2.1 Polar Covalent Bonds: Electronegativity

Chemical bonds

- Ionic bonds
  - Ions held together by electrostatic attractions between unlike charges
  - Bond in sodium chloride
    - Sodium transfers an electron to chlorine to give Na⁺ and Cl⁻

- Nonpolar Covalent bonds
  - Two electrons are shared equally by the two bonding atoms
  - Carbon-carbon bond in ethane
    - Symmetrical electron distribution in the bond

Most bonds are neither fully ionic or covalent.

Polar covalent bonds

- A covalent bond in which the electron distribution between atoms is unsymmetrical
  - Bond polarity is due to difference in electronegativity (EN)
Electronegativity (EN)

- The ability of an atom to attract shared electrons in a covalent bond
- Generally increases across the periodic table from left to right and from bottom to top

Bonds between atoms whose electronegativities differ by less than 0.5 are nonpolar covalent
- Bonds between atoms whose electronegativities differ by 0.5 to 2.0 are polar covalent
- Bonds between atoms whose electronegativities differ by more than 2.0 are largely ionic

Carbon–hydrogen bonds are nonpolar. Bonds between carbon (EN = 2.5) and more electronegative elements, such as oxygen (EN = 3.5) and nitrogen (EN = 3.0) are polar covalent bonds with the bonding electrons drawn towards the more electronegative atoms

Electrostatic potential maps

- Show calculated charge distributions
- Colors indicate electron-rich (red; $\delta^-$) and electron-poor (blue; $\delta^+$) regions
- Methanol, CH$_3$OH, has a polar covalent C-O bond, and methyl lithium has a polar covalent C-Li bond
- A crossed arrow is used to indicate direction of bond polarity
- Electrons are displaced in the direction of the arrow
An atom's ability to polarize a bond is known as the **inductive effect**

**Inductive effect**
- The electron-attracting or electron-withdrawing effect transmitted through σ bonds. Electronegative elements have an electron-withdrawing inductive effect.
- Metals inductively donate electrons.
- Reactive nonmetals inductively withdraw electrons.
- Inductive effects play a major role in understanding chemical reactivity.

**Polar Covalent Bonds: Electronegativity**

Molecules as a whole are often polar.
- Molecular polarity results from the vector summation of all individual bond polarities and lone-pair contributions in the molecule.
- Strongly polar substances are soluble in polar solvents like water.

**Dipole moment (μ)**
- Magnitude of charge Q at either end of molecular dipole times distance r between charges:
  \[ \mu = Q \times r \text{ in debyes (D)} \]
  \[ 1 \text{ D} = 3.336 \times 10^{-30} \text{ coulomb meter (C \cdot m)} \]
- A measure of the net polarity of a molecule.
- Arises when the centers of mass of positive and negative charges within a molecule do not coincide.

**Example calculation:**

If one positive and one negative charge were separated by just less than the length of an average covalent bond (100 pm), the dipole moment would be calculated as follows.

\[ \mu = (1.60 \times 10^{-19} \text{ C})(100 \times 10^{-12} \text{ m})(1 \text{ D} / 3.336 \times 10^{-30} \text{ C \cdot m}) = 4.80 \text{ D} \]
Polar Covalent Bonds: Dipole Moments

Factors Affecting Dipole Moments

- Lone-pair electrons on oxygen and nitrogen project out into space away from positively charged nuclei giving rise to a considerable charge separation and contributing to the dipole moment
- Symmetrical structures of molecules cause the individual bond polarities and lone-pair contributions to exactly cancel

Make a three-dimensional drawing of methylamine, CH₃NH₂, and show the direction of its dipole moment (µ = 1.31)

Worked Example 2.1

Predicting the Direction of a Dipole Moment

Make a three-dimensional drawing of methylamine, CH₃NH₂, and show the direction of its dipole moment (µ = 1.31)
2.3 Formal Charges

**Formal charge**
- The difference in the number of electrons owned by an atom in a molecule and by the same atom in its elemental state
- Formal charges do not imply the presence of actual ionic charges
- Device for electron “bookkeeping”
- Assigned to specific atoms within a molecule
  - Dimethyl sulfoxide \( \text{CH}_3\text{SOCH}_3 \)
    - Sulfur atom has three bonds rather than the usual two and has a formal positive charge
    - Oxygen atom has one bond rather than the usual two and has a formal negative charge

**Formal Charge Determination**

**An isolated carbon atom**

- Owned 4 valence electrons.
- \( \frac{6}{2} = 3 \) valence electrons.

**This carbon atom also owns**

- \( \frac{6}{2} = 3 \) valence electrons.

**An isolated nitrogen atom**

- Owned 5 valence electrons.
- \( \frac{5}{2} + 2 = 4 \) valence electrons.

**This nitrogen atom also owns**

- \( \frac{5}{2} + 2 = 4 \) valence electrons.

**Formal Charges**

\[
\text{Formal charge} = \left( \frac{\text{Number of valence electrons in free atom}}{\text{Number of bonding electrons}} \right) \times \left( \frac{\text{Number of valence electrons in bonded atom}}{2} \right) - \text{Number of nonbonding electrons}
\]

For sulfur:
- Valence electrons = 6
- Bounding electrons = 6
- Nonbounding electrons = 2
- Formal charge = \( 6 - \frac{6}{2} - 2 = -1 \)

For oxygen:
- Valence electrons = 6
- Bounding electrons = 3
- Nonbounding electrons = 6
- Formal charge = \( 6 - \frac{3}{2} - 6 = -1 \)
### Formal Charges

#### Table 2.2: A Summary of Common Formal Charges

<table>
<thead>
<tr>
<th>Atom</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>+1</td>
<td>+2</td>
<td>+3</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Valence electrons</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Number of bonds</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Number of lone pairs</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Formal charge</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
</tbody>
</table>

9/10/2010