Announcements

- Lab week change
  Due to Chancellor's Inauguration Week activities, classes on the afternoon of April 26 are cancelled, so we have to move the lab that day to one week earlier. Since we are having Exam 3 on April 27, it makes sense to move all the labs that week to one week earlier.

Summary: Lab 9 will happen the week of April 17 (this week!). There will be no labs the week of April 24. This is a shift to one week earlier for everyone.

- Exam #3 is next Thursday, April 27
- The final exam is scheduled for Monday, May 15, 8:00-11:00am, in our regularly scheduled lecture hall (S-1-006). I am trying to change the location…stay tuned.
Agenda

- Go over group problem
- Review ionic vs. molecular
- Why do ionic compounds have ionic bonding?
- Why do molecular compounds have covalent bonding?
- The gray area between ionic and molecular and why compounds can’t always be clearly categorized as ionic or molecular
- The Lewis structure model for predicting bonding arrangements in molecular compounds

Map of Chapter 8

- What holds ions together
  - Predicting qualitative trends
- What holds molecules together
  - Predicting enthalpy of reaction from bond energies
- Ionic vs. covalent character of bonds: polarity and electronegativity model
- Lewis structure model
  - Simple structures (octet rule), with single and multiple bonds
  - Resonance structures
  - More complicated structures (breaking the octet rule)
  - Formal charges
- Bond strength and length
  - Using Lewis structures to predict
  - Using Hess’s law and bond enthalpies
Ionic vs. Molecular (what you already know)

1. Ionic bonding
   - Occurs between ions
   - Ions are particles that are charged
     - Atoms that have gained or lost electron(s)
     - Polyatomic ions
   - In solid state, ions are arranged in regular, repeating, alternating + and - lattice structure
   - Strong attractions between + and -, and lattice structure in which every ion surrounded by many ions of opposite charge, make it difficult (energetically) to change solid to liquid
   - As a result, all ionically bonded materials are solids at room temperature and have very high melting points

Ionic vs. Molecular (review)

2. Covalent bonding
   - Occurs between neutral atoms within individual molecules (neutral atoms are not charged)
   - Forces of attraction that hold atoms together inside of molecules result from attractions of each atom’s nucleus (+) toward neighboring atom’s electrons (-) as well as its own electrons (also -)
   - Only valence electrons of atoms interact with valence electrons of other atoms
   - Covalent means ‘shared valence’ electrons
   - When covalently bonded molecules are in solid state, the molecules are arranged in regular, repeating lattice structures. The forces of attraction that hold together molecules in the solid state are weaker than ionic (full + and – monopoles) because inter-molecular forces are between polarized molecules (dipoles) or polarizable molecules ⇒ lower melting points.
Lattice energy in ionic compounds is formation energy

Equal and opposite to energy required to break apart the lattice into separated ions.

**Lattice Energy**

*The energy associated with forming an ionic crystal from atoms*

Why does magnesium chloride (MgCl₂) have a larger lattice energy than calcium chloride (CaCl₂)?

- MgCl₂ has a larger lattice energy than CaCl₂
- More energy is required to disrupt the MgCl₂ lattice
- Ionic bonding is stronger in MgCl₂ than in CaCl₂
- Cl⁻ ions get closer to the center of positive charge (core) in MgCl₂ than in CaCl₂
- Mg²⁺ cations have smaller radius than Ca²⁺ cations
- Magnesium is in period 3
  Calcium is in period 4
Lattice Energy
The energy associated with forming an ionic crystal from atoms

Why does magnesium oxide (MgO) have a larger magnitude by a factor of 4 (more negative) lattice energy than sodium fluoride (NaF)?

Four times more energy is required to disrupt the MgO lattice

Ionic bonding is 4 times stronger in MgO than in NaF

Inter-ion distances are approximately the same in both lattices, but both charges are doubled in MgO compared to NaF

Mg$^{2+}$ and O$^{2-}$ ions have +2 and -2 charges, respectively
Na$^{+}$ and F$^{-}$ ions have +1 and -1 charges, respectively

Magnesium and Sodium are both in period 3. Oxygen and Fluorine are both in period 2.

Period and Group Trends in Lattice Energy

Lattice Energies of Some Ionic Compounds

Data from textbook p. 305
Qualitative trends (comparisons) in strength of ionic bonding

- Recall that Coulomb’s law predicts that force of attraction between two oppositely charged objects depends on magnitudes of charges (direct) and on distance that separates them (indirect)

- Comparing the lattice energies of two ionic compounds depends on two factors:
  - Compare magnitudes of ionic charges over the same separation distance
  - Compare separation distance if the same ionic charges
  - (Both factors can work in the same direction)
  - (If factors work in opposing directions, you need to know more quantitative information to make a prediction)

Bond polarity

- Electronegativity model
- But first, it’s easier to talk about bonds in molecular compounds when we can say something about what those bonds are made of
- Remember, bonds in molecular compounds are called covalent (co=share, valent=made of valence electrons)
- Generally, covalent bonds occur between nonmetals
Lewis Dot Structure Model

Valence number of an atom is the quantity of valence electrons

- Periods 1, 2, 3 have only s and p electrons in valence shell
- Period 3 and higher: d-orbitals are available and can play role in valence shell
- Count only the s and p electrons in the valence shell to make Lewis dot structures

Convention dictates “Hund’s rule” applies to filling the four locations that dots can occupy around a Lewis dot structure for an atom

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Lewis Dot Structure Model

- Powerful model for predicting molecular shapes
- Assists in answering questions:
  - Why do bonds between atoms within a molecule have specific angles?
  - Why are molecules not flat?
  - Why are attractive forces between some molecules stronger/weaker than between other molecules?
  - How is structure related to lots of other chemical and physical properties of covalently bonded materials?
- Theory behind Lewis dot structures is that valence electrons are distributed as either
  - Pairs of electrons that are shared by two atoms (shared pairs)
  - Pairs of electrons that belong to a single atom (unshared, or lone pairs)
Lewis Structures of Simplest Molecules

There is no difference between one electron and another. When a molecule is formed, the electrons have no allegiance to their original atoms.

Octet Rule

A noble gas configuration (8 valence electrons) is stable. Atoms tend to form molecules or polyatomic ions in such a way that each atom is surrounded by 8 electrons (an octet).

There are lots of exceptions. They are interesting and we will study them. But first let’s master the rule.
Lewis Dot Structure Model

- Theory behind Lewis dot structures is that valence electrons are distributed as either
  - Pairs of electrons that are shared by two atoms (shared pairs)
  - Pairs of electrons that belong to a single atom (unshared, or lone pairs)

![Lewis Dot Structures](image)

Try This

Draw the Lewis structures of the following molecules. Don’t forget to show all the valence electrons: both the bonding electrons and the lone pairs. (It might help to check your work by conservation of valence electrons.)

1) N₂
2) CH₄
3) CH₃Cl
4) NH₃
5) H₂CO
Reminder: Electron Affinity

Electron affinity measures how much an atom “likes” electrons

Except not the noble gases

Building Lewis Structures

1. Determine central atom (atom with lowest electron affinity because electron density will spread as far as possible, given the opportunity)
2. Count total number of valence electrons in molecule
3. Arrange atoms around central atom
4. Start with single bonds
5. Place remaining valence electrons
6. Move electrons to form octets, making double or triple bonds where necessary

Check: Make sure you have conservation of electrons
Practicing the Steps

Draw the Lewis structure for ammonium (NH₄⁺)

1. N is central because H atoms can only bond once
2. Total valence electrons
   - 5 on N
   - 1 on each H gives 4 more
   - Ion has +1 charge, meaning one electron is removed
   - Total = 5 + 4 – 1 = 8

The rest of the steps:

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\begin{array}{c}
\text{H} \\
\text{N} \quad \text{H} \\
\text{H} \\
\end{array}
\]

Practicing the Steps

Draw the Lewis structure for the nitrate ion (NO₃⁻)

1. N is central because it has the least electron affinity
2. Total valence electrons
   - 5 on N
   - 6 on each of three O atoms gives 18 more
   - Ion has -1 charge, meaning one electron is added
   - Total = 5 + 18 + 1 = 24

The rest of the steps:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]
Try building these structures:

1) NO$_2^+$
2) CN$^-$
3) SCN$^-$
4) O$_3$

Isoelectronic = same number of (valence) electrons and same number of atoms to distribute them around

Which two of the above structures are isoelectronic?
What is true about isoelectronic species?

Resonance Structures

- What do these structures have in common?
- How are they different?
- Which of these is the actual structure of NO$_3^-$?

Note: This is not a correct Lewis structure. It is drawn this way only to emphasize the bond order.
Bond Order and Bond Length/Strength

- **Bond order**
  - Single bond is bond order 1
  - Double bond is bond order 2
  - Triple bond is bond order 3

- **Bond strength**
  - The greater the bond order, the stronger the bond (the more energy required to break the bond)

- **Bond length**
  - The greater the bond order, the shorter the bond length

Formal Charges

A comparison between the **valence electrons originally contributed by an atom** and the **electrons that it looks like the atom would have if all bonds were broken and electrons reassigned democratically**.

The valence electrons that were **originally** contributed:
- each O had 6
- the N had 5

Electrons assigned democratically if bonds hypothetically broken

Therefore, the formal charges on each atom are

Notice that the sum of the formal charges must equal the ion charge
Formal Charges and Alternative Structures

- If more than one Lewis structure exists, the most stable structure is the one in which the formal charges make most sense
  - Negative formal charges on atoms with large electron affinity
  - Positive formal charges on atoms with small ionization energies (small electron affinity)

\[
\begin{align*}
\text{O} &= \text{C} = \text{N}^- \\
\text{O} &= \text{C} = \text{N}^-
\end{align*}
\]

A Range of Bond Types

Bond “types” are not separable into a true dichotomy between covalent and ionic. Instead there is a range of covalent character vs. ionic character of bonds.

Increasing ionic character of bond
Increasing “bond polarity”

**nonpolar covalent**
- Perfectly covalently shared electrons

**polar covalent**
- Bonding electrons exhibit greater electron density (\(\delta^-\)) on one atom in the bond than on the other (\(\delta^+\))

**ionic**
- Ions with full charges (unshared electrons)
Electronegativity Model to Explain Bond Polarity

- Definition: the attraction that a given atom has for the electrons that are in a bond
- Early idea related to electron affinity (energy required to add an electron to an atom) and ionization energy (energy required to remove an electron from an atom)
- Linus Pauling invented an electronegativity scale of elements based on comparing bond energies of elements bonded to themselves and to other elements

Pauling attributed additional bond strength in HF to extra Coulomb attraction due to partial ionic character of HF bond compared to equal sharing of electrons in H₂ and F₂. Maximum “electronegativity” at F set to 4.0.

Pauling’s Electronegativity Scale

Electronegativity measures the ability of an atom to attract electrons to itself
Predicting Bond Polarity Using Electronegativities

- Electronegativity is a measure of the ability of an atom to attract electrons to itself
- Bond polarity depends on the difference between the electronegativities of the two elements that are in a bond

![Increasing bond polarity diagram]

Predicting Bond Polarity

- Electronegativity measures ability of an atom to attract electrons to itself
- Bond polarity depends on the difference between the electronegativities of the two elements that are in a bond

![Bond polarity types diagram]
Electronegativities Allow You to Compare Bond Polarity

- Which bond is most polar? Which bond is least polar?
- Which end of the bond is the negative pole (greater electron density)? Which end is the positive pole (less electron density)?

The bond between C and N in CN⁻ is less polar than the bond between C and O in H₂CO, which is less polar than the bond between C and F in CH₃F.

Exceptions to Octet Rule

1. Less than an octet on an atom
   - Only happens with Group 3A elements (such as boron) because these elements have 3 valence electrons so they make 3 bonds (not 4)
   - Examples: BF₃, B(OH)₃

2. Odd number of electrons
   - Impossible for all electrons to be paired
   - Lone electron usually resides on atom with lowest electron affinity (which is usually central atom)
   - Called “free radicals”
   - Very reactive because electrons are more stable in pairs
   - Examples: NO (11 valence electrons), NO₂ (17 valence electrons)

3. More than an octet on an atom
   - This is what we will spend the rest of the semester studying