Chapter 8
Bonding

What is a Bond?
- A force that holds atoms together.
- Why?
- We will look at it in terms of energy.
- Bond energy - the energy required to break a bond.
- Why are compounds formed?
- Because it gives the system the lowest energy.

Ionic Bonding
- An atom with a low ionization energy reacts with an atom with high electron affinity.
- A metal and a non-metal
- The electron moves.
- Opposite charges hold the atoms together.

Coulomb’s Law
- \( E = 2.31 \times 10^{-19} \text{ J} \cdot \text{nm} (Q_1Q_2)/r \)
- \( Q \) is the charge.
- \( r \) is the distance between the centers.
- If charges are opposite, \( E \) is negative
- exothermic
- Same charge, positive \( E \), requires energy to bring them together.

What about covalent compounds?
- The electrons in each atom are attracted to the nucleus of the other.
- The electrons repel each other,
- The nuclei repel each other.
- The reach a distance with the lowest possible energy.
- The distance between is the bond length.

![Graph]

Energy

0

Internuclear Distance
Covalent Bonding

- Electrons are shared by atoms.
- These are two extremes.
- In between are polar covalent bonds.
- The electrons are not shared evenly.
- One end is slightly positive, the other negative.
- Indicated using small delta $\delta$. 
Electronegativity

- \( \Delta \) is known for almost every element
- Gives us relative electronegativities of all elements.
- Tends to increase left to right.
- Decreases as you go down a group.
- Most noble gases aren’t discussed.
- Difference in electronegativity between atoms tells us how polar the bond is.

Electronegativity

- The ability of an electron to attract shared electrons to itself.
- Pauling method
- Imaginary molecule HX
- Expected H-X energy = \( \frac{H-H \text{ energy} + X-X \text{ energy}}{2} \)
- \( \Delta = (H-X)_{\text{actual}} - (H-X)_{\text{expected}} \)

Electronegativity difference

- Zero
- Intermediate
- Large

Bond Type

- Covalent
- Polar
- Ionic

Covalent Character decreases

Ionic Character increases
Dipole Moments
- A molecule with a center of negative charge and a center of positive charge is dipolar (two poles),
- or has a dipole moment.
- Center of charge doesn’t have to be on an atom.
- Will line up in the presence of an electric field.

How It is drawn
\[ \text{H - F} \]
\[ \delta^+ \quad \delta^- \]

Which Molecules Have Dipoles?
- Any two atom molecule with a polar bond.
- With three or more atoms there are two considerations.
  1) There must be a polar bond.
  2) Geometry can’t cancel it out.

Geometry and polarity
- Three shapes will cancel them out.
- Linear

Geometry and polarity
- Three shapes will cancel them out.
- Planar triangles
Geometry and polarity
- Three shapes will cancel them out.
  - Tetrahedral

Geometry and polarity
- Others don’t cancel
  - Bent

Geometry and polarity
- Others don’t cancel
  - Trigonal Pyramidal

Ions
- Atoms tend to react to form noble gas configuration.
- Metals lose electrons to form cations
- Nonmetals can share electrons in covalent bonds.
  - When two non-metals react (more later)
- Or they can gain electrons to form anions.

Ionic Compounds
- We mean the solid crystal.
- Ions align themselves to maximize attractions between opposite charges, and to minimize repulsion between like ions.
- Can stabilize ions that would be unstable as a gas.
- React to achieve noble gas configuration

Size of ions
- Ion size increases down a group.
- Cations are smaller than the atoms they came from.
- Anions are larger.
- Across a row they get smaller, and then suddenly larger.
- First half are cations.
- Second half are anions.
Periodic Trends

- Across the period nuclear charge increases so they get smaller.
- Energy level changes between anions and cations.

Size of Isoelectronic ions

- Positive ions have more protons so they are smaller.

Forming Ionic Compounds

- Lattice energy - the energy associated with making a solid ionic compound from its gaseous ions.
- $M^+(g) + X^-(g) \rightarrow MX(s)$
- This is the energy that “pays” for making ionic compounds.
- Energy is a state function so we can get from reactants to products in a round about way.

Na(s) + $\frac{1}{2}$F$_2$(g) → NaF(s)

- First sublime Na
  - Na(s) → Na(g)  \( \Delta H = 109 \text{ kJ/mol} \)
- Ionize Na(g)
  - Na(g) → Na$^+(g) + e^-$  \( \Delta H = 495 \text{ kJ/mol} \)
- Break F-F Bond
  - $\frac{1}{2}$F$_2$(g) → F(g)  \( \Delta H = 77 \text{ kJ/mol} \)
- Add electron to F
  - F(g) + e$^-$ → F$^-(g)$  \( \Delta H = -328 \text{ kJ/mol} \)

Na(s) + $\frac{1}{2}$F$_2$(g) → NaF(s)

- Lattice energy
  - Na$^+(g) + F^-(g) \rightarrow NaF(s)$  \( \Delta H = -928 \text{ kJ/mol} \)

Calculating Lattice Energy

- Lattice Energy = $k(Q_1Q_2 / r)$
- $k$ is a constant that depends on the structure of the crystal.
- $Q$’s are charges.
- $r$ is internuclear distance.
- Lattice energy is with smaller ions
- Lattice energy is greater with more highly charged ions.
Calculating Lattice Energy

- This bigger lattice energy “pays” for the extra ionization energy.
- Also “pays” for unfavorable electron affinity.
- \( \text{O}^{2-}(\text{g}) \) is unstable, but will form as part of a crystal.

Bonding

Partial Ionic Character

- There are probably no totally ionic bonds between individual atoms.
- Calculate % ionic character.
- Compare measured dipole of \( X-Y \) bonds to the calculated dipole of \( X^+Y^- \) the completely ionic case.
- \( \% \text{ dipole} = \frac{\text{Measured } X-Y}{\text{Calculated } X^+Y^-} \times 100 \)
- In the gas phase.

The Covalent Bond

- The forces that causes a group of atoms to behave as a unit.
- Why?
- Due to the tendency of atoms to achieve the lowest energy state.
- It takes 1652 kJ to dissociate a mole of \( \text{CH}_4 \) into its ions.
- Since each hydrogen is hooked to the carbon, we get the average energy = 413 kJ/mol.

How do we deal with it?

- If bonds can’t be ionic, what are ionic compounds?
- And what about polyatomic ions?
- An ionic compound will be defined as any substance that conducts electricity when melted.
- Also use the generic term salt.
CH3Cl has 3 C-H, and 1 C - Cl
the C-Cl bond is 339 kJ/mol
The bond is a human invention.
It is a method of explaining the energy change associated with forming molecules.
Bonds don’t exist in nature, but are useful.
We have a model of a bond.

What is a Model?
• Explains how nature operates.
• Derived from observations.
• It simplifies them and categorizes the information.
• A model must be sensible, but it has limitations.

Properties of a Model
• A human inventions, not a blown up picture of nature.
• Models can be wrong, because they are based on speculations and oversimplification.
• Become more complicated with age.
• You must understand the assumptions in the model, and look for weaknesses.
• We learn more when the model is wrong than when it is right.

Covalent Bond Energies
• We made some simplifications in describing the bond energy of CH4
• Each C-H bond has a different energy.
  • CH4 → CH3 + H \(\Delta H = 435 \text{ kJ/mol}\)
  • CH3 → CH2 + H \(\Delta H = 453 \text{ kJ/mol}\)
  • CH2 → CH + H \(\Delta H = 425 \text{ kJ/mol}\)
  • CH → C + H \(\Delta H = 339 \text{ kJ/mol}\)
• Each bond is sensitive to its environment.

Averages
• There is a table of the averages of different types of bonds pg. 365
• single bond- one pair of electrons is shared.
• double bond- two pair of electrons are shared.
• triple bond- three pair of electrons are shared.
• More bonds, more bond energy, but shorter bond length.

Using Bond Energies
• We can estimate \(\Delta H\) for a reaction.
• It takes energy to break bonds, and end up with atoms (+).
• We get energy when we use atoms to form bonds (-).
• If we add up the energy it took to break the bonds, and subtract the energy we get from forming the bonds we get the \(\Delta H\).
• Energy and Enthalpy are state functions.
Find the energy for this

\[
2 \text{CH}_2 = \text{CHCH}_3 + 2\text{NH}_3 + \text{O}_2 \\
\rightarrow 2 \text{CH}_2 = \text{CHC}=\text{N} + 6 \text{H}_2\text{O}
\]

- C-H 413 kJ/mol
- C\equiv C 614 kJ/mol
- N-H 391 kJ/mol
- C-C 347 kJ/mol
- O-H 467 kJ/mol
- O=O 495 kJ/mol
- C≡N 891 kJ/mol

Localized Electron Model
- Simple model, easily applied.
- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.
- Three Parts
  1) Valence electrons using Lewis structures
  2) Prediction of geometry using VSEPR
  3) Description of the types of orbitals (Chapt 9)

Lewis Structure
- Shows how the valence electrons are arranged.
- One dot for each valence electron.
- A stable compound has all its atoms with a noble gas configuration.
- Hydrogen follows the duet rule.
- The rest follow the octet rule.
- Bonding pair is the one between the symbols.
- One dot for each valence electron.

Rules
- Sum the valence electrons.
- Use a pair to form a bond between each pair of atoms.
- Arrange the rest to fulfill the octet rule (except for H and the duet).
- H\_2\text{O}
- A line can be used instead of a pair.

Quiz Answers
1. D
2. B
3. A
4. D
5. C
6. E
7. D
8. E
9. E

A useful equation
- \((\text{happy-have}) / 2 = \text{bonds}\)
- CO\_2 C is central atom
- PO\_Cl\_3 P is central atom
- SO\_4^{2-} S is central atom
- SO\_3^{2-} S is central atom
- PO\_4^{3-} P is central atom
- SCl\_2 S is central atom
Exceptions to the octet
• BH$_3$
• Be and B often do not achieve octet
• Have less than an octet, for electron deficient molecules.
• SF$_6$
• Third row and larger elements can exceed the octet
• Use 3d orbitals?
• I$_3^-$

Exceptions to the octet
• When we must exceed the octet, extra electrons go on central atom.
• (Happy – have)/2 won’t work
• ClF$_3$
• XeO$_3$
• ICl$_4^-$
• BeCl$_2$

Resonance
• Sometimes there is more than one valid structure for a molecule or ion.
• NO$_3^-$
• Use double arrows to indicate it is the “average” of the structures.
• It doesn’t switch between them.
• NO$_2^-$
• Localized electron model is based on pairs of electrons, doesn’t deal with odd numbers.

Formal Charge
• For molecules and polyatomic ions that exceed the octet there are several different structures.
• Use charges on atoms to help decide which.
• Trying to use the oxidation numbers to put charges on atoms in molecules doesn’t work.

Formal Charge
• The difference between the number of valence electrons on the free atom and that assigned in the molecule or ion.
• We count half the electrons in each bond as “belonging” to the atom.
• SO$_4^{2-}$
• Molecules try to achieve as low a formal charge as possible.
• Negative formal charges should be on electronegative elements.

Examples
• XeO$_3$
• NO$_4^{3-}$
• SO$_2$Cl$_2$
VSEPR
- Lewis structures tell us how the atoms are connected to each other.
- They don’t tell us anything about shape.
- The shape of a molecule can greatly affect its properties.
- Valence Shell Electron Pair Repulsion Theory allows us to predict geometry.

VSEPR
- Molecules take a shape that puts electron pairs as far away from each other as possible.
- Have to draw the Lewis structure to determine electron pairs.
- bonding
- nonbonding lone pair
- Lone pair take more space.
- Multiple bonds count as one pair.

VSEPR
- The number of pairs determines – bond angles
  – underlying structure
- The number of atoms determines – actual shape

VSEPR

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<th>Bond Angles</th>
<th>Underlying Shape</th>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
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Actual shape

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### Actual Shape

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### Examples

- SiF$_4$
- SeF$_4$
- KrF$_4$
- BF$_3$
- PF$_3$
- BrF$_3$

### No central atom

- Can predict the geometry of each angle.
- Build it piece by piece.

### How well does it work?

- Does an outstanding job for such a simple model.
- Predictions are almost always accurate.
- Like all simple models, it has exceptions.
- Doesn’t deal with odd electrons

### Polar molecules

- Must have polar bonds
- Must not be symmetrical
- Symmetrical shapes include
  - Linear
  - Trigonal planar
  - Tetrahedral
  - Trigonal bipyramidal
  - Octahedral
  - Square planar