Chem 103, Section F0F
Unit VI - Compounds Part II: Covalent Compounds
Lecture 16

- Bond energies and chemical change
- Electronegativity and bond polarity
- Depicting Molecules and Ions with Lewis Structures

Lecture 16 - Covalent Bonding

Reading in Silberberg

- Chapter 9, Section 4
  - *Bond Energy and Chemical Change*
- Chapter 9, Section 5
  - *Electronegativity and Bond Polarity*
- Chapter 10, Section 1
  - *Depicting Molecules and Ions with Lewis Structures*

Lecture 16 - Introduction

In this lecture we will look in more detail at covalent bonding

- Bond energies and how they can be used to predict the enthalpy change for a reaction.
- We will see that the distinction between ionic and covalent bonds is not an all-or-nothing situation, but rather a continuum.
- The concept of electronegativity and how it can be used to predict the ionic or covalent character of a bond.
- Lewis structures, or Lewis formulas, and how they can be used to predict the covalent bonding within a molecule.

Lecture 16 - Bond Energies & Chemical Change

The only component of the internal energy that changes significantly during a chemical reaction is the energy of attraction between the atomic nuclei and the electrons that they share in covalent bonds.

- This energy is called bond bond energy

$$H_2\,(g) + F_2\,(g) \longrightarrow 2\,HF\,(g)$$

$$H\text{—}H + F\text{—}F \longrightarrow H\text{—}F + H\text{—}F$$

In this reaction, an H–H bond and an F–F bond are broken, and two H–F bonds are formed

Lecture 16 - Bond Energies & Chemical Change

The bond energy is the enthalpy (heat energy) that is required to break a covalent bond.

Lecture 16 - Bond Energies & Chemical Change

Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
Single Bonds									
	H—H	432	74	N—H	391	101	Si—H	323	148
	H—F	565	92	N—N	160	146	Si—Si	226	234
	H—Cl	427	127	N—P	209	177	Si—O	368	161
	H—Br	363	141	N—O	201	144	Si—S	226	210
	H—I	295	161	N—F	272	139	Si—F	565	156
				N—Cl	200	191	Si—Cl	381	204
	C—H	413	109	N—Br	243	214	Si—Br	310	216
	C—C	347	154	N—I	159	222	Si—I	234	240
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	C—P	264	187	O—O	204	148	P—P	200	221
	C—S	259	181	O—S	265	151	P—F	490	156
	C—F	453	133	O—F	190	142	P—Cl	331	204
	C—Cl	339	177	O—Cl	203	164	P—Br	272	222
	C—Br	276	194	O—Br	234	172	P—I	184	243
	C—I	216	213	O—I	234	194			

Lecture 16 - Bond Energies & Chemical Change

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Lecture 16 - Bond Energies & Chemical Change

Bond energies can be used to calculate the enthalpy change for a reaction (ΔH^o_{rxn}).

- In the lab, ΔH^o_{rxn} is the heat that you felt, which was either absorbed or released during a reaction.
  - $\Delta H^o_{rxn} < 0$ (exothermic)
    - Heat was *released* and the beaker got warmer
  - $\Delta H^o_{rxn} > 0$ (endothermic)
    - Heat was *absorbed* and the beaker got colder

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Lecture 16 - Bond Energies & Chemical Change

Bond energies can be used to calculate the enthalpy change for a reaction (ΔH^o_{rxn}).

- This is done by summing together the energy that is released when all of the bonds in the products form
- And subtracting from this, the sum of the energy it takes to break all of the bonds in the reactants.

$$\Delta H^o_{rxn} = \sum \Delta H^o_{\text{reactant bonds broken}} - \sum \Delta H^o_{\text{product bonds formed}}$$

$$\Delta H^o_{rxn} = \sum \text{BE}_{\text{reactant bonds broken}} - \sum \text{BE}_{\text{product bonds formed}}$$

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Lecture 16 - Bond Energies & Chemical Change

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The BE's are the bond energies tabulated in Table 9.2

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Lecture 16 - Bond Energies & Chemical Change

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Hess's Law allows us to equate this difference to ΔH^o_{rxn}

Lecture 16 - Bond Energies & Chemical Change

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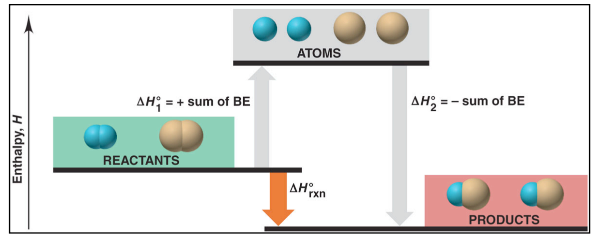
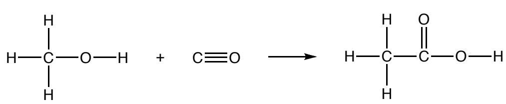


Lecture 081117 - Question 1

An important industrial route to synthesizing extremely pure acetic acid is the reaction of methanol with carbon monoxide: Is this reaction



A) exothermic?

B) endothermic?

Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
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	C—Br	276	194	O—Br	234	172	P—I	184	243	Br—I	175	248
	C—I	216	213	O—I	234	194				I—I	151	266
Multiple Bonds												
	C=C	614	134	N=N	418	122	C C	839	121	N N	945	110
	C=N	615	127	N=O	607	120	C N	891	115	N O	631	106
	C=O	745	123	O_2	498	121	C O	1070	113			
		(799 in CO_2)										

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Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945

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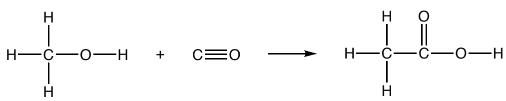


A) exothermic?

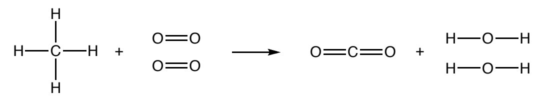
B) endothermic?

Lecture 081117 - Bond Energies & Chemical Change

Combustion reactions, involving fuels or foods, release a lot of enthalpy.

- This means that the bonds in the fuel or food that are broken are weaker that the bonds in the CO_2 and H_2O that form.

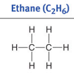
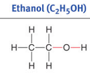
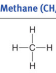
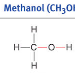
$$CH_4\,(g) \;+\; 2\,O_2\,(g) \longrightarrow CO_2\,(g) \;+\; 2\,H_2O\,(g)$$



Lecture 081117 - Bond Energies & Chemical Change

Combustion reactions, involving fuels or foods, release a lot of enthalpy.

Table 9.4 Heats of Reaction (ΔH_{rxn}) for the Combustion of Some Carbon Compounds

	Two-Carbon Compounds		One-Carbon Compounds	
	Ethane (C_2H_6)	Ethanol (C_2H_5OH)	Methane (CH_4)	Methanol (CH_3OH)
Structural formula				
Sum of C—C and C—H bonds	7	6	4	3
Sum of C—O and O—H bonds	0	2	0	2
ΔH_{rxn} (kJ/mol)	−1560	−1367	−890	−727
ΔH_{rxn} (kJ/g)	−51.88	−29.67	−55.5	−22.7

Lecture 081117 - Bond Energies & Chemical Change

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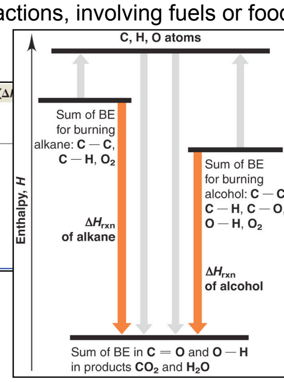
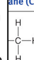
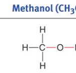


Table 9.4 Heats of Reaction (Δ

	One-Carbon Compounds	
	ane (CH_4)	Methanol (CH_3OH)
Structural formula		
Sum of C—C and C—H bonds	4	3
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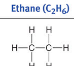
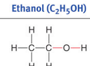
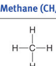
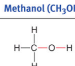
Structural formula				
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Lecture 16 - Electronegativity & Bond Polarity

An atom's electronegativity is a measure of how strongly that atom is attracted to the electrons that it shares with another atom in a covalent bond.

Lecture 16 - Electronegativity & Bond Polarity

Linus Pauling observed that the bond energy for a covalent bond between two dissimilar atoms was not equal to the average of the bond energy for the covalent bond of each atoms with itself, as might be expected:

$$H_2\,(g) + F_2\,(g) \longrightarrow 2\,HF\,(g)$$

$$H{-}H \;+\; F{-}F \longrightarrow H{-}F \;+\; H{-}F$$

	H—H	F—F	H—F	H—F
Expected BE:	432	159	296	296
Actual BE:	432	159	565	565

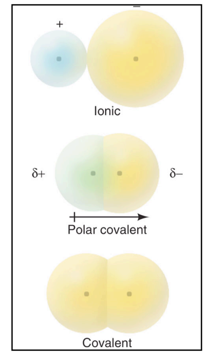
$$\left(BE = \frac{432 + 159}{2} = 296 \right)$$

Lecture 16 - Electronegativity & Bond Polarity

Pauling proposed that the electrons that were being shared, were not shared equally.

- And that this lead to covalent bond that was partially ionic.
- Such bonds are called **polar covalent bonds**.

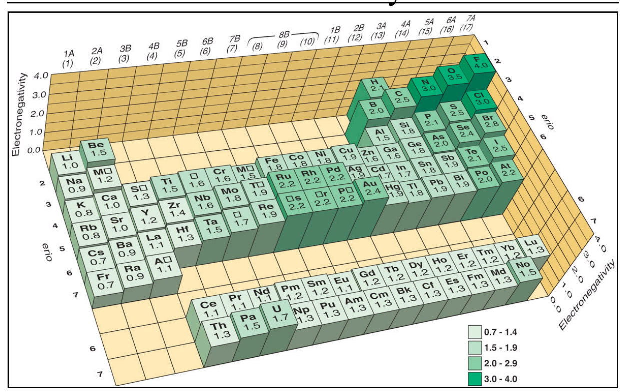
The ionic contribution increases the bond energy for the bond.



Lecture 16 - Electronegativity & Bond Polarity

Pauling created an index for each atom, called the **electronegativity index**, which can be used to predict the polarity of a bond between two atoms.

Lecture 16 - Electronegativity & Bond Polarity



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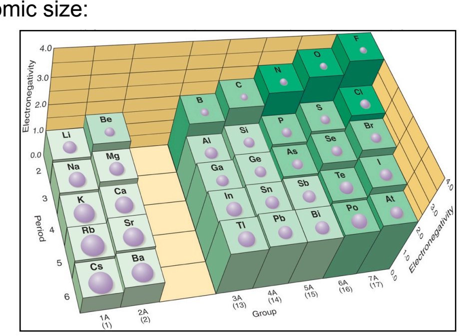
Lecture 16 - Electronegativity & Bond Polarity

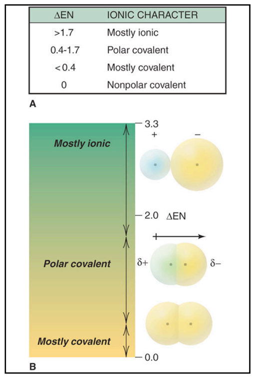
The electronegativity index follows the same periodic trend as the atomic size:



Lecture 16 - Electronegativity & Bond Polarity

The electronegativity index is used to determine the polarity of a bond.

- The magnitude of the difference in the electronegativity (EN) index for the two atoms participating in a bond is proportional to the polarity of the bond.
- This places covalent and ionic bonds on a continuum

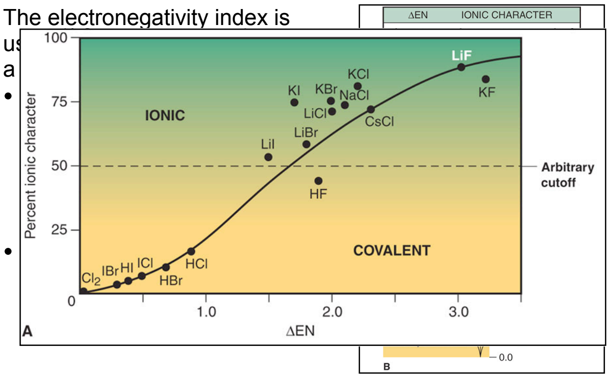


Lecture 16 - Electronegativity & Bond Polarity

The electronegativity index is

us

a



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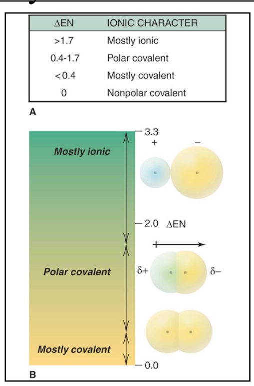
- This places covalent and ionic bonds on a continuum



Lecture 16 - Questions

Which of the following lists correctly arranges the bonds in *increasing* polarity:

A) Si–Si < S–Cl < Si–Cl < P–Cl

B) Si–Si < S–Cl < P–Cl < Si–Cl

C) P–Cl < Si–Cl < Si–Si < S–Cl

D) Si–Cl < P–Cl < S–Cl < Si–Si

Lecture 16 - Electronegativity & Bond Polarity

The electronegativity index is also used to determine which atom is assigned the bonding electrons when determining oxidation numbers

1. The more electronegative atom in a bon is assigned *all* the *shared* electrons; the less electronegative atom is assigned *none*.
2. Each atom in a bond is assigned *all* of its *unshared* electrons.
3. The oxidation number is given by

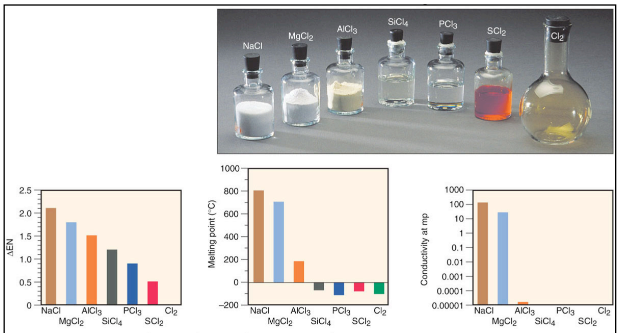
O.N. = no. of valence e^- - (no. of shared e^- + no. of unshared e^-)

Lecture 16 - Electronegativity & Bond Polarity

ΔEN can be used to predict the strength of intermolecular interactions

- Which, we will see, are reflected in melting points and boiling points.

Lecture 16 - Electronegativity & Bond Polarity



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Lecture 16 - Electronegativity & Bond Polarity

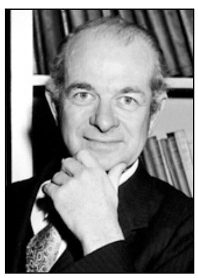
ΔEN can be used to predict the strength of intermolecular interactions

- Which, we will see, are reflected in melting points and boiling points.

Lecture 16 - Electronegativity & Bond Polarity

For his contributions to our undersanding of the nature of the chemical bond, Linus Pauling received the 1954 Nobel Prize in Chemistry

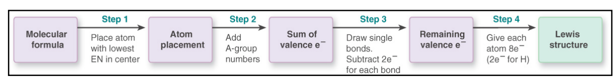
- Eight years later, Pauling received the 1962 Nobel Peace Prize, for his work in establishing nuclear test band treaties.
- Pauling also made significant contributions in the area of protein chemistry



Lecture 16 - Lewis Structures

Lewis structures provide a simplified, systematic way of predicting molecular structures.

- Later these will be used as the first step to predicting the 3–dimensional structures for molecules.
- Arriving at a Lewis structure starts with a 4-step process, starting with the molecular formula.

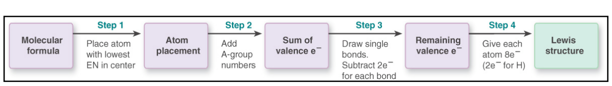


Lecture 16 - Lewis Structures

Using the "octet rule" to write Lewis Structures.

- Structures with single bonds, *e.g.* NF_3

Step 1: Place the atoms relative to each other with the element having the lowest group number in the center.



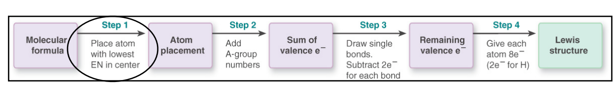
Lecture 16 - Lewis Structures

Using the "octet rule" to write Lewis Structures.

- Structures with single bonds, *e.g.* NF_3

Step 1: Place the atoms relative to each other with the element having the lowest group number in the center.

F
N
F F



Lecture 16 - Lewis Structures

Using the “octet rule” to write Lewis Structures.

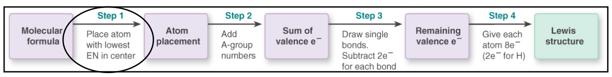
- Structures with single bonds, *e.g.* NF_3

Step 2: Determine the total number of valence electrons available from the group (A-group) numbers.

F

N

F F



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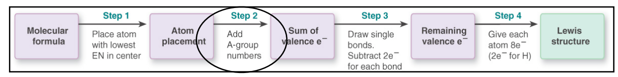


Lecture 16 - Lewis Structures

Using the “octet rule” to write Lewis Structures.

- Structures with single bonds, *e.g.* NF_3

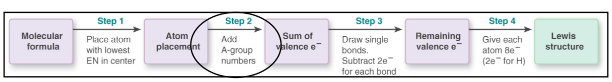
Step 2: Determine the total number of valence electrons available from the group (A-group) numbers.

- 1 X 5 for N + 3 X 7 for F = 26 valence e^-’s

F

N

F F



Lecture 16 - Lewis Structures

Using the “octet rule” to write Lewis Structures.

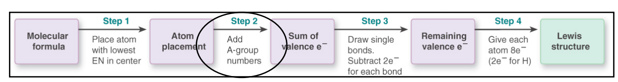
- Structures with single bonds, *e.g.* NF_3

Step 3: Draw a single bond from each surrounding atom to the central atom and subtract two valence e^-’s for each bond.

F

N

F F



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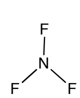
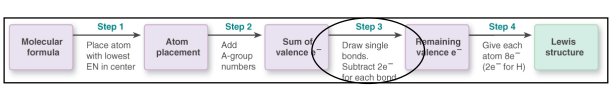




Lecture 16 - Lewis Structures

Using the “octet rule” to write Lewis Structures.

- Structures with single bonds, *e.g.* NF_3

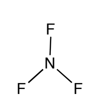
Step 3: Draw a single bond from each surrounding atom to the central atom and subtract two valence e^-’s for each bond.

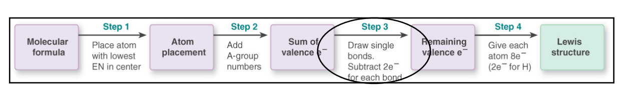
- 26 valence e^-’s – 3 X 2 for each bond = 20 e^-’s remaining

F

N

F F





Lecture 16 - Lewis Structures

Using the “octet rule” to write Lewis Structures.
- Structures with single bonds, *e.g.* NF_3

Step 4: Distribute the remaining electrons in pairs sot that each atoms ends up with eight electons (or 2 for H).
- Start with the surrounding atoms.

Lecture 16 - Lewis Structures

Using the “octet rule” to write Lewis Structures.
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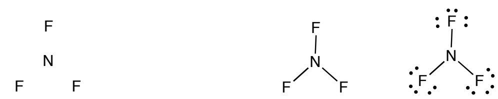

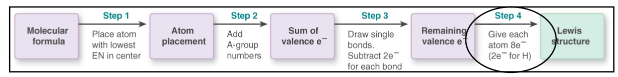

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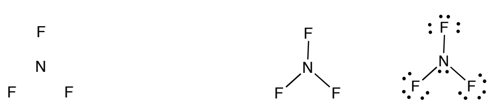
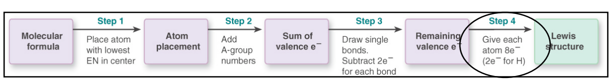
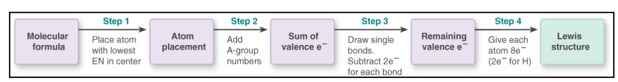




Lecture 16 - Lewis Structures

Some basic guidelines for drawing bonds:
- Hydrogen atoms form only one bond.
- Carbon atoms form four bonds.
- Nitrogen atoms form three bonds.
- Oxygen atoms form two bonds
- Halogens (F, Cl, Br, I) form one bond when they are the surrounding atoms.
  - fluorine is always a surrounding atom



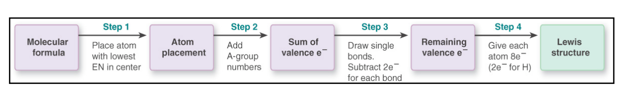
Lecture 16 - Question

Draw a Lewis structure of PH_4^+. (The number of valance electrons should be reduced by 1 e^- to give PH_4^+ its positive charge.)

Lecture 16 - Lewis Structures

For molecules with multiple bonds, there is an additional step
- After the first 4 steps, the central atoms will be left with a deficit of electrons (less than 8)

Step 5: If after step 4, the central atom still does not have an octet, make a multiple bond by changing a lone pair from one of the surrounding atoms into a bonding pair to the central atom.



Lecture 16 - Question

Draw a Lewis structure of the nitrate ion (NO_3^-):

Lecture 16 - Lewis Structures

Molecules with multiple bonds often have more than one possible structure.

- These are called resonance structures

If the resonance structures are equally probable, the true structure is usually considered as an average of the resonance structures

- This produces bonds with fractional bond orders.

Example:

- NO_3^- has three resonance structures.
- The average structure has 3 bonds, each with a bond order of 1 1/3.

Lecture 16 - Lewis Structures

Some molecules have resonance structures that are not equally probable.

- Calculating a formal charge for each atom in a Lewis structure can be used to distinguish which of the resonance structures is more probable.

Formal charges are calculated in a way similar to calculating oxidation numbers.

- However, instead of giving the bonding pairs of electrons to the more electronegative atom, they are instead, divided equally between the two atoms that share the electrons.

Lecture 16 - Lewis Structures

Calculating the formal charge:

Formal charge of atom =

no. of valence e^- – (no. of unshared valence e^- + 1/2 no. of shared valence e^-)

Example:

- NO_3^-.

Lecture 16 - Lewis Structures

The more probable resonance structure adhere to the following criteria:

- Smaller formal charges are preferred to larger ones.
- The same nonzero formal charge on neighboring atoms is not preferred.
- The more negative formal charge should reside on the more electronegative atom.

Example:

- Thiocynate (NCO^-).

Lecture 16 - Lewis Structures

There are some exceptions to the octet rule

- Electron deficient molecules that contain berylium or boron.
  - These atoms are not electronegative enough to form multiple bonds to solve this problem.
  - Even though berylium is a metal, it can form covalent molecules.

Examples:

- $BeCl_2$ and BF_3
  - Formal charges show that structures with multiple bonds are not as probable.

Lecture 16 - Lewis Structures

There are some exceptions to the octet rule

- Larger atoms (period 3 and higher), such as S and P, can form more than 4 bonds.
  - This is called an **expanded valence shell**
  - The empty outer *d* orbitals are used in addition to the *s* and *p* orbitals to hold valence electrons.

Examples

- SF_6, PCl_5.

Lecture 16 - Lewis Structures

An expanded valence shell can also be used to form multiple bonds

- Example: H_2SO_4.

The expanded valence shell model and formal charges may not always predict the most probable Lewis structure for these molecules.

Unit VI - Up Next

Lecture 17 - Molecular Shape and Polarity

- Using the Valence-Shell Electron-Pair Repulsion (VSEPR) Theory to predict molecular shapes
- Molecular shape and polarity

The End