Chapter 10

The Shapes of Molecules

Chapter 10

Molecular Lewis Structures

- We can use Lewis dot symbols to build molecules, to show the bonding between atoms, and to predict the three-dimensional molecular structure of the resulting compound
- Powerful tool to predict molecular structure
  - Start thinking in 3-D
- How to determine the central atom for polyatomic molecules (H₂O, CH₄)?
- Use a systematic approach

Molecular Lewis Structures

A Systematic Approach

1. Identify the central atom based on electronegativities of the constituents atoms. The central atom is the one with low electronegativity value. Exception: Hydrogen (always be the terminal atom)
2. Recognize the number of bonds each atom should make to satisfy its octet
3. Determine the total number of valence electrons in the molecule.
4. Place one pair of electrons between each pair of bonded atoms to form a single bond.
5. Use any remaining pairs as lone pairs around each terminal atom (except H) so that each terminal atom is surrounded by eight electrons
6. If the central atom has fewer than eight electrons at this point, move one or more of the lone pairs on the terminal atoms into a position intermediate between the center and the terminal atom to form double or triple bonds
Molecular Lewis Structures

- Hydrogen needs one e− to achieve a noble gas configuration — thus it forms one covalent bond.

- Carbon

- Nitrogen

- Oxygen

- Fluorine

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Molecular Lewis Structures

- Formaldehyde, CH₂O
  - Which is the central atom?
  - Total valence electrons = ?

  - Check the octet of C, is it satisfied?

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Molecular Lewis Structures

- Ammonia, NH₃
  - Which is the central atom?
  - Total valence electrons = ?

  - Check the octet of N, is it satisfied?
Molecular Lewis Structures

- NF₃
  - Which is the central atom?
  - Total valence electrons = ?
  - Bonding electrons

  - How many electrons remain and where do they go?
  - Check the octets of N and F, are they satisfied?

Molecular Lewis Structures

- Ethane, C₂H₆
  - Total valence electrons = ?
  - Bonding electrons

  - Check the "octets", are they satisfied?

Molecular Lewis Structures

- Ethylene, C₂H₄
  - Total valence electrons = ?
  - Bonding electrons

  - How many electrons are left over and where do they go?
  - Check the "octets", are they satisfied?
Molecular Lewis Structures
- Phosgene, COCl₂
- Hydrazine, N₂H₄
- Hydrogen peroxide, H₂O₂

Polyatomic Ions
- Covalent bonding can also occur in polyatomic ions
  - Sulfate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺) for example
- To generate Lewis structures, use the systematic approach except …
Polyatomic Ions

- Nitrate, $\text{NO}_3^-$
- Total valence electrons = ?
- Bonding electrons

- How many electrons are left over and where do they go?
- Check the octets of O and N, are they satisfied?
- Place brackets around the structure: overall charge is 1-

Polyatomic Ions

- Another example, $\text{PO}_4^{3-}$

Polyatomic Ions

- Chlorate, $\text{ClO}_3^-$
Delocalized Electron-pair Bonding: Resonance

- $\text{O}_3$
- $\text{CO}_3^{2-}$

Which One is the Real Structure?

Actual representation of the molecule is a hybrid of many different [Lewis Structures] i.e. resonance forms "[Resonance Hybrid]"
Which One is the Real Structure?

Or:

Formal Charge

- What is it?
  
  Formal charge = Group number - \[\text{LPE} + \frac{1}{2}(\text{BE})\]
  
  LPE: lone pair electrons
  BE: number of bonding electrons

- Examples:
  1. H\(_2\)O
  2. OH\(^-\)

Overall charge of a molecule or polyatomic ion = summation of formal charges of all the atoms in a molecule / polyatomic ion

Formal Charge

- Hypochlorous acid: HOCI or HClO?
- ClO\(^-\)

- Hydrogen cyanide: HNC or HCN?
- CN\(^-\)
Formal Charge

- Formal charge and resonance structures
  1) NO$_3^-$
  2) CH$_3$COO$^-$

Octet Rule Exceptions

Electron-deficient Molecules:

- BF$_3$
- BeH$_2$

Expanded Octets

- PCl$_5$
- SiF$_5^-$
- SF$_6$
More Exceptions

- ClF_4^-
- BrF_5
- NO_2

Molecule with odd number of electrons: free radicals

Chemical Bonding and Molecular Geometry

Molecular Shape

- Most molecules are not flat as they appear in two-dimensional Lewis structures
- Molecules have three-dimensional shapes
- Shape can be predicted using Valence Shell Electron Pair Repulsion (VSEPR) theory
Shape via VSEPR

- First obtain the Lewis structure
- Then apply the VSEPR rules:
  - All valence shell electron pairs (electron charge clouds) are treated equally whether they are bonding or nonbonding
  - Stereoelectronically significant electron pairs
  - Double and triple bonds are treated as single bonds for predicting molecular shapes
  - Electron pairs orient in space to get as far away from neighbors as possible

Balloon models of electron-pair geometries

Molecular Shapes with Two Electron Pairs

- CO₂
  - 180°
  - Linear
- BeCl₂
Molecular Shapes with Three Electron Pairs

- BF$_3$
  - Molecular shape is determined by the positions of atoms
  - Trigonal planar

Molecular Shapes with Four Electron Pairs

- CH$_4$
  - Tetrahedral

Molecular Shapes with Five Electron Pairs
**Molecular Shapes with Four Electron Pairs**

Examples: $\text{SF}_6$, $\text{ClO}_3^-$

**A Summary of Common Molecular Shapes**

**Shape via VSEPR**

- $\text{NH}_4^+$
- $\text{PF}_5$
Shape via VSEPR

- H₂O
  Structure is ___________
- ClF₂⁺
  Structure is ___________

Shape via VSEPR

- Central atoms with expanded octets and lone pairs
  - ClF₄⁺
  - ICl₄⁻
  - BrF₅

Molecular Shapes with More Than One Central Atom
We can use the polarity of individual bonds to predict the polarity of overall molecules.

**Polar Molecule** = a molecule that contains polarized bonds AND has the resulting partial charges distributed unsymmetrically.

- Polarity induces a dipole or a separation of charge.

**Molecule Polarity and Dipole Moment**

- A quantitative measure of the degree of charge separation in a molecule.
- Product of partial charges and the distance by which they are separated.
- Unit: Debye (D); 1 D = 3.34 x 10^{-30} C.m
- A vector quantity, having both a magnitude and a direction.

**Nonpolar molecule** = a molecule that has nonpolar bonds (like H\(_2\) or I\(_2\)) or a molecule that has polarized bonds AND has the resulting partial charges distributed symmetrically.

- Dipoles cancel out (point in opposite directions) resulting in a nonpolar molecule.
Molecule Polarity

Polar or non-polar?

- CO₂
- H₂O

More examples:

- BF₃
- NH₃

Trigonal planar
Trigonal pyramidal
Molecule Polarity

- CS₂ – polar or nonpolar?
- CCl₄ – polar or nonpolar?
- SF₆ – polar or nonpolar?

Molecule Polarity

- NH₃ – polar or nonpolar?
- SO₃ – polar or nonpolar?
- SO₂Cl₂ – polar or nonpolar?

Molecule Polarity

- SCl₂ – polar or nonpolar?
- SF₄ – polar or nonpolar?
- XeF₄ – polar or nonpolar?