*** electrons and electrons in **unfilled *d*** and ***f*** sublevels are considered valence electrons.
- We will primarily concern ourselves with main group elements, so we will usually consider only the ***s*** and ***p*** electrons.

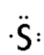
Element Electron Dot Structures

- Electron Dot Structures of atoms assume that s and p orbitals have the same energy (because of hybridization).
- Consider each "side" of an element symbol as an orbital:

- We must observe Hund's rule when we fill electrons. Sulfur has six valence electrons:

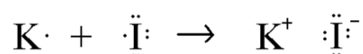


- Or, simply:



Ionic Compounds

- **Ionic Compounds –** Atoms form ions in order to achieve an OCTET – 8 valence electrons.



Covalent Compounds

- **Covalent Compounds –** Atoms share electrons in covalent bonds in order to achieve an octet.
- Consider:
  - Carbon Tetrachloride (CCl_4)
  - Water (H_2O)
  - Silicon Disulfide (SiS_2)

Note that the least electronegative atom goes in the center.

Predicting Simple Covalent Formulas

- What formula might we expect for a compounds containing:
  - Phosphorus and Chlorine?
  - Hydrogen and Sulfur?

Bond Order

- **Bond Order –** The number of electrons shared between atoms determines the number of bonds between 2 atoms.
  - Single bond – sharing of 2 electrons .
  - Double bond – sharing of 4 electrons.
  - Triple bond – sharing of 6 electrons.

Electron Dot Structures for Simple Covalent Molecules or Ions

Write electron dot structures for the following covalent compounds. Make sure that all of the atoms (except H) have an octet:

- **SF_2**
- **CH_4**
- **NH_4^+**
- **CO_3^{2-}**
- **CO_2**
- **C_2H_6**
- **$COCl_2$**
- **C_2H_2**

Add an electron for each negative charge and remove an electron for each positive charge.

Exceptions to the octet rule :

- Hydrogen needs only 2 valence electrons.
- Group 2A and 3A elements (**Be** and **B** columns) do not need and should not have octets.
- Central atoms in the third row of the periodic table or below may get 10-12 valence electrons.
  - This is an ***expanded octet.***
  - These atoms have opened up an energy level with *d* orbitals, but have no electrons in that *d* sublevel.
  - These *d*-orbitals are available for bonding with other atoms.

Electron Dot Structures for Simple Covalent Molecules

- Write electron dot structures for the following covalent compounds. Some may not follow the octet rule.
  - SF_6
  - SF_4
  - $AlBr_3$
  - BeI_2
  - PCl_5
  - XeF_4

Oxides & Oxoanions

- Write an electron dot structure for the following polyatomic ions:

  SO_3^{2-} NO_3^{-}

- Some electron dot structures for molecules and polyatomic ions are difficult to determine by simply looking at the electron dot structures of the atoms.

Drawing Lewis Dot Structures

General rules for covalent compounds and polyatomic ions with a central atom.

1. Find the Total number of valence electrons:
   - Add up valence electrons for all atoms.
   - For each negative (-) charge, add one electron.
   - For each positive (+) charge, subtract one electron.
2. Put the least electronegative atom in the center (but ***not*** Hydrogen).
3. Put other atoms around central atom and connect with a single bond.
4. Fill octets on outer atoms as lone pairs.

Drawing Lewis Dot Structures General Rules (continued)

5. If any electrons are unused, put those remaining electrons on the central atom as lone pairs.
6. If needed, move lone pairs from outer atoms to bond with the central atom to form an octet on the central atom. This will make double or triple bonds.
7. Minimize (or properly distribute) formal charge by changing lone pairs to bonds.
   Only violate the octet if allowed.

Formal Charge

To assign formal charge to an atom in a dot structure:

- Find the number of electrons in the valence shell of an atom of the element (from the periodic table).
- Assign valence electrons to the atom in the Lewis structure:
  - 1 electron per bond
  - 2 electrons per lone pair.
- Then, subtract the number of electrons assigned in the dot structure from the number assigned on the Periodic table:

Formal Charge = # assigned on PT – # assigned in dot structure

Formal Charge (continued)

- The formal charges on all of the atoms MUST add up to the overall charge on the molecule or polyatomic ion.
- No atom or ion should have a formal charge >+1 or <-1.
- When all atoms are not zero, then generally, more electronegative elements will have a negative formal charge and less electronegative elements will have a positive formal charge.
- Group 2A and Group 3A elements have fewer than 4 electrons in their atomic electron configurations. Giving them an octet in a Lewis structure will give them a negative formal charge, which is not likely as they have low electronegativities.

Examples

- Oxoanions
- Oxoacids
- Various

Resonance

- A means of representing bonding in a molecule when a single electron dot structure cannot adequately describe the bonding in a molecule.
- Consider NO_3^-

Resonance

- No single structure gives a complete picture of the bonding in nitrate ion.
- Originally, chemists thought that the double bonds would alternate between being single and double bonds.
- However, empirical evidence shows that the actual molecule can be thought of as a resonance hybrid of these three molecules.

Bond Order

- Bond Order − The number of electron pairs shared between two atoms in a molecule or polyatomic ion.
- Single bonds, double bonds, & triple bonds are common.
- Fractional Bond Orders − When a molecule has more than one resonance structure, partial bonds are possible.
- $\text{Bond Order} = \dfrac{\text{Total number of shared pairs}}{\text{Total number of bonding regions}}$
- Consider NO_3^-

Bond Length

- Bond Length − Distance between the nuclei of 2 bonded atoms.
- Atomic radii and bond order both influence bond length.
- As bond order increases, bond length decreases.

Bond	Length (pm)
N−O	136
N−N	140
N−P	180
C−C	154
C=C	134
C≡C	124

Bond Length

- Consider the NO bond lengths below:

Bond	Length (pm)
N−O	136
N=O	115

- Consider the NO_2^- ion:
- Bond order = 1.5
- The observed bond length, 125 pm, is intermediate between a single and double bond.

Bond Energy

- Bond Dissociation Energy – also called simply ***bond energy***. It is the energy that is required (positive value) to break a chemical bond.
- Bond Formation Energy – The energy released (negative vale) when a chemical bond is formed.
- ***Table 9.2*** is a list of bond dissociation energies.
- Bond energy increases as bond order increases.

Bond Energy

Bond	Energy (kJ/mol)
N−N	163
N=N	418
N≡N	945

- Bond dissociation energies may be used to estimate heats of reaction (ΔH_{rxn})
- $\Delta H_{rxn} = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$
- $\Delta H_{rxn} = \Sigma(\text{reactant bonds}) - \Sigma(\text{product bonds})$

ΔH from Bond Energy Approximations

- Estimate the ΔH of hydrogenation of ethene (C_2H_4) based on bond energy approximations.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$