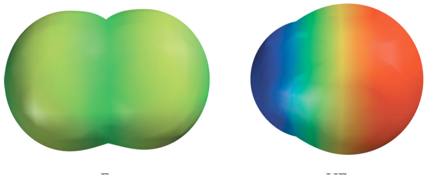
Ch09

# Electronegativity

Sharing isn’t always equal sharing.

Fine tuning the electronic structure of molecules.

version 1.5



# Electronegativity

- Bond Polarity
  - Covalent bonds
    - electron affinity
    - polar covalent bonds
  - Electronegativity
    - Pauling values
    - bond polarity, ΔEN
      - covalent, ΔEN = 0-0.4
      - polar covalent, ΔEN = 0.4-2.0
      - ionic, ΔEN = 2.0+
  - Dipole moment
    - μ = qr
    - percent ionic character
- Writing Lewis Structures
  - Five Steps.
    - Take stock.
    - Draw a skeleton.
    - Distribute Electrons.
    - Push Electrons.
    - Evaluate Result.

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  - What formal charge is not
  - How to calculate formal charge
  - Formal Charge indicates the best possible structure
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- Exceptions to the Octet Rule
  - Odd Electron Systems
  - That prefer less than 8
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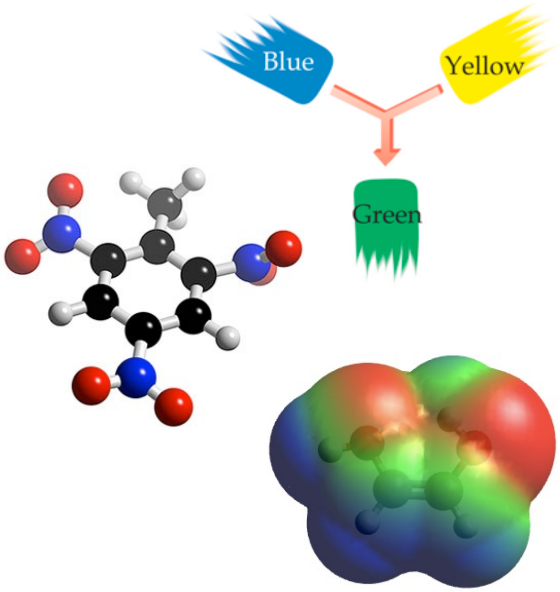
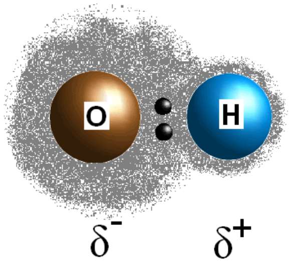
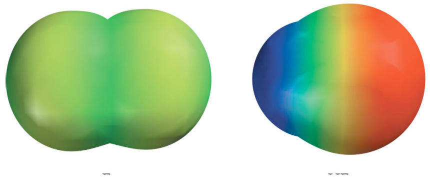
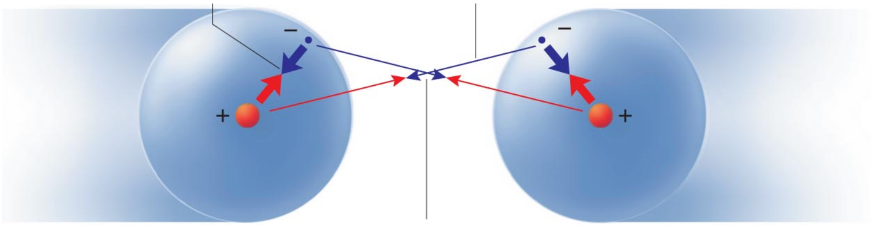
  - What multiple bonds mean.
  - Bond Lengths
  - Bond Energies
    - Enthalpy of Reactions



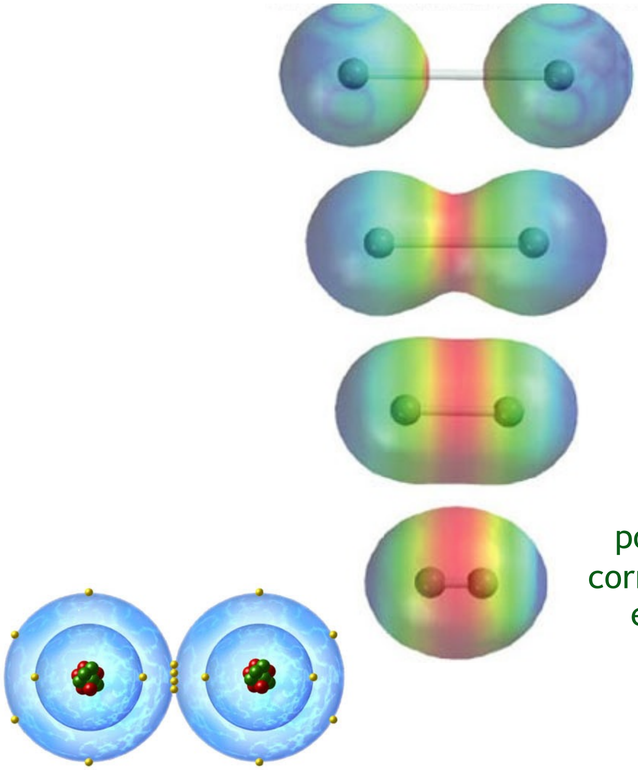




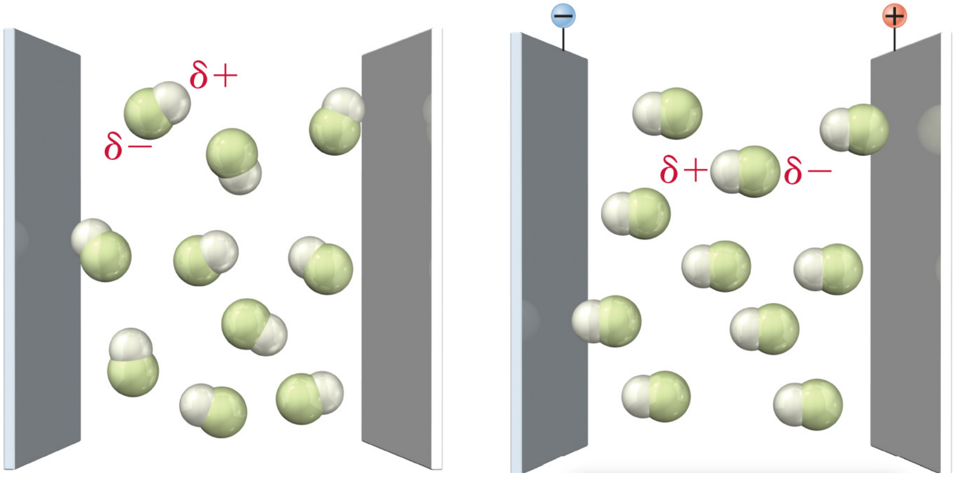
# Covalent Bonds



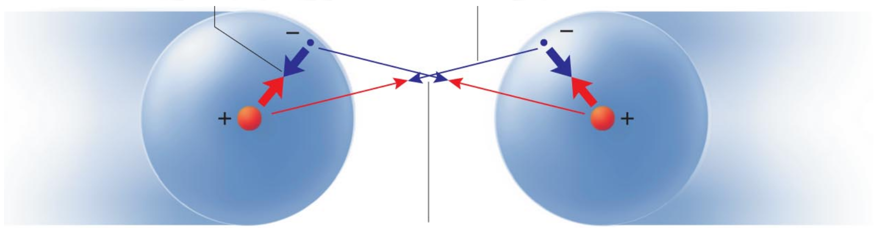
- Covalent Bonds are a result of atoms pulling on each others electrons.
- The atoms lock into a fixed distance from each other, entangling their orbitals.
- The shared electrons complete each atoms octet, making a stable combined arrangement of electrons.
- Some molecules placed in a electric field don’t spin.
  - These molecules share electrons symmetrically, there is no positive of negative end to align with the field.
- Other molecules spin and align with the field.
  - These molecules must have a positive and negative end.
  - They don’t share electrons symmetrically.



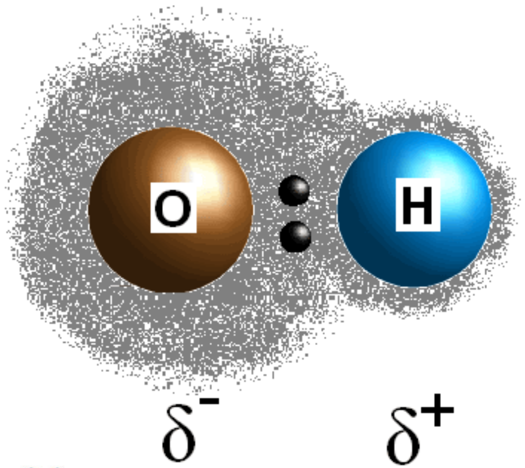
(in electrostatic potential maps red corresponds to greater electron density, blue indicates lesser density)

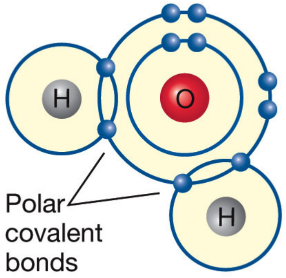


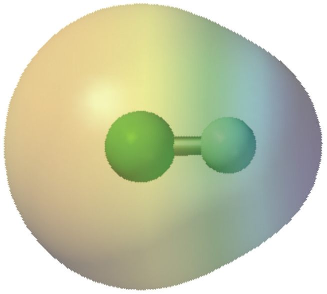
# Polar Covalent Bonds

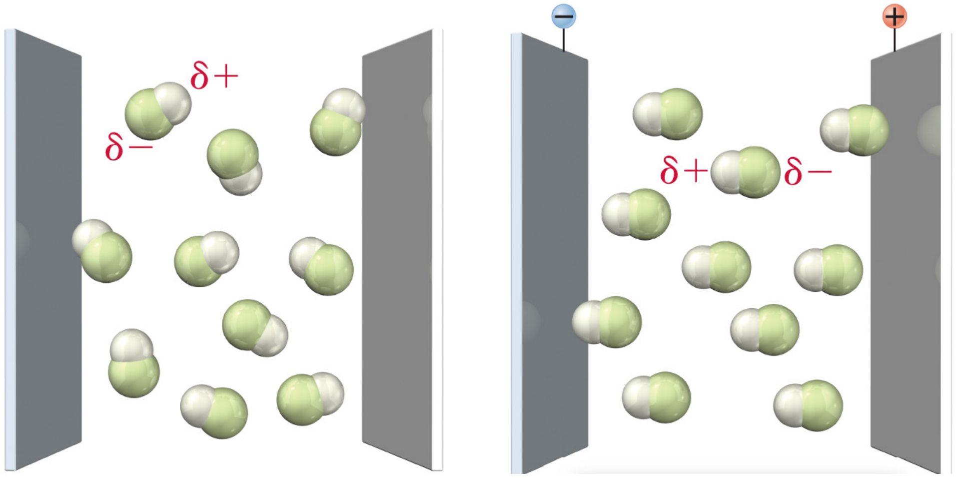


- Pure covalent bonds are symmetric.
  - Not all covalent bonds are pure.
- Sometimes one atom pulls stronger on the shared electrons than the other.
- Polar covalent bonds are covalent bonds with asymmetric sharing of the bonding pair.



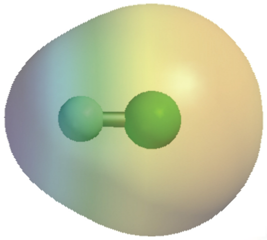


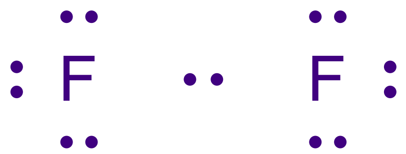


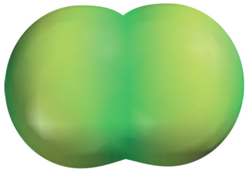


# Energy of Polar Covalent Bonds

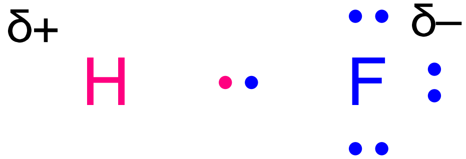
- It takes 436 kJ to break the covalent bond in $F_2$.
  - Each F is holding the electrons with 218 kJ.
    - ½ of 436 kJ = 218 kJ
- It takes 155 kJ to break the covalent bond in $H_2$.
  - Each H is holding the electrons with 77.5 kJ.
    - ½ of 155 kJ = 77.5 kJ
- So how strong is a HF bond?
  - You'd think 218 kJ + 77.5kJ = 296 kJ — it's not.
  - It's actually more.  It's 565 kJ.
- The two atoms of HF don't act equally.
- Linus Pauling suggested that Fluorine will pull more on the shared electrons between it and hydrogen, resulting in them being pulled deeper into fluorine's shell, resulting in a partial separation of charge.
  - δ (lower case delta) indicates a charge less than 1.
  - The partial separation of charge provides an electrostatic attraction between atoms.
    - The resulting bond is partly ionic and partly covalent.
- Polar covalent bonds are covalent bonds with some ionic character.
- Pure covalent bonds are covalent bonds with no ionic character.

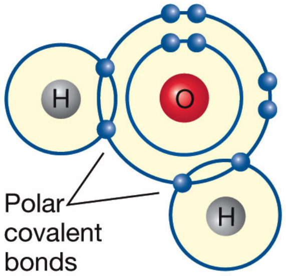


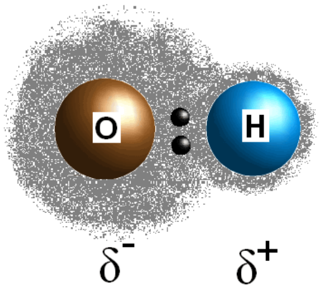


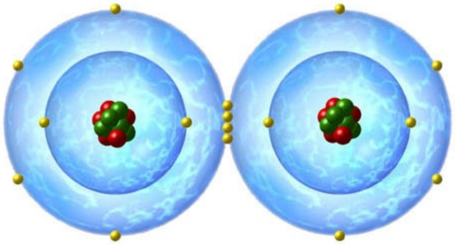


H •• H







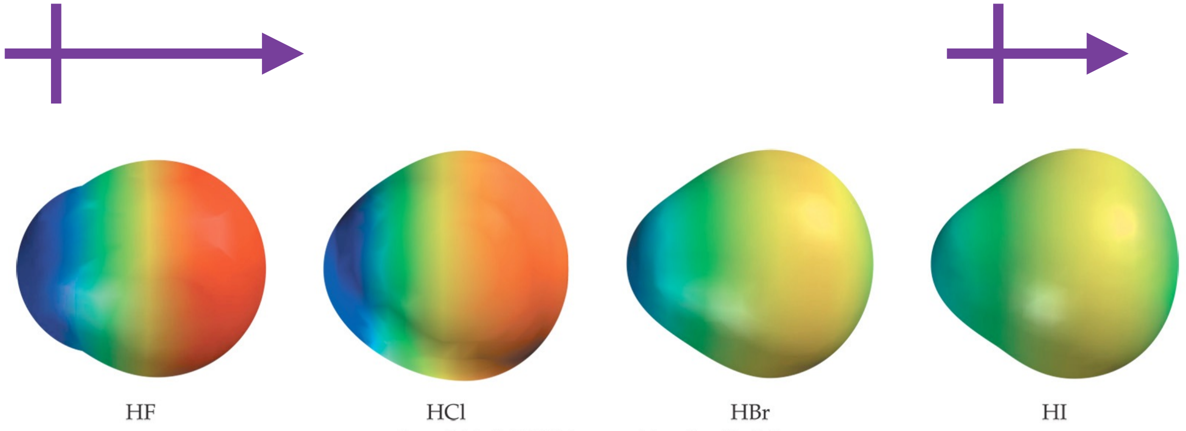


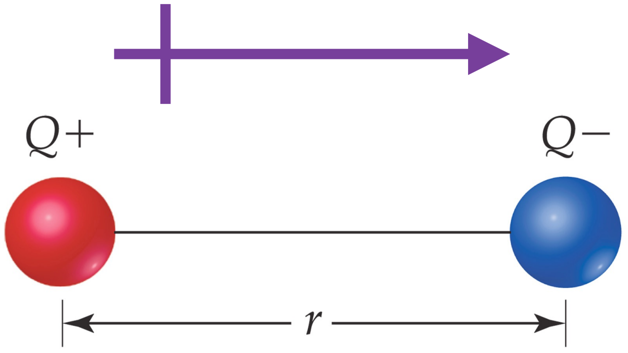
# Bond Dipoles

- A separation of charge causes a dipole moment.
- The dipole moment, μ, produced by two equal but opposite charges separated by a distance, r, is calculated:

$$\mu = Qr$$

- Dipoles are measured in debyes (D).
- Q is measured in coulombs (C), r in meters (m).
- Dipoles are indicated graphically by an arrow pointing from the positive charge to the negative charge, with a cross on the positive end of the arrow.
- Polar covalent bonds have partial separation of charge, therefore have a dipole.
- The size of the dipole is indicated by the length of the arrow.
    - Longer arrows induce a larger dipole.
- To put numbers to polarity and dipoles we need a measure of the partial charge separation that occurs in polar covalent bonds.

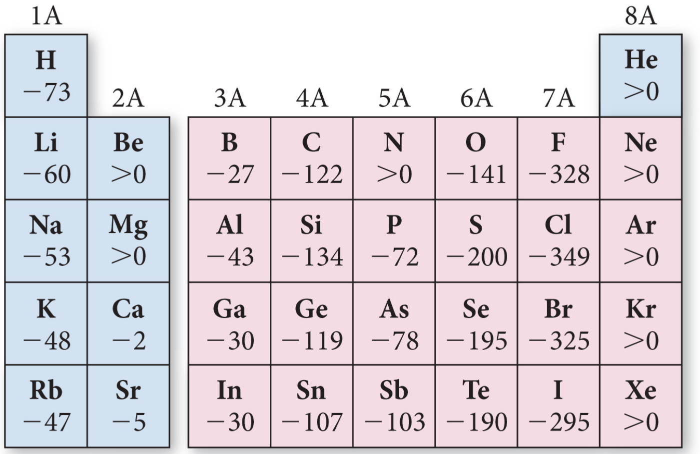




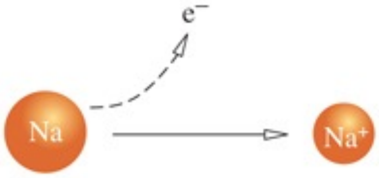
# Electron Affinity (EA)

- Electron affinity is the energy released by adding an electron to an atom.
- Covalent bonding is a result of sharing electrons between atoms with high electron affinity.
- Less energy is released as we go down the periodic table.
- More energy is released as we go across the periodic table (left to right).
  - Noble Gases have a positive EA, no energy is released when they accept an electron.
    - They aren't very reactive.
  - Non-metals tend to have high EA, we get a lot of energy by giving them electrons.
    - Pure non-metals tend to be very reactive, they even react with themselves.
    - $N_2$, $O_2$, $Cl_2$, $Br_2$

**Electron Affinities (kJ/mol)**



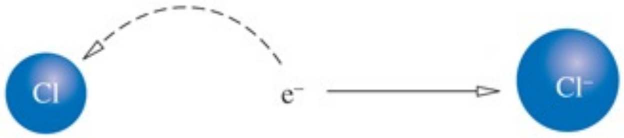
| 1A | 2A | 3A | 4A | 5A | 6A | 7A | 8A |
|---|---|---|---|---|---|---|---|
| **H**<br>−73 | | | | | | | **He**<br>>0 |
| **Li**<br>−60 | **Be**<br>>0 | **B**<br>−27 | **C**<br>−122 | **N**<br>>0 | **O**<br>−141 | **F**<br>−328 | **Ne**<br>>0 |
| **Na**<br>−53 | **Mg**<br>>0 | **Al**<br>−43 | **Si**<br>−134 | **P**<br>−72 | **S**<br>−200 | **Cl**<br>−349 | **Ar**<br>>0 |
| **K**<br>−48 | **Ca**<br>−2 | **Ga**<br>−30 | **Ge**<br>−119 | **As**<br>−78 | **Se**<br>−195 | **Br**<br>−325 | **Kr**<br>>0 |
| **Rb**<br>−47 | **Sr**<br>−5 | **In**<br>−30 | **Sn**<br>−107 | **Sb**<br>−103 | **Te**<br>−190 | **I**<br>−295 | **Xe**<br>>0 |



## Ionization Energy (IE)

$\Delta H$ = +496 kJ/mol — endothermic

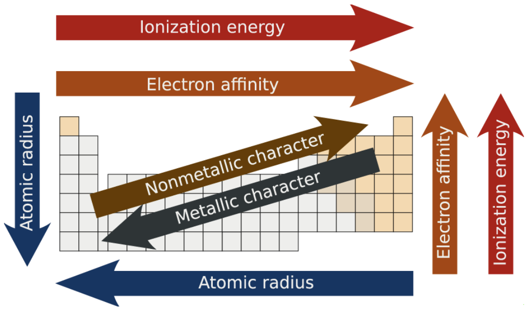
forming cations *consumes* energy



## Electron Affinity (EA)

$\Delta H$ = -349 kJ/mol — exothermic

forming anions *releases* energy



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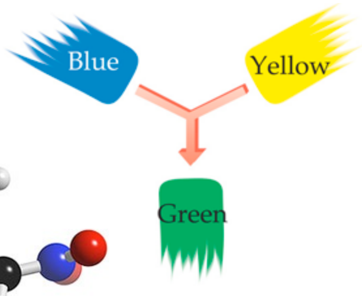
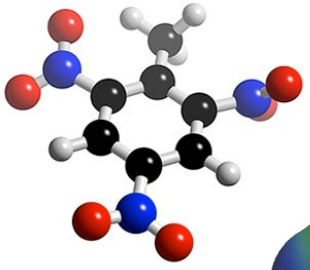
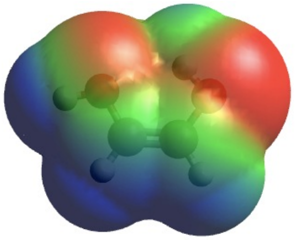
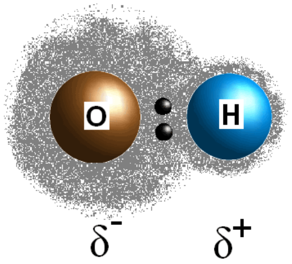
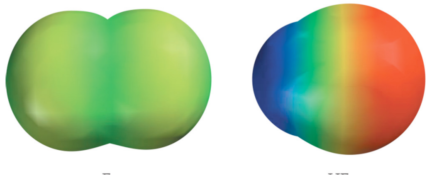




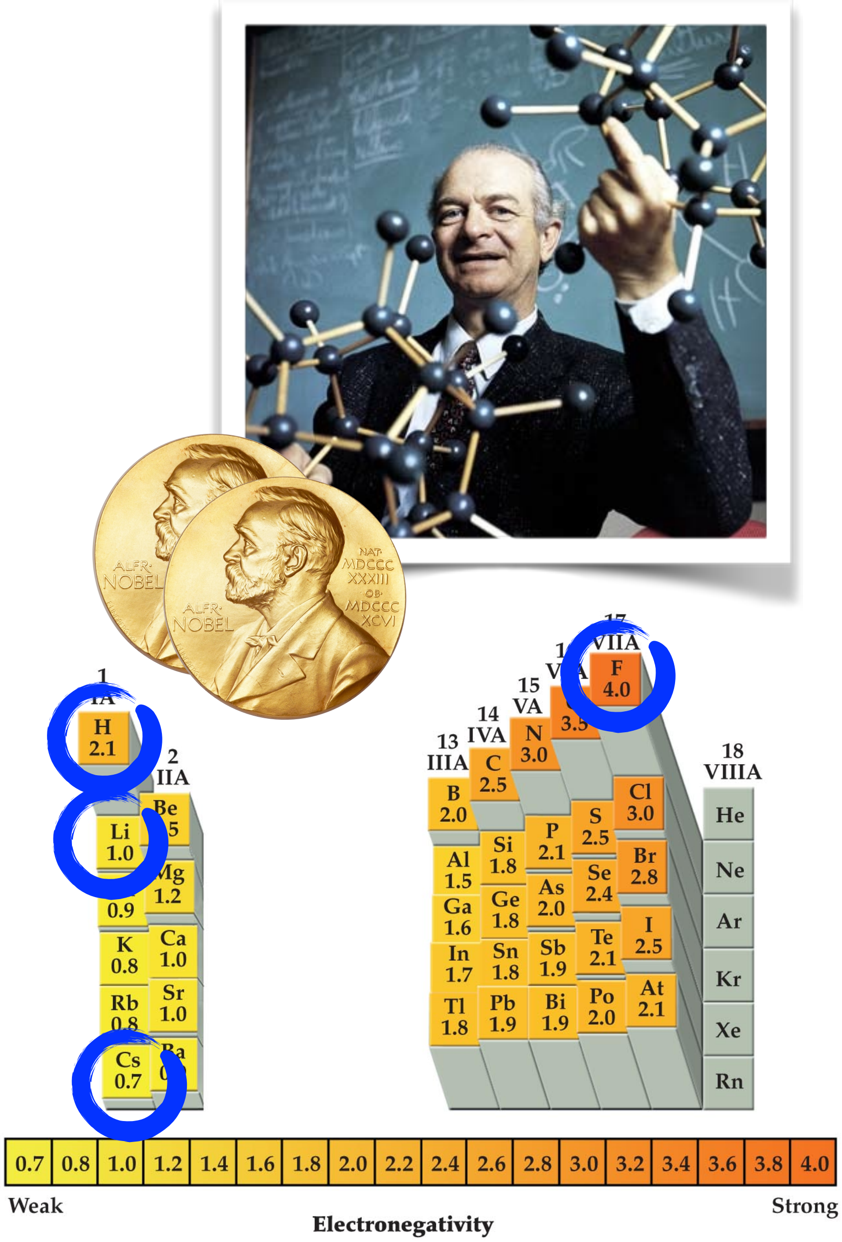






# The Pauling Electronegativity Scale

- Electronegativity is a property of atoms <u>within a molecule</u> that is related to the electron affinity of that element.
- Electronegativity is the relative strength of an element pulling on electrons within the molecule.
- Unlike Electron Affinity and Ionization Energy…
    - Electronegativity is not measured in units of energy.
    - Electronegativity is not a threshold to forming ions.
- The electronegativity scale was established by CalTech professor Linus Pauling in 1932.
- Pauling was awarded the Nobel Prize in 1954 “for his research into the nature of the chemical bond” … and was also awarded the Nobel Peace Prize in 1962 for his work towards ending nuclear bomb testing.
- Linus Pauling is the only person to have every won two unshared Noble prizes.
- Electronegativity numbers are in Pauling units.  Units are not shown.
- The electronegativity scale was established by looking at ratios of polar covalent bond strengths.
- You need to <u>memorize four electronegativity</u> values:
    - The values are based by the arbitrary assignment of 4.0 to Fluorine and 1.0 to Lithium.
        - As you go across the second period each element differs by 0.5.
    - Cesium has he lowest electronegativity of 0.7.
    - Hydrogen has a value of 2.1

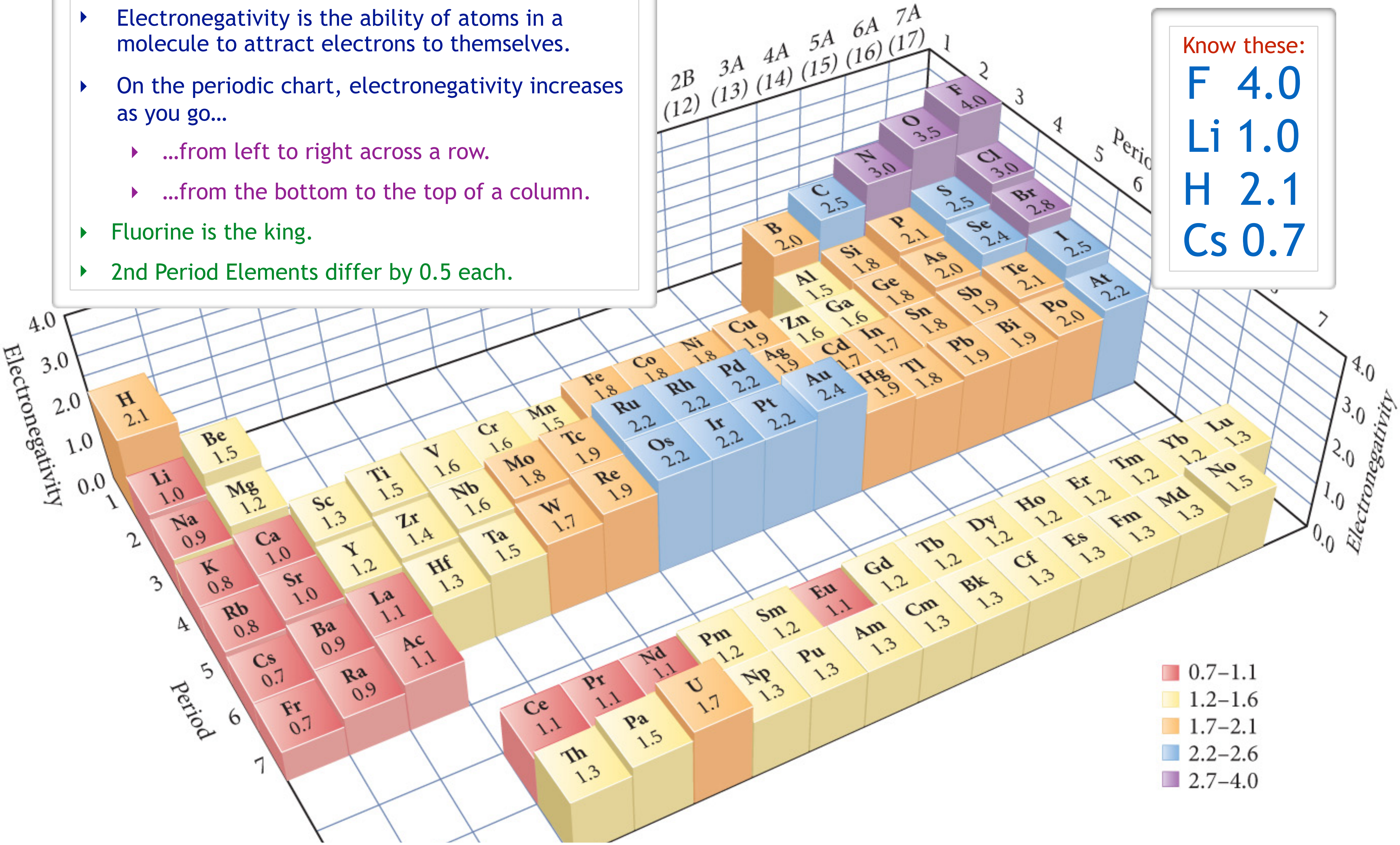


# Electronegativity Trends

- Electronegativity is the ability of atoms in a molecule to attract electrons to themselves.
- On the periodic chart, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.
- Fluorine is the king.
- 2nd Period Elements differ by 0.5 each.

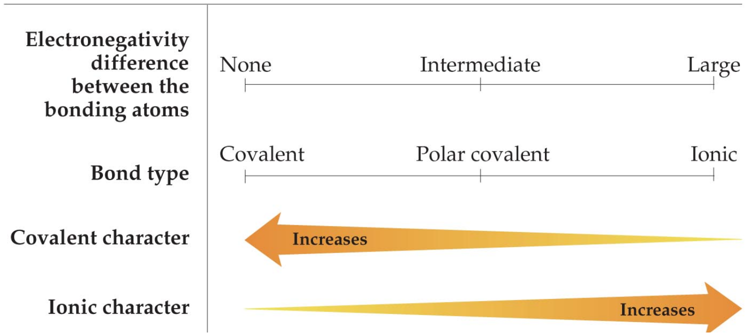
Know these:

F 4.0
Li 1.0
H 2.1
Cs 0.7



# Identifying Bonding Types

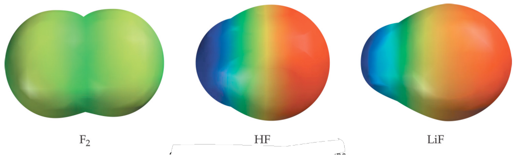
- Lewis dot structures assume all bonds are covalent bonds.
- They’re not.
- Bonding indicated by Lewis structures may turn out to be either:
  - Covalent (no dipole on the bond)
  - Polar Covalent (dipole along the bond)
  - Ionic (bond snaps and atoms become charged)
- Use the difference in electronegativity (ΔEN) to estimate the bond type.
  - The line between covalent & polar covalent is ΔEN >= 0.4
  - The line between polar covalent & ionic is ΔEN >= 2.0
    - Important: These lines are not exact, depending on the molecular structure there are many exceptions. But this is where we’ll draw the lines for purposes of this class.

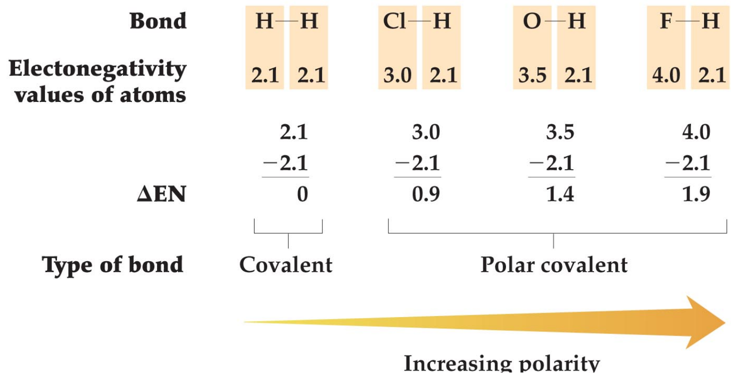


| Electronegativity difference between the bonding atoms | None | Intermediate | Large |
|---|---|---|---|
| Bond type | Covalent | Polar covalent | Ionic |

Covalent character — Increases

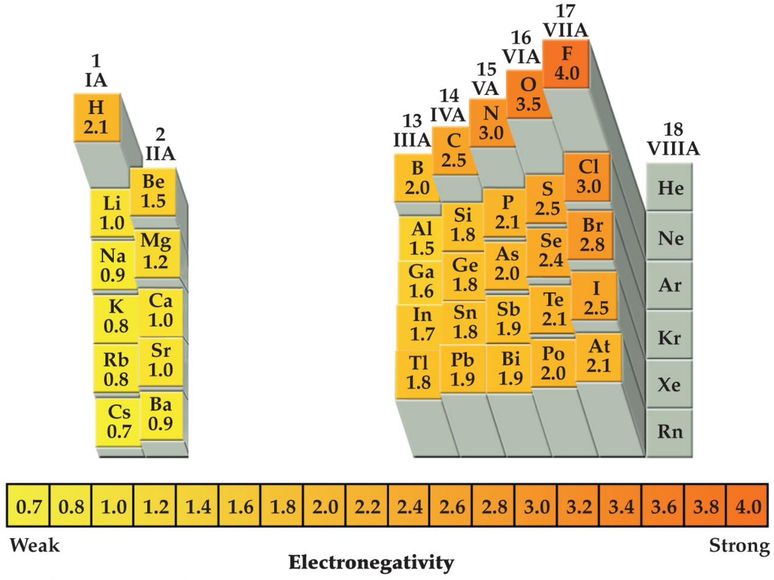
Ionic character — Increases

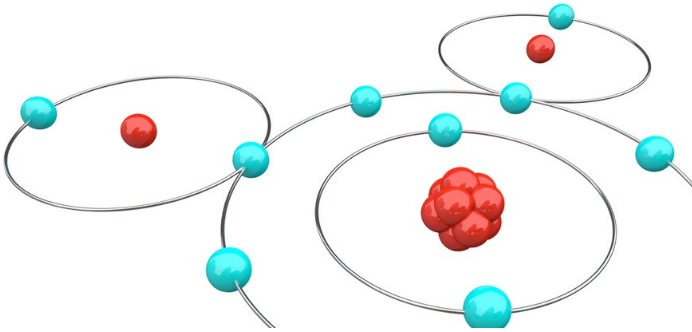




| Bond | H—H | Cl—H | O—H | F—H |
|---|---|---|---|---|
| Electonegativity values of atoms | 2.1 2.1 | 3.0 2.1 | 3.5 2.1 | 4.0 2.1 |
| ΔEN | 2.1 −2.1 0 | 3.0 −2.1 0.9 | 3.5 −2.1 1.4 | 4.0 −2.1 1.9 |
| Type of bond | Covalent | Polar covalent | | |

Increasing polarity





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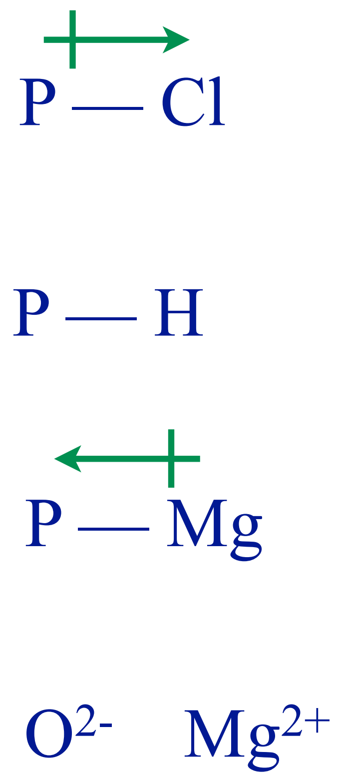
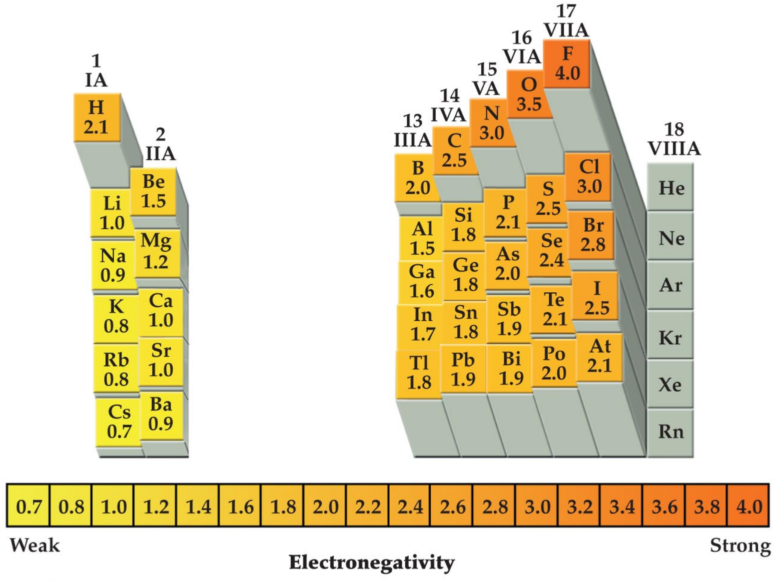


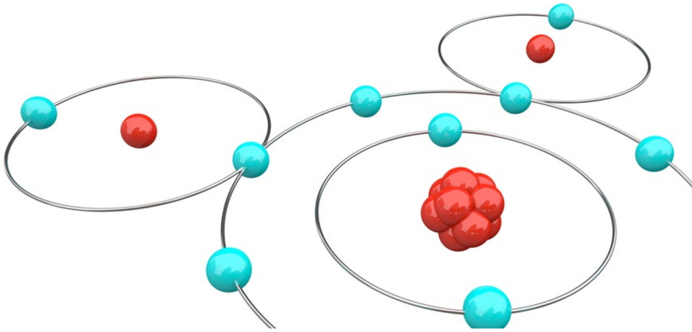
($PCl_3$) P — Cl ΔEN = 0.9 Polar Covalent

($PH_5$) P — H ΔEN = 0 Covalent

($Mg_3P_2$) P — Mg ΔEN = 0.9 Polar Covalent

(MgO) $O^{2-}$ $Mg^{2+}$ ΔEN = 2.3 Ionic





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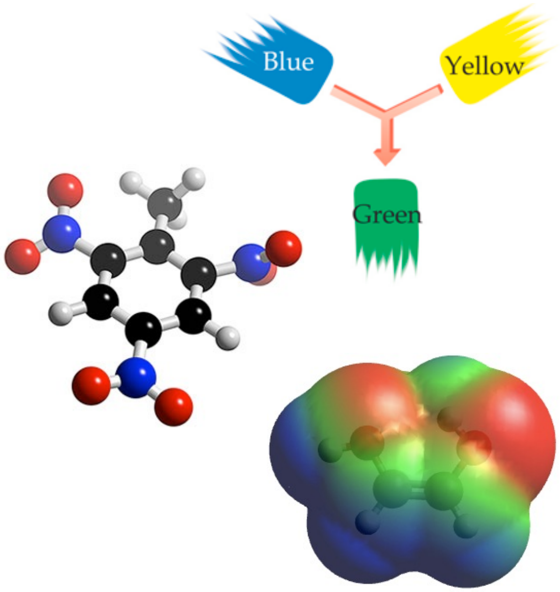
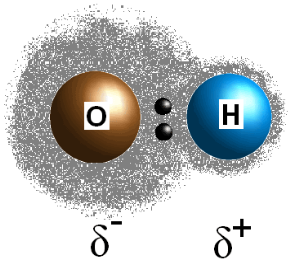
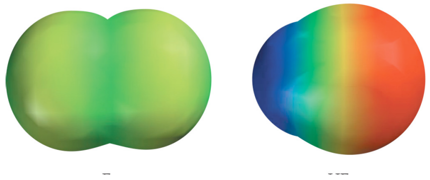


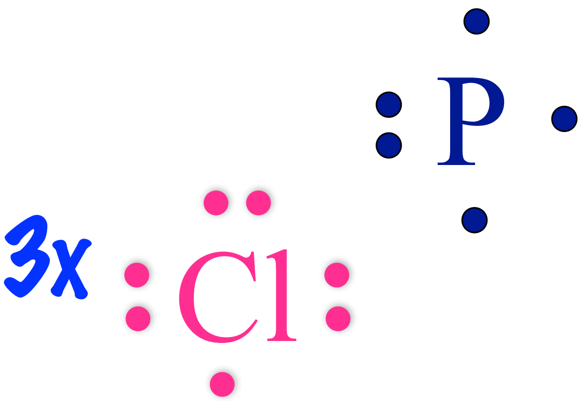


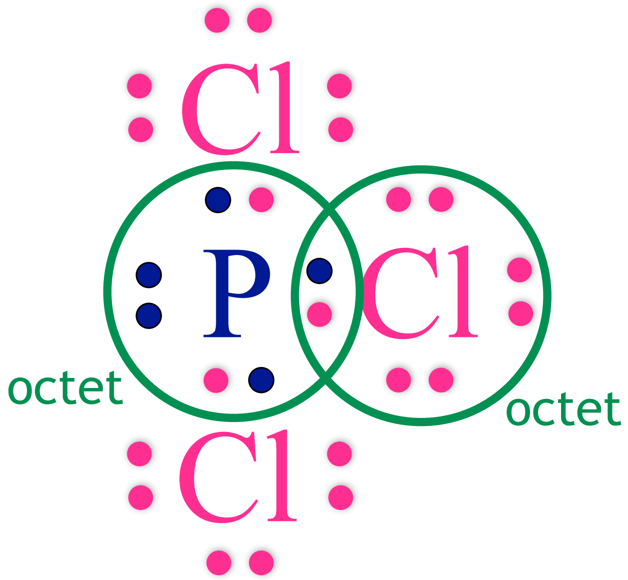


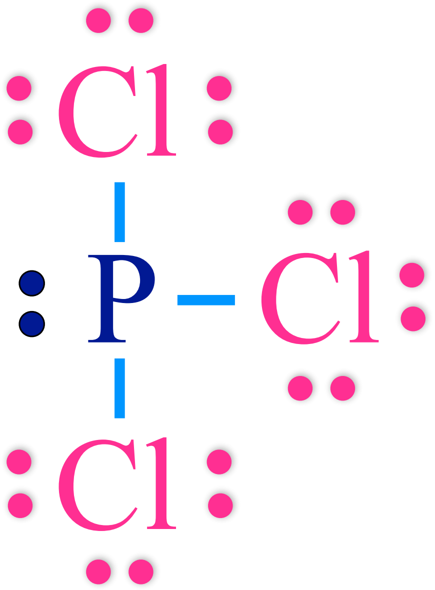
# Lewis Structures

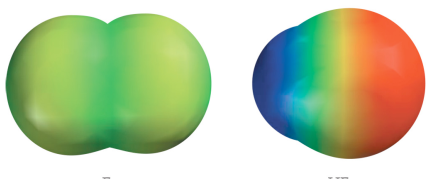
- A compound is formed by creating bonds between atoms.
- A compound is the result of atoms entangling their valence electrons, forming bonds.
- A Lewis structure is a description of a compound that shows where all the electrons of the atoms end up when the valence shells of the atoms entangle (form bonds).
- Good Lewis structures allow each atom to see an octet of electrons.
- A good Lewis structure is an accurate predictor of where bonds form in a compound.
- It helps us understand where bonds occur.
- Electrons group in pairs. Pairs are either shown as two dots or a single line.

$PCl_3$









# How to make a Lewis Structure:

- Lewis structures are created by pooling all the electrons in a compound or ion and assigning them to bonds (shared electrons) and lone pairs (electrons dedicated to one atom).
- Use these five steps:
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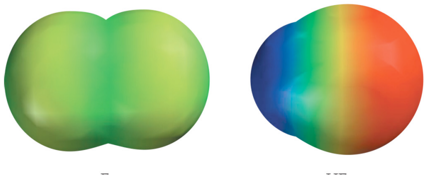
    - (if needed)
  - Step 5: Show any Charge

$CH_2O$



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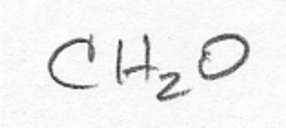

$CH_2O$

1. **Take Stock:** Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
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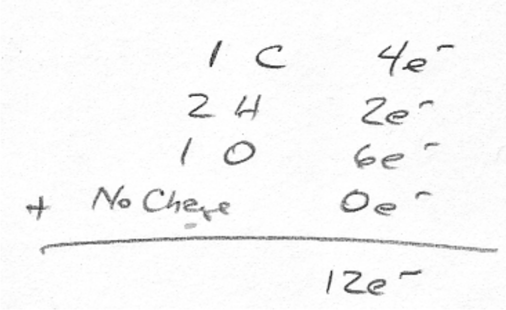
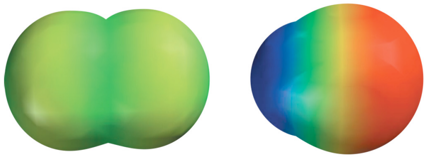


| | |
|---|---|
| 1 C | $4e^-$ |
| 2 H | $2e^-$ |
| 1 O | $6e^-$ |
| + No Charge | $0e^-$ |
| | $12e^-$ |



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|---|---|---|
| | 1 C | $4e^-$ |
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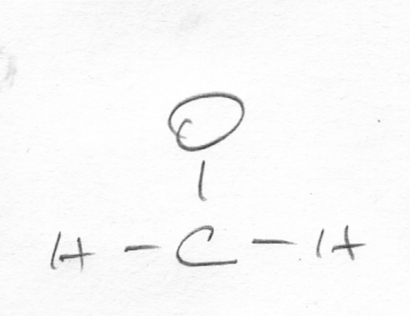
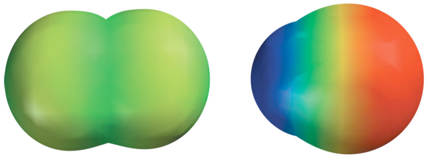
| + | No Charge | $0e^-$ |
| | | $12e^-$ |
| − | 3 bonds | $6e^-$ |
| | | $6e^-$ |

$CH_2O$



2. Draw a Simple Skeleton: The central atom is the *least* electronegative element that isn't hydrogen. Connect the outer atoms to it by single bonds.



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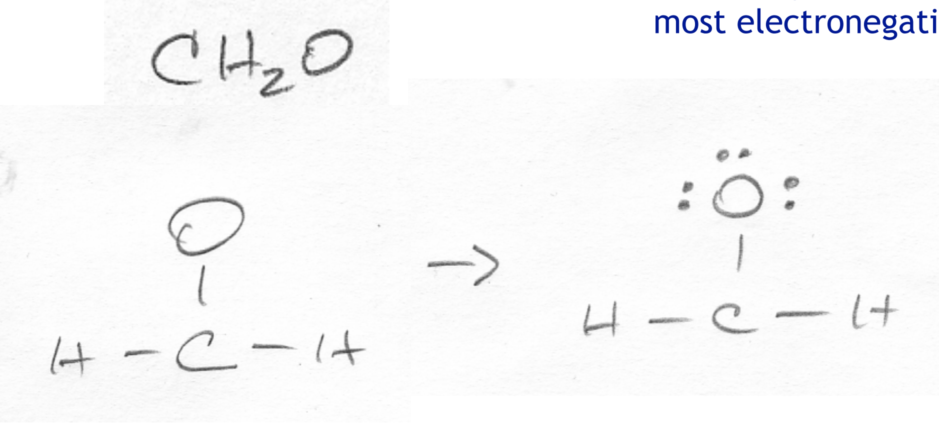
    - (if needed)
  - Step 5: Show any Charge

3. **Fill in the Octets:** Use the rest of the electrons to fill in the octets of remaining atoms, starting with the most electronegative atoms.



1 C $4e^-$
2 H $2e^-$
1 O $6e^-$
+ No Charge $0e^-$

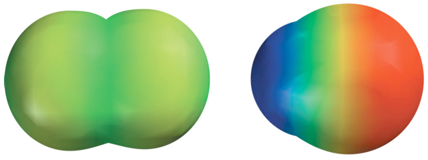
$12e^-$

− 3 bonds $6e^-$

$6e^-$

− 3 lp's $6e^-$

0



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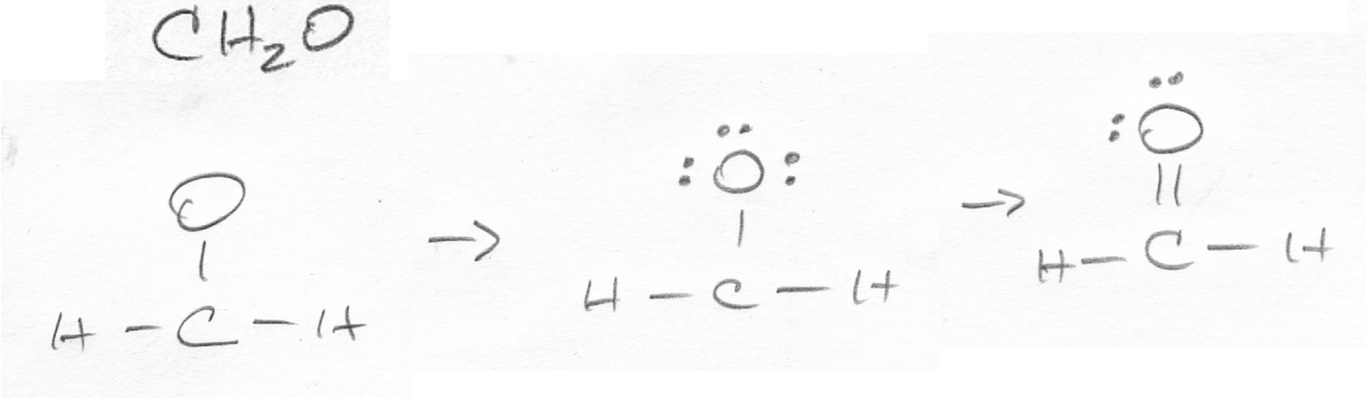

| | | |
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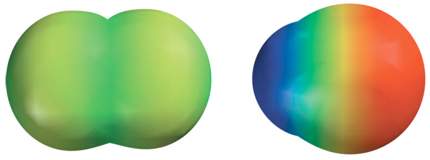
| | 1 O | $6e^-$ |
| + | No Charge | $0e^-$ |
| | | $12e^-$ |
| − | 3 bonds | $6e^-$ |
| | | $6e^-$ |
| − | 3 lp's | $6e^-$ |
| | | 0 |

4. **Push LP’s into Bonds:** If you run out of electrons before the central atom has an octets — form multiple bonds until it does.



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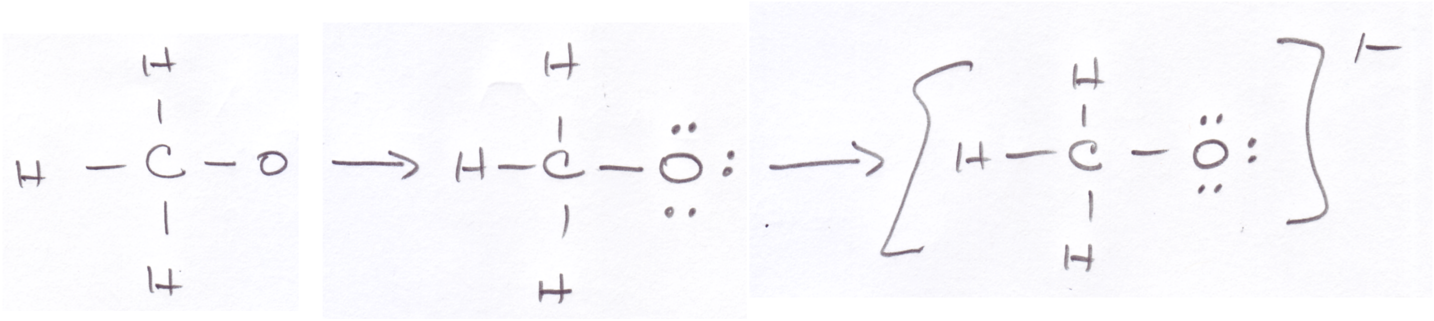
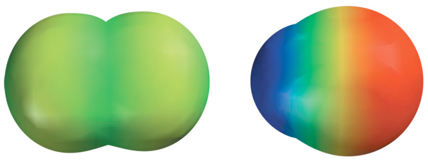
    - (if needed)
  - Step 5: Show any Charge

| | |
|---|---|
| C | $4e^-$ |
| 3 (H) | $3e^-$ |
| O | $6e^-$ |
| -1 chg | $1e^-$ |
| | $14e^-$ |

| | |
|---|---|
| 4 bonds | $8e^-$ |
| | $6e^-$ |

$CH_3O^-$





# Try these…

- (1) Take Stock:
  - Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
    - If it is an anion, add one electron for each negative charge.
    - If it is a cation, subtract one electron for each positive charge.
- (2) Draw a skeleton:
  - The central atom is the least electronegative element that isn't hydrogen.
  - Look for chains or group hints in the formula.
  - Connect the atoms by single bonds (only).
- (3) Pass out the rest of the electrons:
  - Fill the octets of the outer atoms (most electronegative).
  - Fill the octet of the central atoms (least electronegative).
- (4) Push electrons:
  - If you run out of electrons before everyone has an octet…

    …form multiple bonds until they do.
- (5) Assign charge:
  - Show any overall charge.
  - Look at formal charge.
    - For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
    - Subtract that from the number of valence electrons for that atom: the difference is its formal charge.

$CO_2$

$CH_3OH$

$CH_3CO_2^-$

$NH_3$

$HCN$

$C_2H_4$

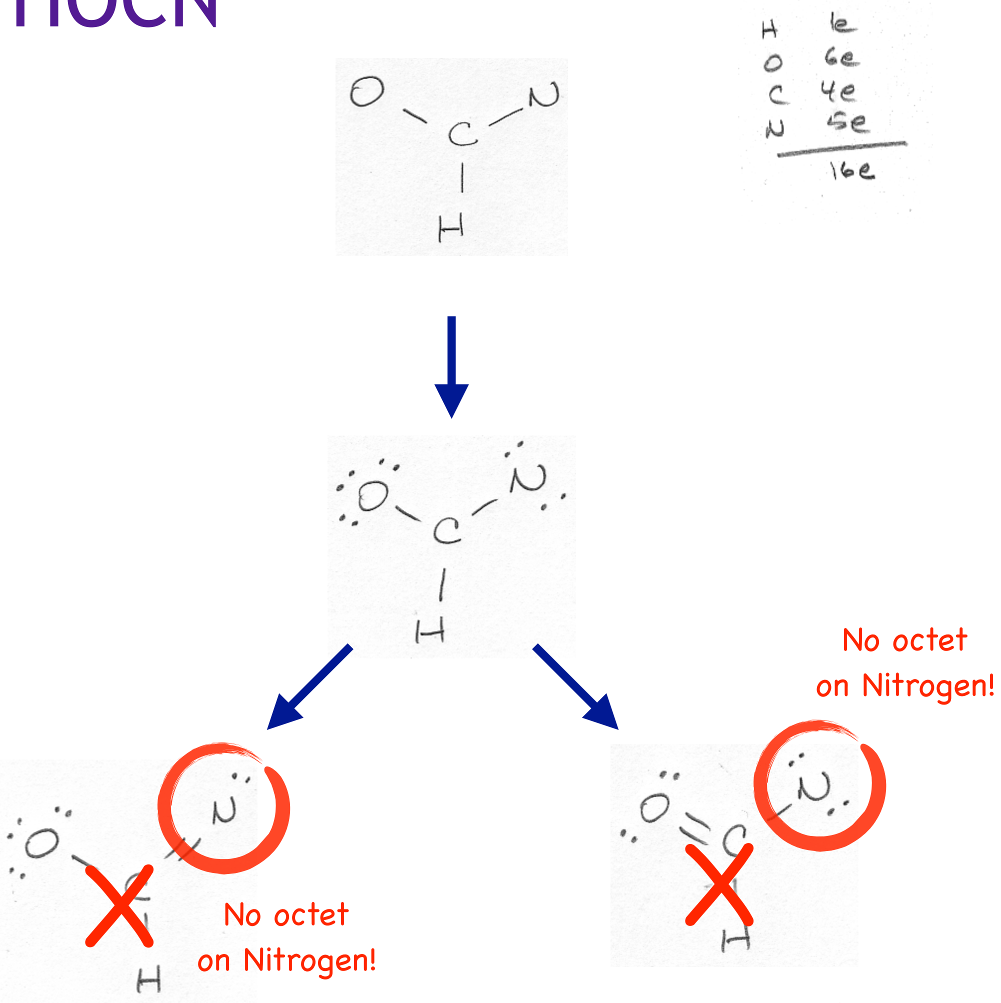
$NH_4^+$

$CHOCH_3$

# Some skeleton's won't give you a valid structure.

- Use these five steps:
  - Step 1: Take Stock
  - Step 2: Draw a Simple Skeleton
  - Step 3: Fill in the Octets
  - Step 4: Push LP's into Bonds
    - (if needed)
  - Step 5: Show any Charge

## HOCN



No octet on Nitrogen!

No octet on Nitrogen!

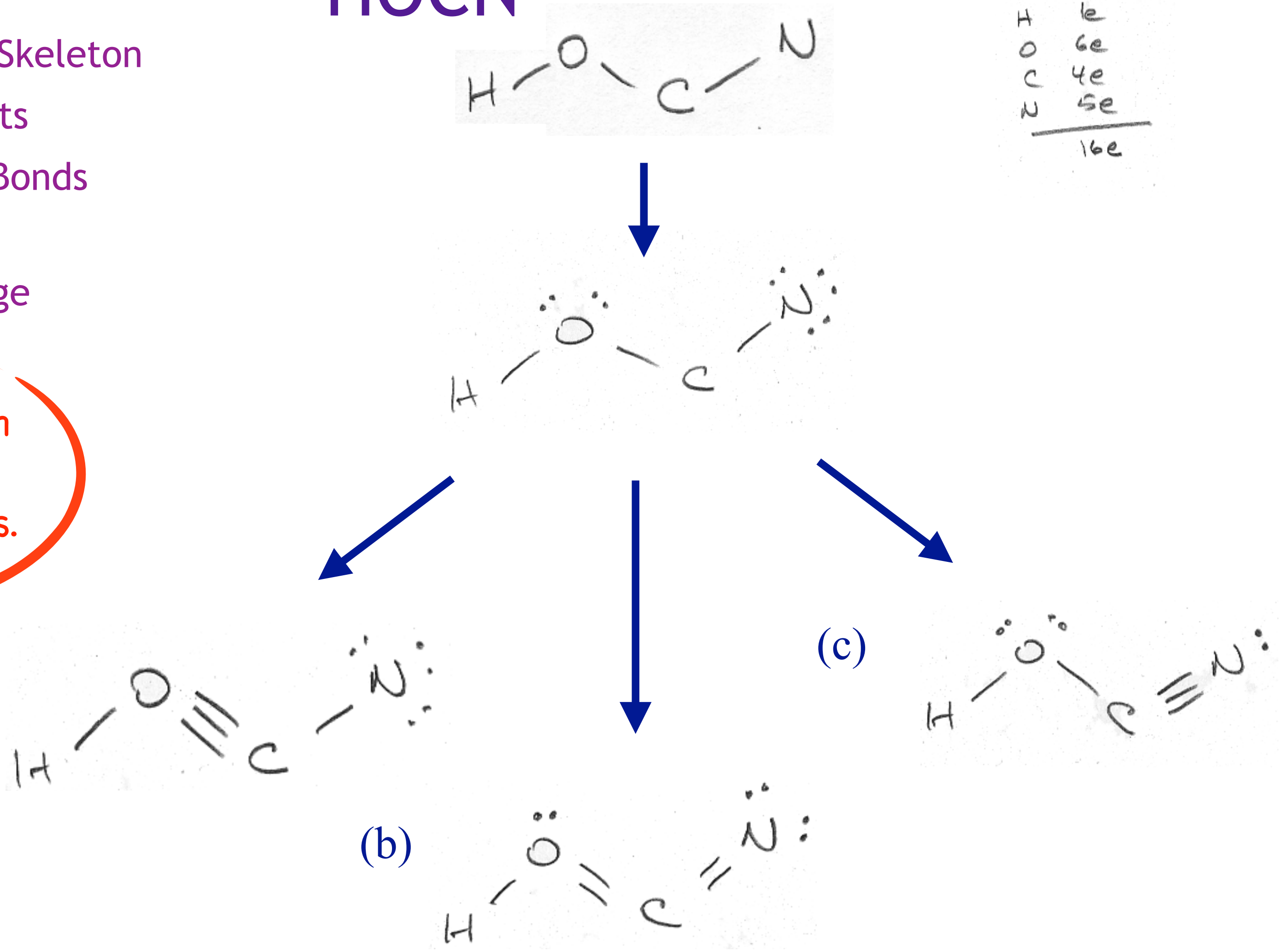
Neither structure is good.
Start over.

# … and sometimes you'll get more than one.

- Use these five steps:
  - Step 1: Take Stock
  - Step 2: Draw a Simple Skeleton
  - Step 3: Fill in the Octets
  - Step 4: Push LP's into Bonds
    - (if needed)
  - Step 5: Show any Charge

Formal charge can help us compare possible structures.

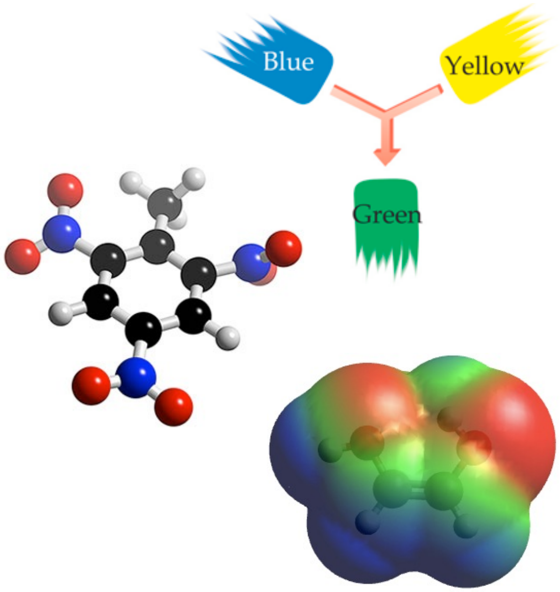
HOCN

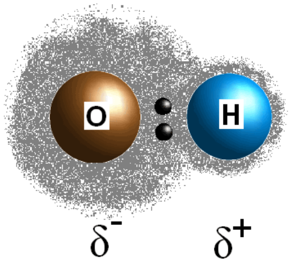


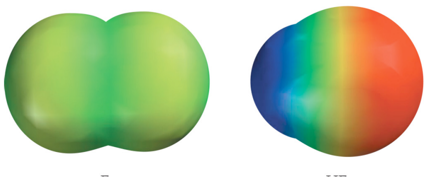
H 1e
O 6e
C 4e
N 5e
16e

# Electronegativity

- Bond Polarity
  - Covalent bonds
    - electron affinity
    - polar covalent bonds
  - Electronegativity
    - Pauling values
    - bond polarity, ΔEN
      - covalent, ΔEN = 0-0.4
      - polar covalent, ΔEN = 0.4-2.0
      - ionic, ΔEN = 2.0+
  - Dipole moment
    - $\mu = qr$
    - percent ionic character
- Writing Lewis Structures
  - Five Steps.
    - Take stock.
    - Draw a skeleton.
    - Distribute Electrons.
    - Push Electrons.
    - Evaluate Result.
- Resonance & Formal Charge
  - What formal charge is not
  - How to calculate formal charge
  - Formal Charge indicates the best possible structure
  - Resonance
- Exceptions to the Octet Rule
  - Odd Electron Systems
  - That prefer less than 8
  - Expanded Octets (more than 8)
- Bond Thermodynamics
  - What multiple bonds mean.
  - Bond Lengths
  - Bond Energies
    - Enthalpy of Reactions





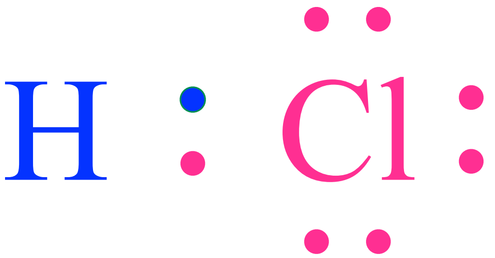


# What Formal Charge is not.

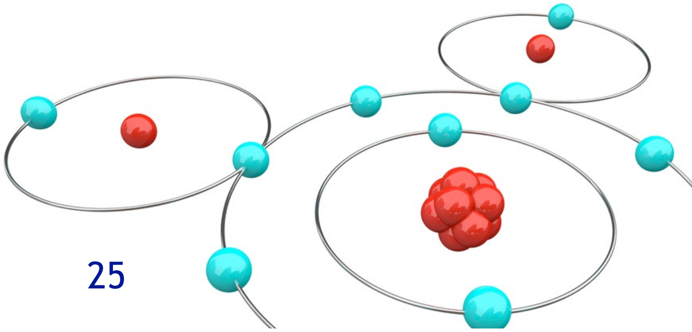
- Formal Charge is not checking the octet.
  - When we build a Lewis structure, we try and make sure every atom is in a comfortable neighborhood.
  - Checking the octet is about finding out if atom sees the correct number of electrons around it.
  - This is not formal charge.
    - Chlorine has an octet, this has nothing to do with it’s formal charge.
- Formal Charge is not oxidation number.
  - When we do redox chemistry, we ask ourselves what charge would an atom end up with if we broke every bond to create separate ions.
  - Chlorine normally has a -1 charge.
  - This is not formal charge.
    - It’s oxidation number is -1, this has nothing to do with it’s formal charge.

Formal charge can help us compare possible structures.

HCl



| | | |
|---|---|---|
| Valence | 2e (duet) | 8e (octet) |
| Oxidation Number: | +1 | -1 |
| Formal Charge: | 0 | 0 |



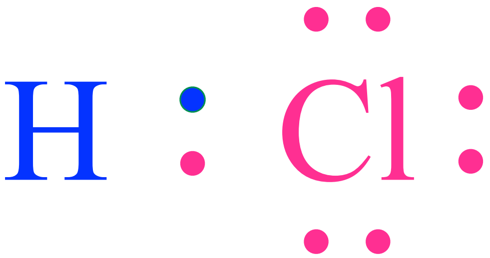
# What Formal Charge is.

- Formal Charge is the formal "ownership" of electrons.
  - When we hypothesize a Lewis structure, we ask ourselves what price atoms paid to enter into that cooperative arrangement.
  - We ask ourselves how many electrons it ended up owning, and how many did it start with.
    - The difference is formal charge.
      - ( # electrons in lone pairs + ½ in each of it's bonds - valence electrons for it's neutral atom )
    - Note: Any gains for one atom must be paid by another, so the sum of all formal charges must equal the total charge on the molecule or ion.
  - The higher the price, the less likely atoms will enter into that structure — formal charge let's us evaluate possible Lewis structures.

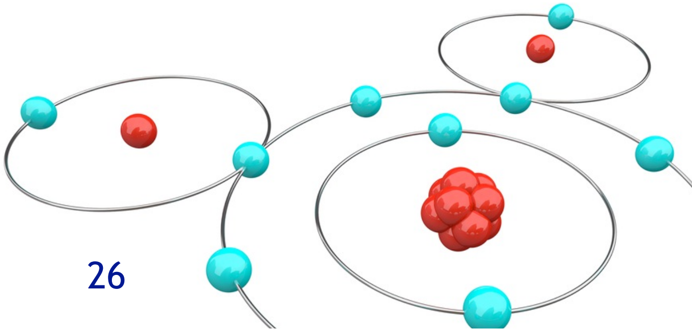
- Formal Charge tells us what each atom gave up or gained to create the shared arrangement in the molecule.
- Everyone wants an octet, but formal charge tells us what price was paid to get that octet.

Formal charge can help us compare possible structures.

HCl



| | | |
|---|---|---|
| Valence | 2e (duet) | 8e (octet) |
| Oxidation Number: | +1 | -1 |
| Formal Charge: | 0 | 0 |



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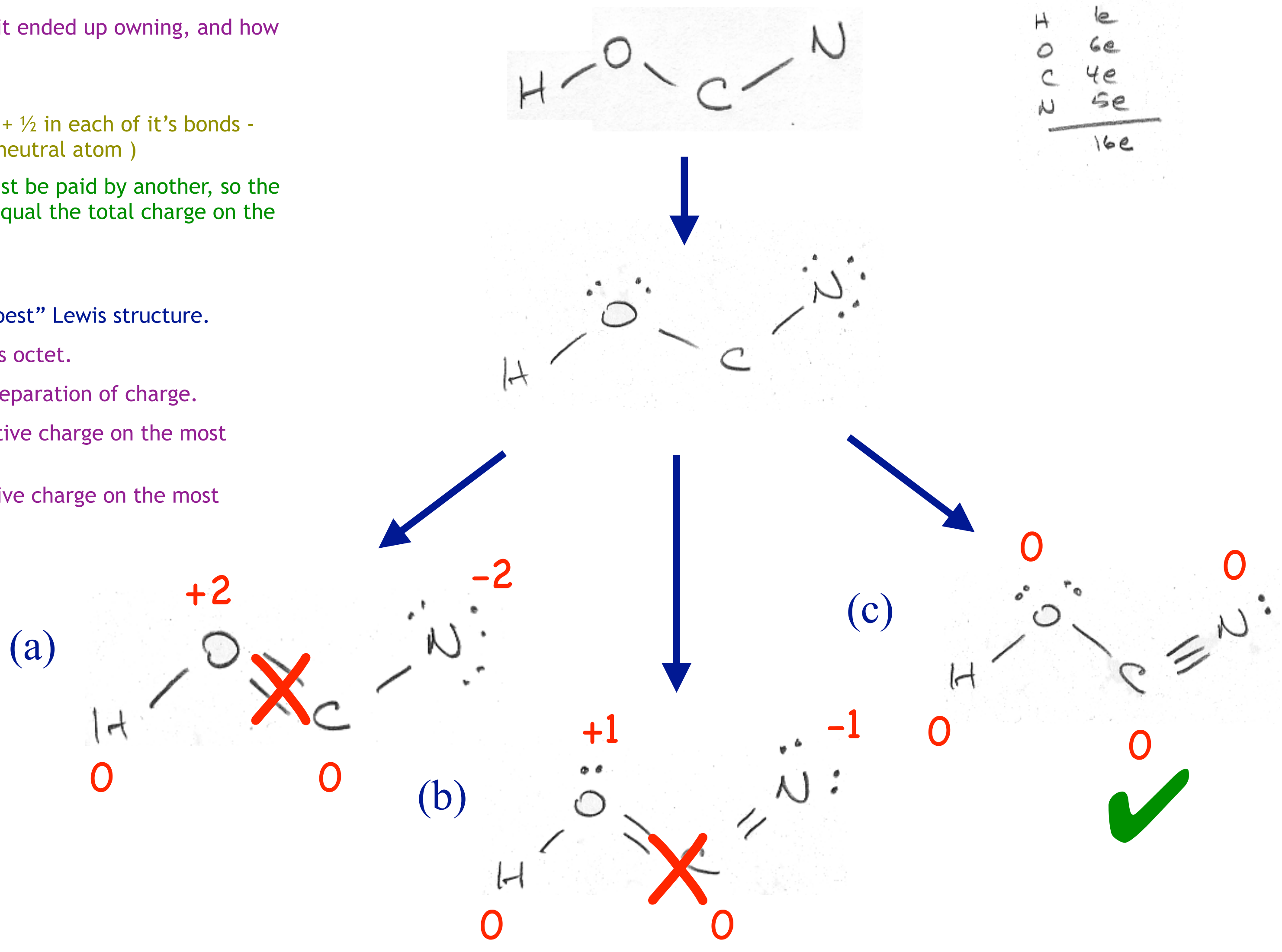
    - Note: Any gains for one atom must be paid by another, so the sum of all formal charges must equal the total charge on the molecule or ion.

- Formal charge can be used to identify the “best” Lewis structure.
  - The best structure satisfies each atoms octet.
  - The best structure has a minimum of separation of charge.
  - The best structure places formal negative charge on the most electronegative elements.
  - The best structure places formal positive charge on the most electropositive elements.

## HOCN



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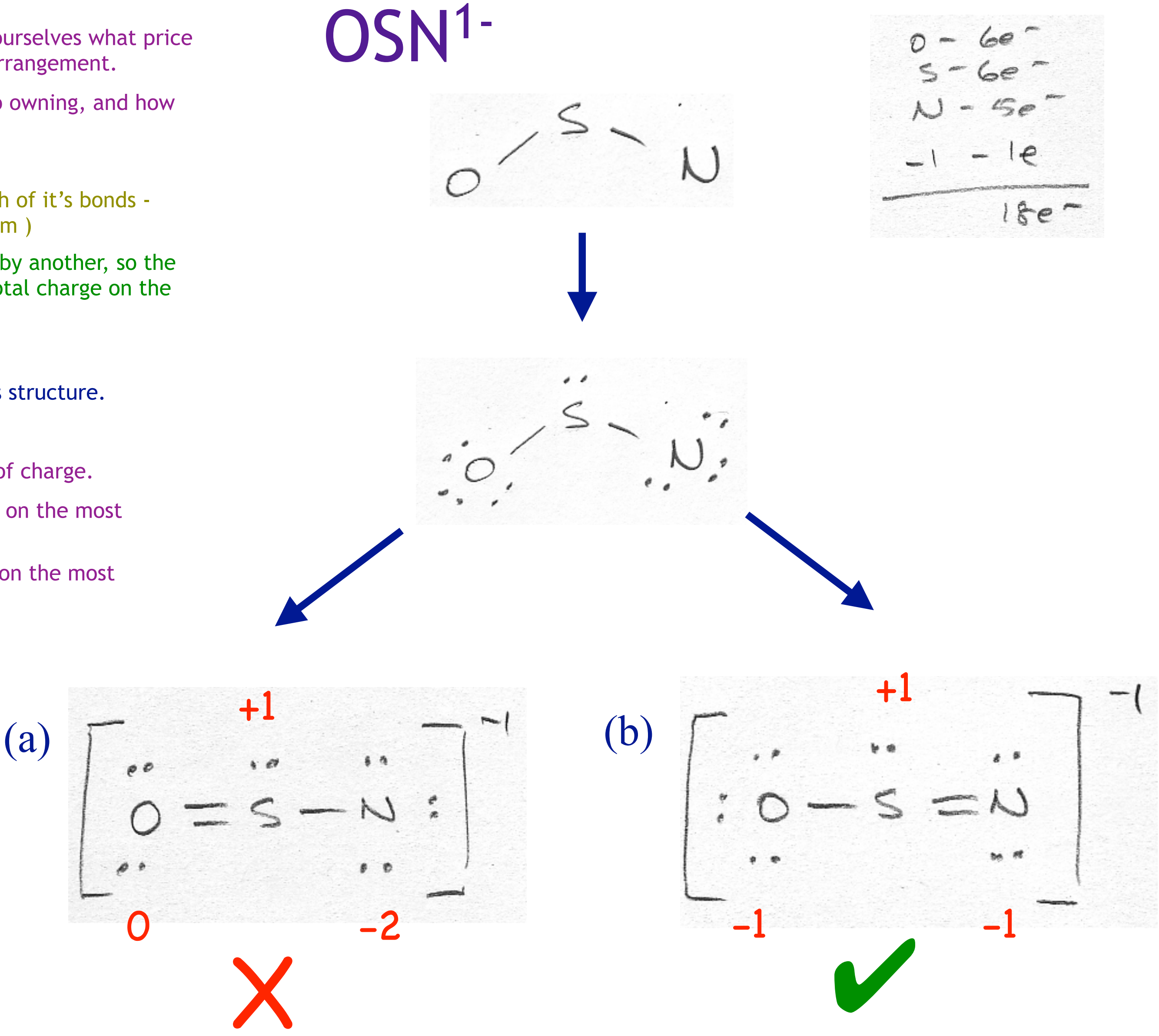
$OSN^{1-}$



O - 6e⁻
S - 6e⁻
N - 5e⁻
-1 - 1e
18e⁻

Formal charge can help us compare possible structures.

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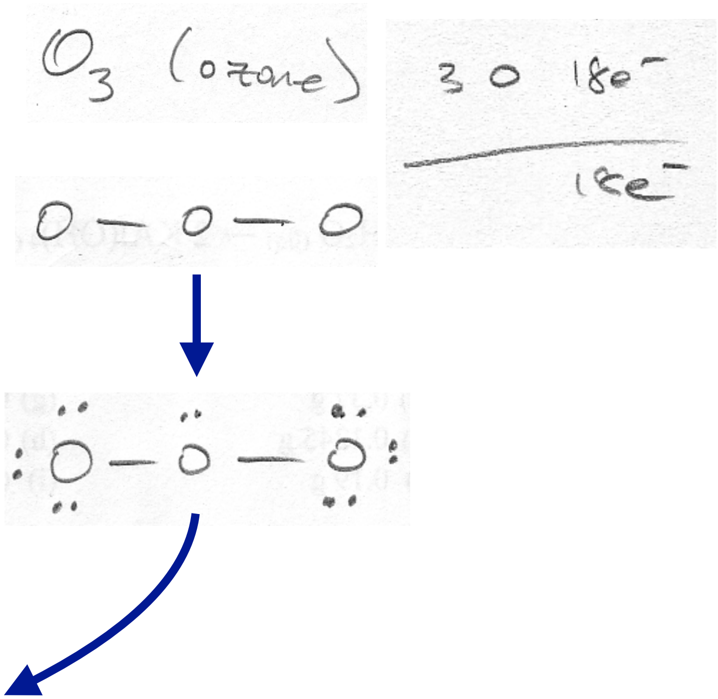
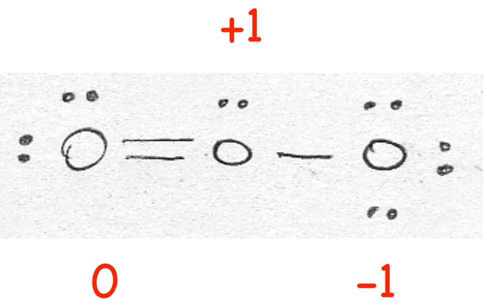
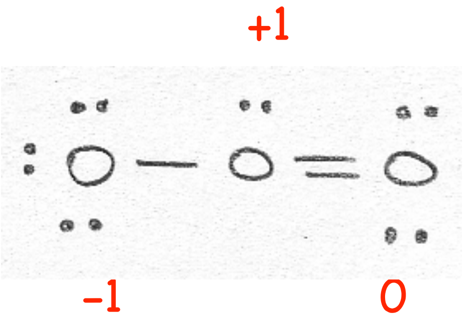


(a)



(b)



Let's look at experiment...

# Resonance Structures

- Our Lewis analysis suggests that:
  - One of the two oxygen — oxygen bonds should be a double bond.
    - Double bonds are shorter and have more electron density between the atoms.
  - One of the terminal oxygen atoms should have greater electron density around it.
    - Three lone pairs of oxygen on one, only two on the other.
- In ozone ($O_3$) we find experimentally:
  - Both bond lengths are the same.
    - And the bond length is some where between what we'd expect for a double bond and single bond.
  - Electron density is evenly spread over both terminal atoms.
- We conclude the structure is neither A nor B, but a blending of the two.

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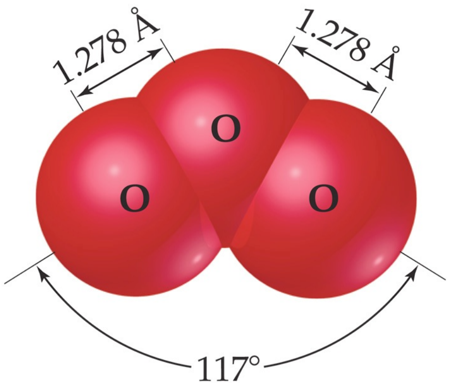

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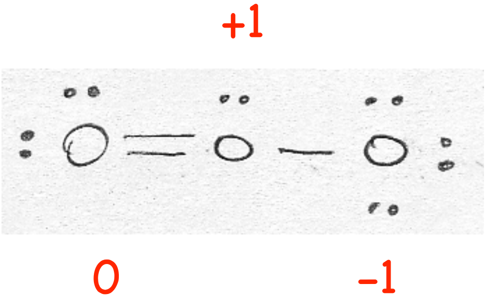

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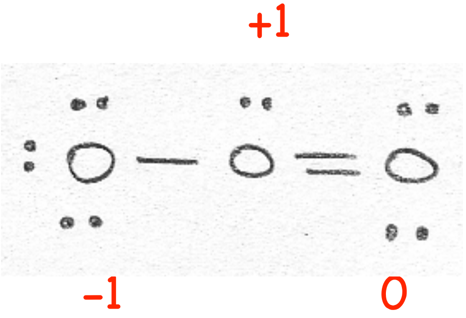

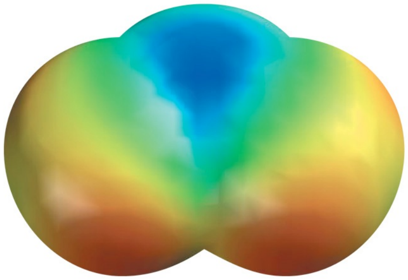

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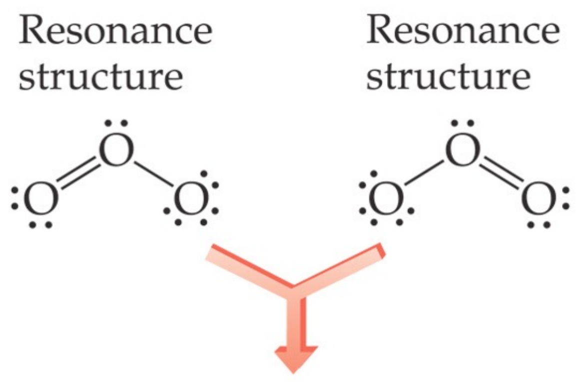
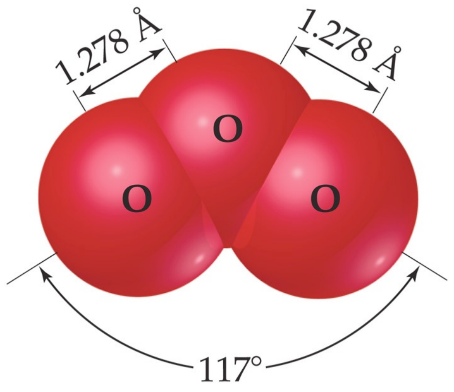
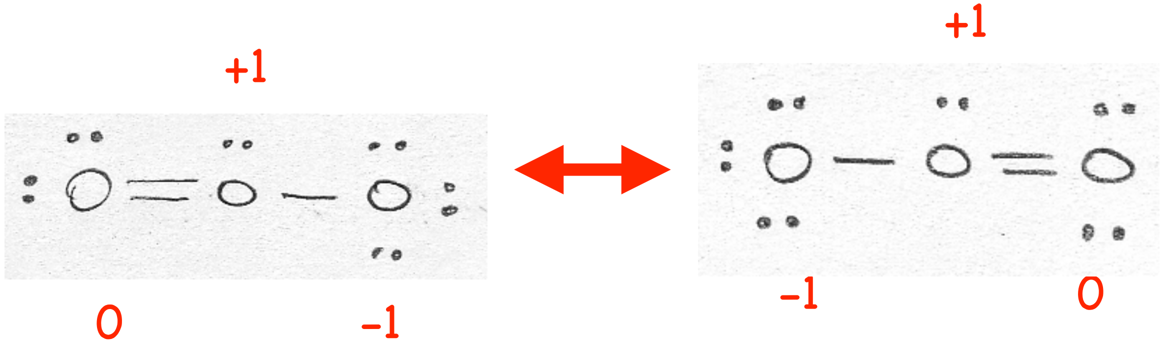
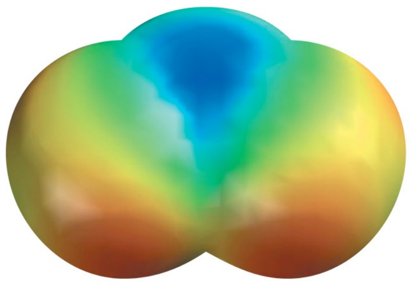
- Resonance structures are two or more structures that represent aspects of a more complex structure. We use ↔ to indicate resonance structures.



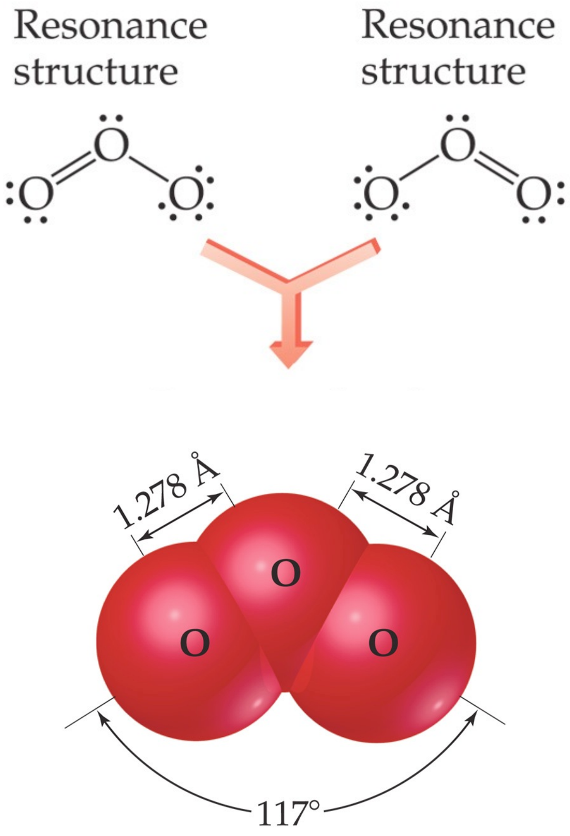


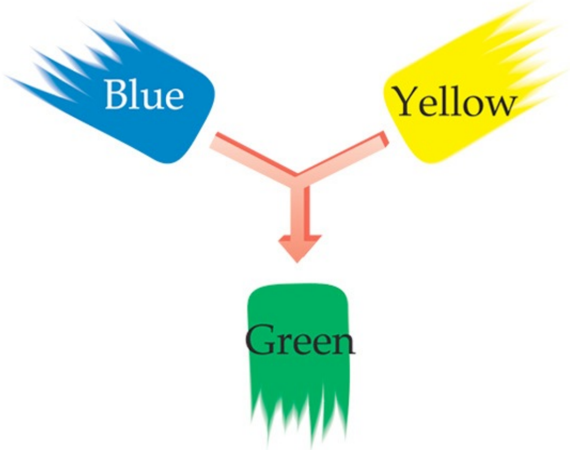


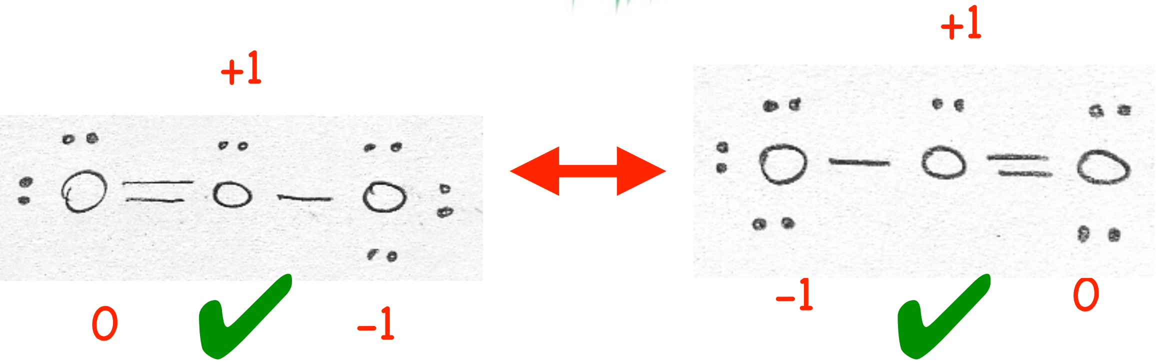


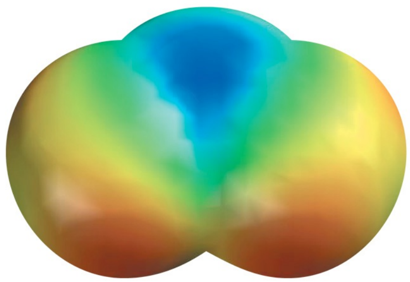
# Resonance Structures

- Resonance structures are two or more structures that represent aspects of a more complex structure. We use ↔ to indicate resonance structures.
  - Note: the two structures do not interconvert. It’s not like equilibrium where things are going back and forth.
  - Instead, the double headed arrow indicates that the single true structure lies between the two or more extremes.
  - The true structure is a blending of the simpler depictions.



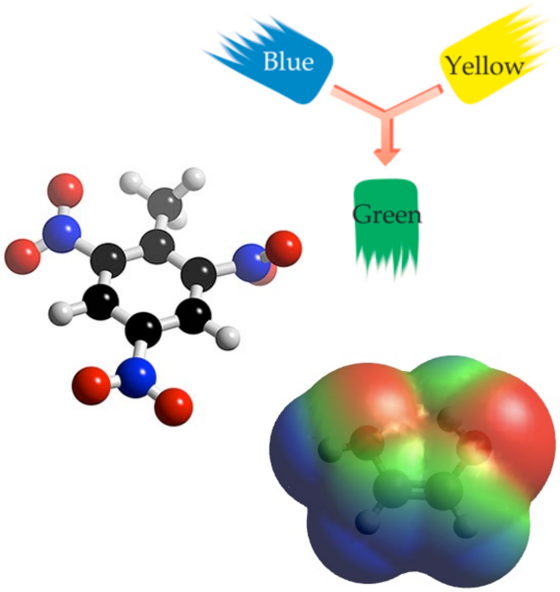


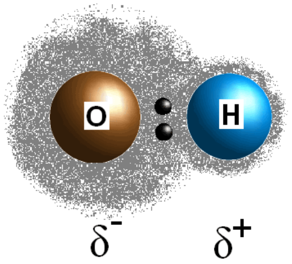


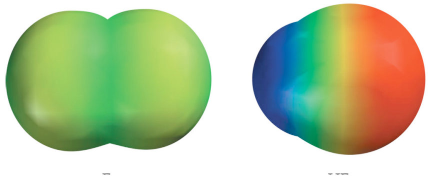


# Electronegativity

- Bond Polarity
  - Covalent bonds
    - electron affinity
    - polar covalent bonds
  - Electronegativity
    - Pauling values
    - bond polarity, ΔEN
      - covalent, ΔEN = 0-0.4
      - polar covalent, ΔEN = 0.4-2.0
      - ionic, ΔEN = 2.0+
  - Dipole moment
    - $\mu = qr$
    - percent ionic character
- Writing Lewis Structures
  - Five Steps.
    - Take stock.
    - Draw a skeleton.
    - Distribute Electrons.
    - Push Electrons.
    - Evaluate Result.
- Resonance & Formal Charge
  - What formal charge is not
  - How to calculate formal charge
  - Formal Charge indicates the best possible structure
  - Resonance
- Exceptions to the Octet Rule
  - Odd Electron Systems
  - That prefer less than 8
  - Expanded Octets (more than 8)
- Bond Thermodynamics
  - What multiple bonds mean.
  - Bond Lengths
  - Bond Energies
    - Enthalpy of Reactions







# Octet Rule

- Atoms like a complete shell.
- Atoms will bond to share or acquire a filled valence shell.
  - for most atoms this is 8 electrons — $ns^2np^6$
- This produces predictable bonding tendencies:
  - atoms with 8 valence electrons form 0 bonds [Ne, Ar, Kr, etc]
  - atoms with 7 valence electrons form 1 bond [Cl, F, Br, etc]
  - atoms with 6 valence electrons form 2 bonds [O, S, Se, etc]
  - atoms with 5 valence electrons form 3 bonds [N, P, As, etc]
  - atoms with 4 valence electrons form 4 bonds [C, Si, etc]
    - 8 + 0 = 7 + 1 = 6 + 2 = 5 + 3 = 4 + 4 = 8
  - These are tendencies, not guarantees!
- The general tendency of atoms to like a filled shell is called the octet rule.
- There are exceptions to the octet rule. Three observed exceptions are:
  1. Molecules or ions with odd numbers of electrons.
  2. Atoms that prefer less than 8 electrons.
  3. Central atoms that can accommodate more than 8 electrons.

# Exception #1: Odd Number of Electrons

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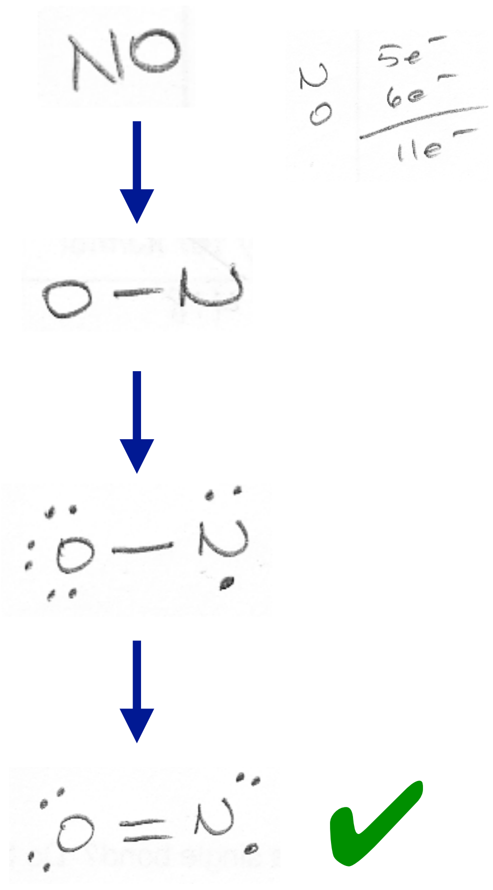

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

# Exception #2: Prefer Less than 8

- Atoms like a complete shell.
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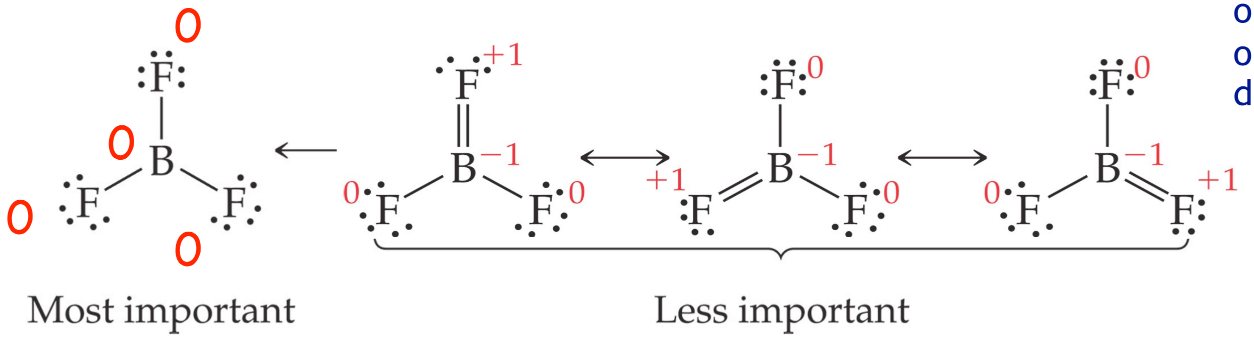
$BF_3$

- Consider $BF_3$:
  - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
  - This would not be an accurate picture of the distribution of electrons in $BF_3$.
- Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.
- The lesson is: if filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



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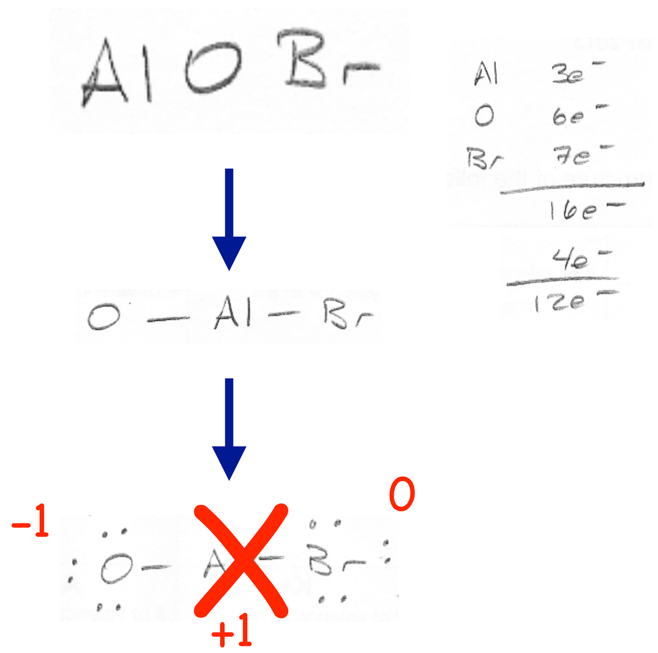

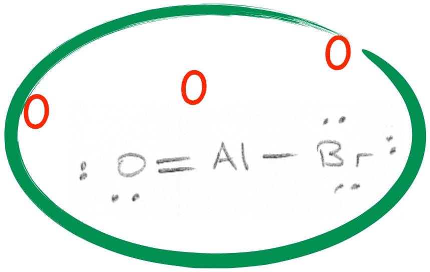

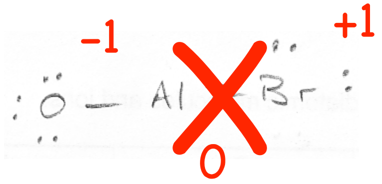

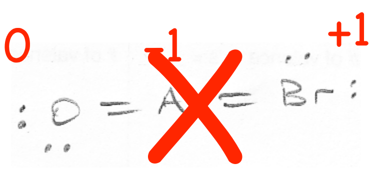

Negative charge on the least electronegative element!

# Exception #3: Expanded Octet

- Atoms like a complete shell.
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- This produces predictable bonding tendencies:
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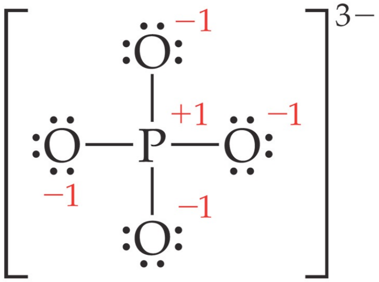
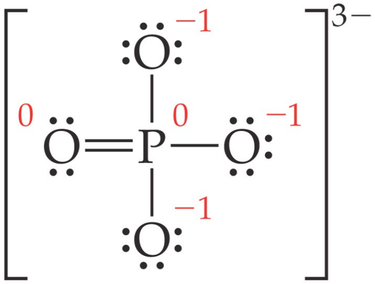
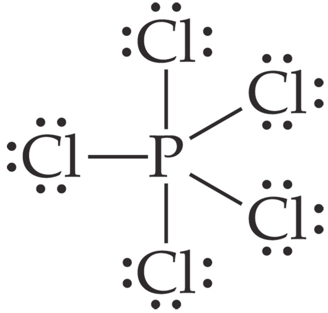




- The only way PCl5 can exist is if phosphorus has 10 electrons around it.
    - Atoms are allowed to expand the octet in the 3rd row or below.
    - Presumably d orbitals in these atoms participate in bonding.



- Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, the better structure puts a double bond between the phosphorus and one of the oxygens.
- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: when the central atom in on the 3rd row or below and expanding its octet eliminates some formal charges, do so.

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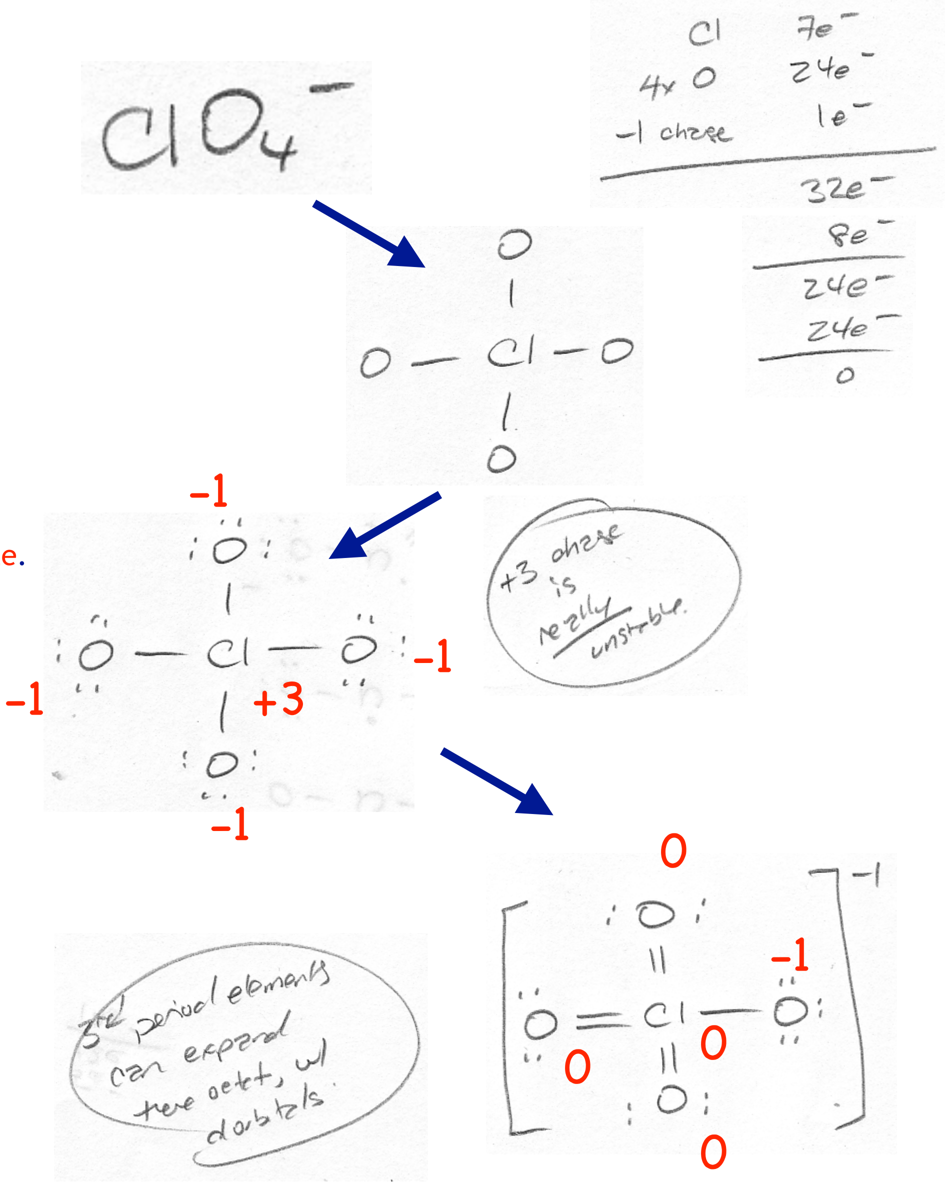


# Lewis Rules

- Rule #1: Take Stock.
  - Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
    - If it is an anion, add one electron for each negative charge.
    - If it is a cation, subtract one electron for each positive charge.
- Rule #2: Pick a Skeleton.
  - The central atom is the least electronegative element that isn't hydrogen.
  - Connect the outer atoms to it by single bonds. Don't write multiple bonds!
  - Subtract the electrons you used from your stockpile
- Rule #3: Pay out whatever electrons you have left.
  - Fill the octets of the outer atoms first.
    - Start with the most electronegative element
  - Fill the octet of the central atom last — it might get shortchanged.
- Rule #4: Push electrons.
  - If you run out of electrons before the central atom has an octet…
    - Form multiple bonds until it does.
    - Form multiple bonds by pushing electrons into the center.
- Rule #5: Assign formal charges; see if you like your structure.
  - For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
    - This is what the atom owns now. Don't confuse this with whether or not it sees an octet!
  - Subtract that from the number of valence electrons for that element.
    - This is what it had before it became part of the molecule.
  - The difference is its formal charge.
    - The formal charge is what the atom gained or lost by joining the molecule.
      - In addition to seeing an octet of electrons — a separate issue.
  - If you don't like the structure, go to step #2.

$AlH_3$ $XeF_4$

$CH_2O$

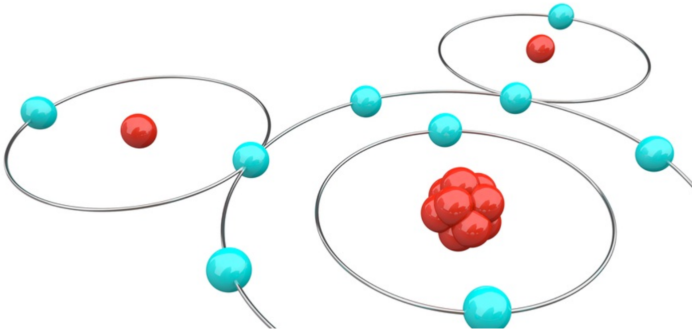
$ClO_4^-$

$C_2H_6$

$NH_4^+$

$Si_2H_4$

$CH_2NH$



# Electronegativity

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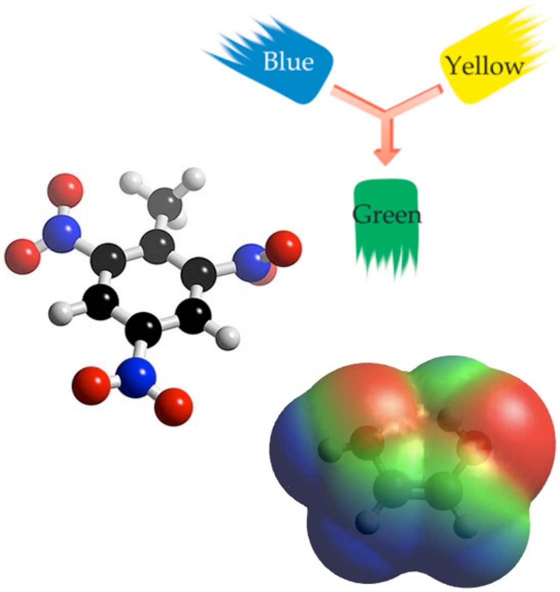
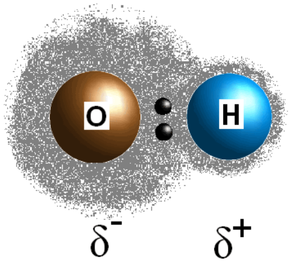
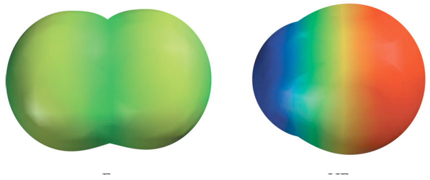
  - Bond Energies
    - Enthalpy of Reactions

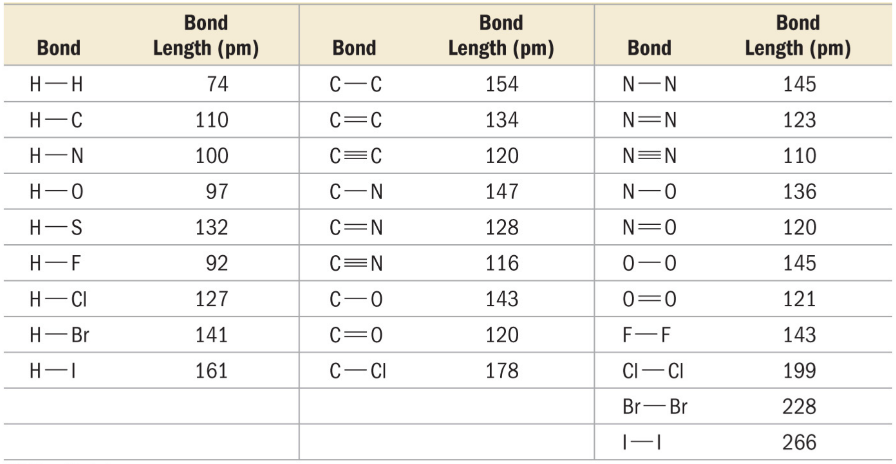




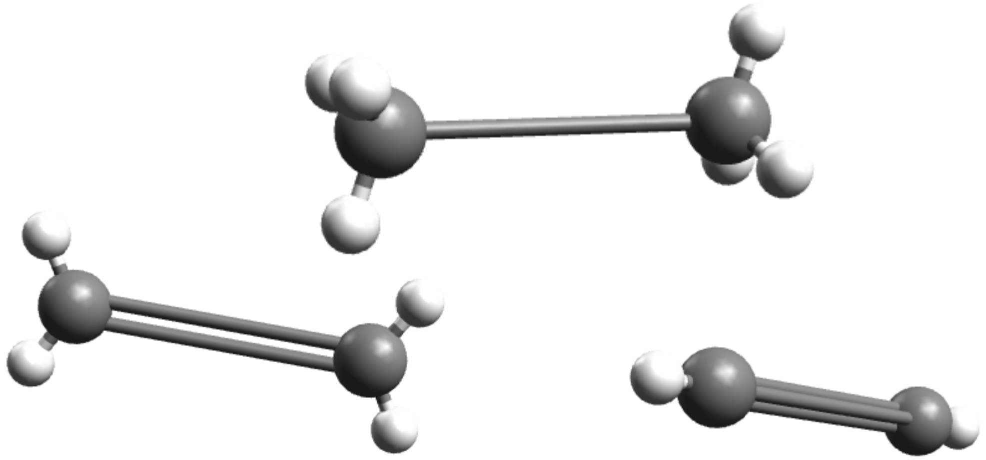


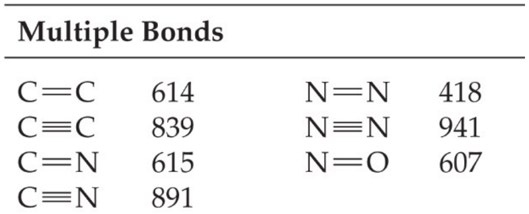
# Bond Order

- What is a double bond?
  - Bond order refers to whether a bond is a single, double or triple bond.
- A multiple bond isn't just many single bonds.
- We see this because:
  - As bond order increases, bond length decreases.
    - Single bonds are longer than double bonds.
    - Double bonds are longer than triple bonds.
  - As bond order increases, bond enthalpy increases
    - Single bonds are weaker than double bonds.
    - Double bonds are weaker than triple bonds.
  - But the enthalpy is not a multiple of the single bond energy.
    - A C-C double bond is 1.75x the strength of a C-C single bond.
    - A N-N double bond is 2.6x the strength of a N-N single bond.
- We will explore higher order bonding and it's effects on molecule shape in the next chapter.



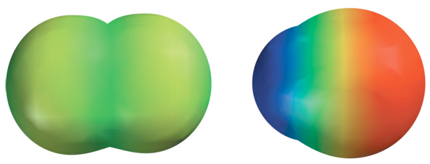
| Bond | Bond Length (pm) | Bond | Bond Length (pm) | Bond | Bond Length (pm) |
|---|---|---|---|---|---|
| H—H | 74 | C—C | 154 | N—N | 145 |
| H—C | 110 | C═C | 134 | N═N | 123 |
| H—N | 100 | C≡C | 120 | N≡N | 110 |
| H—O | 97 | C—N | 147 | N—O | 136 |
| H—S | 132 | C═N | 128 | N═O | 120 |
| H—F | 92 | C≡N | 116 | O—O | 145 |
| H—Cl | 127 | C—O | 143 | O═O | 121 |
| H—Br | 141 | C═O | 120 | F—F | 143 |
| H—I | 161 | C—Cl | 178 | Cl—Cl | 199 |
| | | | | Br—Br | 228 |
| | | | | I—I | 266 |





**Multiple Bonds**

| | | | |
|---|---|---|---|
| C═C | 614 | N═N | 418 |
| C≡C | 839 | N≡N | 941 |
| C═N | 615 | N═O | 607 |
| C≡N | 891 | | |



# Bond Enthalpy

$Cl{-}Cl(g) \longrightarrow 2\,Cl\cdot(g)$

- The strength of a bond is measured by determining how much energy is required to break the bond.
- This is the bond enthalpy.
  - The bond enthalpy for a Cl Cl single bond (Cl-Cl), is measured to be 242 kJ/mol.
  - We've tabulated the average bond enthalpies for many different types of bonds.
- Average bond enthalpies are positive
  - You need to use energy to force apart atoms in a molecule.
  - Bond breaking is an endothermic process.
- You get energy back, by putting atoms into low energy configurations.  By forming bonds.
  - Forming a bond is an exothermic process.
  - So the table also tells you how much energy you'd get back if you formed that bond (you just have to reverse the sign).
- Chemical reactions involve breaking and making bonds, using and getting back enthalpy.
- Since Enthalpy is a state function, we can calculate the head of reaction but keeping track of how many bonds are made and broken in a reaction.

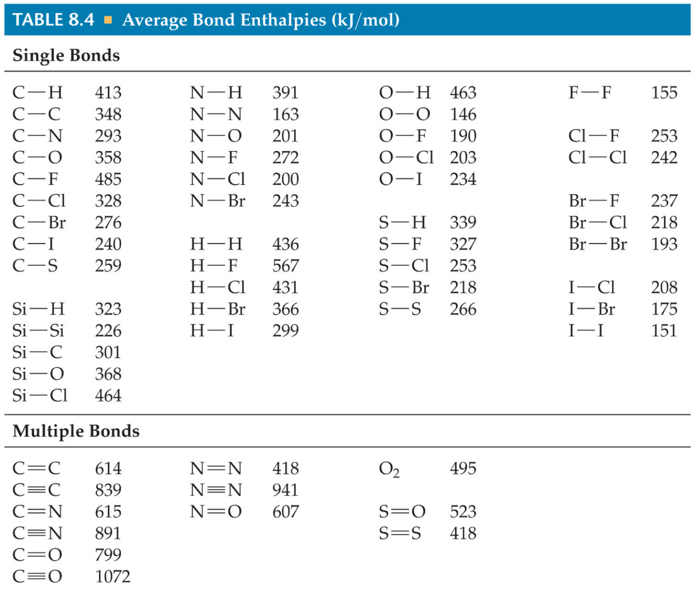
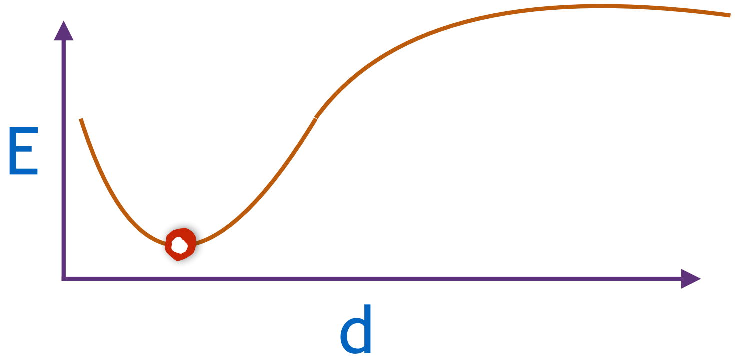
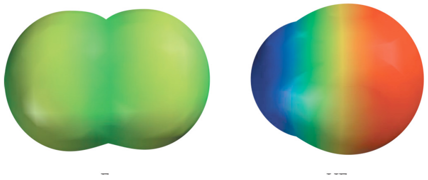


**TABLE 8.4 ■ Average Bond Enthalpies (kJ/mol)**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Single Bonds** | | | | | | | |
| C—H | 413 | N—H | 391 | O—H | 463 | F—F | 155 |
| C—C | 348 | N—N | 163 | O—O | 146 | | |
| C—N | 293 | N—O | 201 | O—F | 190 | Cl—F | 253 |
| C—O | 358 | N—F | 272 | O—Cl | 203 | Cl—Cl | 242 |
| C—F | 485 | N—Cl | 200 | O—I | 234 | | |
| C—Cl | 328 | N—Br | 243 | | | Br—F | 237 |
| C—Br | 276 | | | S—H | 339 | Br—Cl | 218 |
| C—I | 240 | H—H | 436 | S—F | 327 | Br—Br | 193 |
| C—S | 259 | H—F | 567 | S—Cl | 253 | | |
| | | H—Cl | 431 | S—Br | 218 | I—Cl | 208 |
| Si—H | 323 | H—Br | 366 | S—S | 266 | I—Br | 175 |
| Si—Si | 226 | H—I | 299 | | | I—I | 151 |
| Si—C | 301 | | | | | | |
| Si—O | 368 | | | | | | |
| Si—Cl | 464 | | | | | | |
| **Multiple Bonds** | | | | | | | |
| C=C | 614 | N=N | 418 | $O_2$ | 495 | | |
| C≡C | 839 | N≡N | 941 | | | | |
| C=N | 615 | N=O | 607 | S=O | 523 | | |
| C≡N | 891 | | | S=S | 418 | | |
| C=O | 799 | | | | | | |
| C≡O | 1072 | | | | | | |



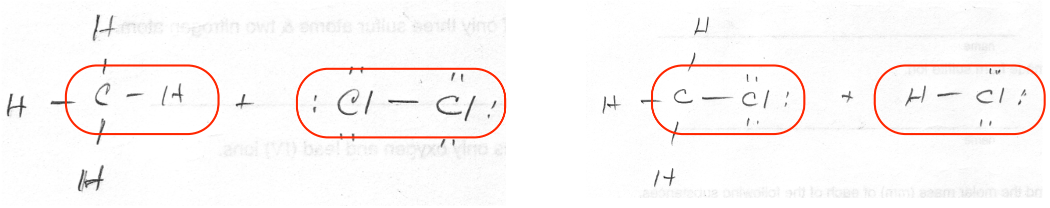


NOTE:  These are *average* bond enthalpies, not absolute bond enthalpies; the C-H bonds in methane, $CH_4$, will be a little bit different than the C-H bond in chloroform, $CHCl_3$.  But average bond enthalpies are good approximations.

# ΔH of Reaction from Bond Enthalpies

- Hess’s law let’s us just consider what was gained and lost from a system to find the change in enthalpy of that system.
- We can estimate ΔH for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.

$$CH_4\ (g) + Cl_2\ (g) \longrightarrow CH_3Cl\ (g) + HCl\ (g)$$



$$H_3CH \quad + \quad ClCl \longrightarrow H_3CCl \quad + \quad HCl$$

In this example, one C-H bond and one Cl-Cl bond are broken;
one C-Cl bond and one H-Cl bond are formed.

*— the rest of the bonds don’t change, so we don’t have to consider them in finding the change in enthalpy!*

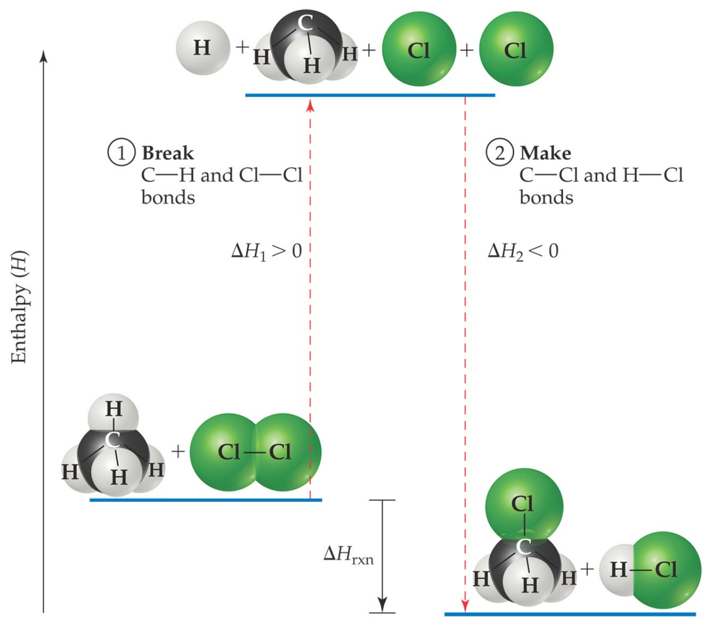
So,

$$\Delta H = [\Delta H(\text{C-H}) + \Delta H(\text{Cl-Cl})] - [\Delta H(\text{C-Cl}) + \Delta H(\text{H-Cl})]$$

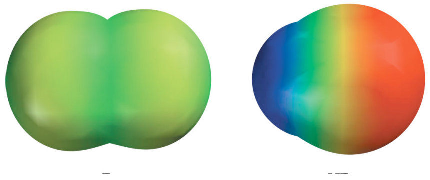
$$= [(413\ \text{kJ}) + (242\ \text{kJ})] - [(328\ \text{kJ}) + (431\ \text{kJ})]$$

$$= (655\ \text{kJ}) - (759\ \text{kJ})$$

$$= -104\ \text{kJ}$$



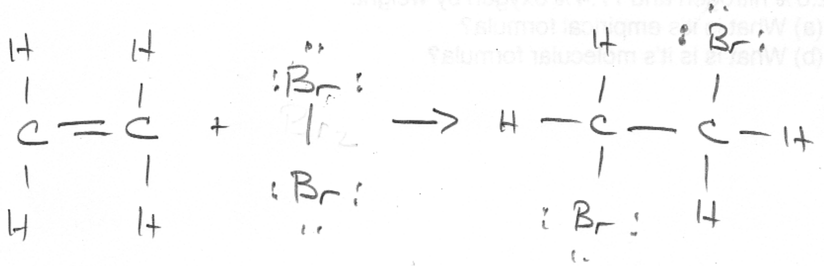
In other words, $\Delta H_{rxn} = \Sigma$(bond enthalpies of bonds broken) - $\Sigma$(bond enthalpies of bonds formed)



# ΔH of Reaction from Bond Enthalpies

Determine the heat of reaction for the following reaction:

$$CH_2CH_2\ (g) + Br_2\ (g) \longrightarrow CBrH_2CBrH_2\ (g)$$



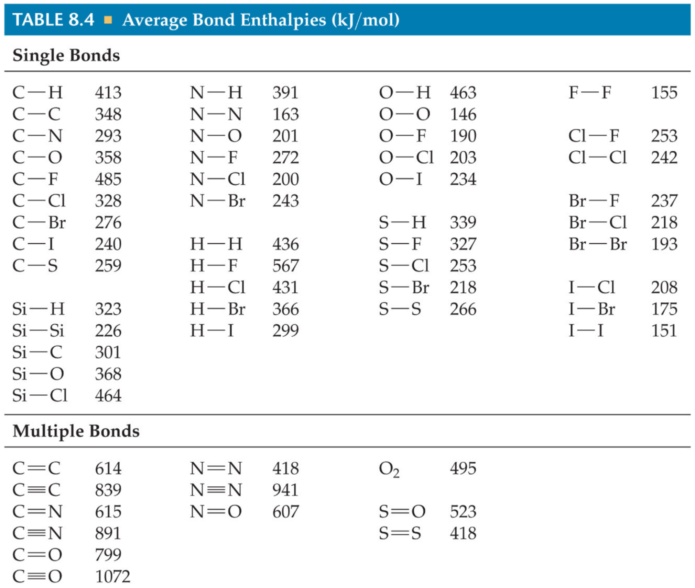


**TABLE 8.4 ■ Average Bond Enthalpies (kJ/mol)**

**Single Bonds**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C—H | 413 | N—H | 391 | O—H | 463 | F—F | 155 |
| C—C | 348 | N—N | 163 | O—O | 146 | | |
| C—N | 293 | N—O | 201 | O—F | 190 | Cl—F | 253 |
| C—O | 358 | N—F | 272 | O—Cl | 203 | Cl—Cl | 242 |
| C—F | 485 | N—Cl | 200 | O—I | 234 | | |
| C—Cl | 328 | N—Br | 243 | | | Br—F | 237 |
| C—Br | 276 | | | S—H | 339 | Br—Cl | 218 |
| C—I | 240 | H—H | 436 | S—F | 327 | Br—Br | 193 |
| C—S | 259 | H—F | 567 | S—Cl | 253 | | |
| | | H—Cl | 431 | S—Br | 218 | I—Cl | 208 |
| Si—H | 323 | H—Br | 366 | S—S | 266 | I—Br | 175 |
| Si—Si | 226 | H—I | 299 | | | I—I | 151 |
| Si—C | 301 | | | | | | |
| Si—O | 368 | | | | | | |
| Si—Cl | 464 | | | | | | |

**Multiple Bonds**

| | | | | | |
|---|---|---|---|---|---|
| C═C | 614 | N═N | 418 | $O_2$ | 495 |
| C≡C | 839 | N≡N | 941 | | |
| C═N | 615 | N═O | 607 | S═O | 523 |
| C≡N | 891 | | | S═S | 418 |
| C═O | 799 | | | | |
| C≡O | 1072 | | | | |

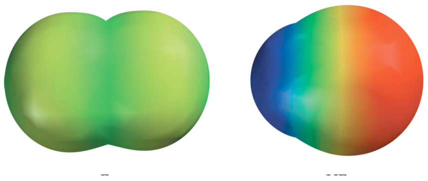
$$\Delta H = \sum \text{Bonds Broken} - \sum \text{Bonds Formed}$$

$$= \left[1\,(C{=}C) + 1\,(Br{-}Br)\right] - \left[1\,(C{-}C) + 2\,(C{-}Br)\right]$$

$$= \left[839\text{ kJ} + 193\text{ kJ}\right] - \left[348\text{ kJ} + 2(276\text{ kJ})\right]$$

$$= 1{,}032\text{ kJ} - 900.\text{ kJ}$$

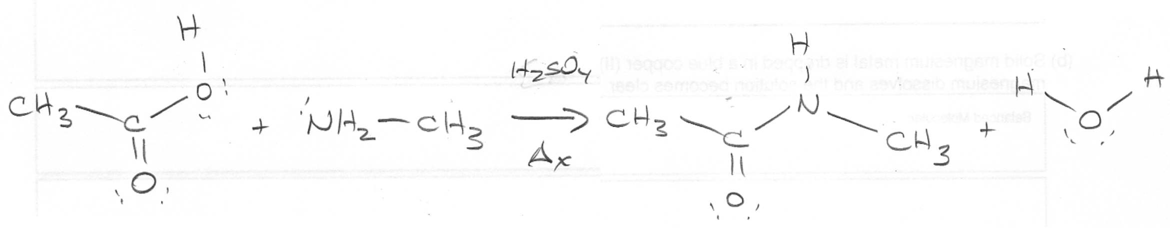
$$= \boxed{132\text{ kJ}}\ \text{(Endothermic)}$$



# ΔH of Reaction from Bond Enthalpies

Determine the heat of reaction for the following reaction:

$CH_3CO_2H + NH_2CH_3 \longrightarrow CH_3CONHCH_3 + H_2O$



$$\Delta H = \sum \text{Bonds Broken} - \sum \text{Bonds Formed}$$

$$= [1(C-O) + 1(N-H)] - [1(C-N) + 1(O-H)]$$

$$= [358\text{ kJ} + 391\text{ kJ}] - [293\text{ kJ} + 463\text{ kJ}]$$

$$= 749\text{ kJ} - 756\text{ kJ}$$

$$= \boxed{-7\text{ kJ}}\ (\text{Exothermic})$$

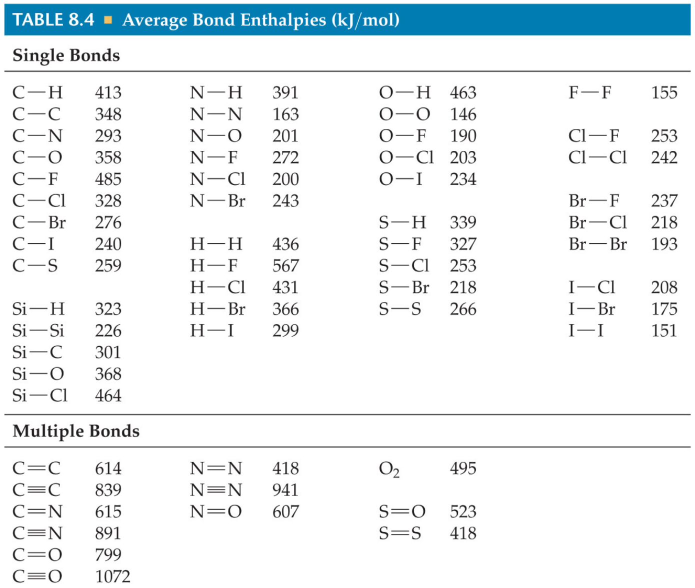


**TABLE 8.4 ■ Average Bond Enthalpies (kJ/mol)**

**Single Bonds**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C—H | 413 | N—H | 391 | O—H | 463 | F—F | 155 |
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| C—N | 293 | N—O | 201 | O—F | 190 | Cl—F | 253 |
| C—O | 358 | N—F | 272 | O—Cl | 203 | Cl—Cl | 242 |
| C—F | 485 | N—Cl | 200 | O—I | 234 | | |
| C—Cl | 328 | N—Br | 243 | | | Br—F | 237 |
| C—Br | 276 | | | S—H | 339 | Br—Cl | 218 |
| C—I | 240 | H—H | 436 | S—F | 327 | Br—Br | 193 |
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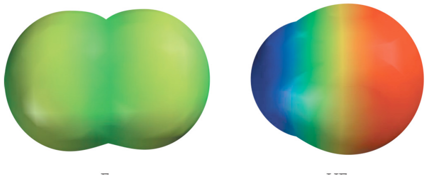
| | | H—Cl | 431 | S—Br | 218 | I—Cl | 208 |
| Si—H | 323 | H—Br | 366 | S—S | 266 | I—Br | 175 |
| Si—Si | 226 | H—I | 299 | | | I—I | 151 |
| Si—C | 301 | | | | | | |
| Si—O | 368 | | | | | | |
| Si—Cl | 464 | | | | | | |

**Multiple Bonds**

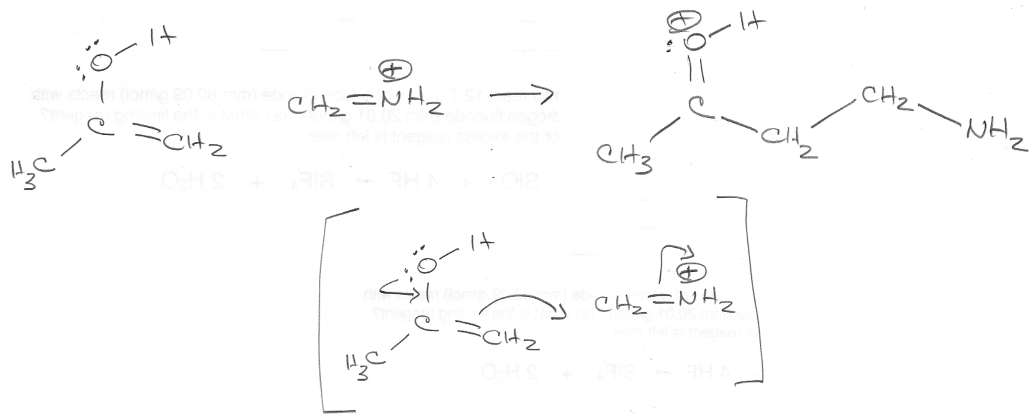
| | | | | | |
|---|---|---|---|---|---|
| C=C | 614 | N=N | 418 | $O_2$ | 495 |
| C≡C | 839 | N≡N | 941 | | |
| C=N | 615 | N=O | 607 | S=O | 523 |
| C≡N | 891 | | | S=S | 418 |
| C=O | 799 | | | | |
| C≡O | 1072 | | | | |



# ΔH of Reaction from Bond Enthalpies

Determine the heat of reaction for the following reaction:

$$H_3COHCH_2 + CH_2NH_2^{1+} \longrightarrow CH_3COHCH_2CH_2NH_2^{1+}$$



$$\Delta H = \Sigma \text{ Bonds Broken} - \Sigma \text{ Bonds Formed}$$

$$= [1(C{=}C) + 1(C{=}N)] - [1(O{=}C) + 1(C{-}C) + 1(C{-}N)]$$

$$= [614\text{ kJ} + 615\text{ kJ}] - [799\text{ kJ} + 348\text{ kJ} + 293\text{ kJ}]$$

$$= 1{,}229\text{ kJ} - 1{,}440.\text{ kJ}$$

$$= \boxed{-211\text{ kJ}} \text{ (Exothermic)}$$

**TABLE 8.4 ■ Average Bond Enthalpies (kJ/mol)**

**Single Bonds**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C—H | 413 | N—H | 391 | O—H | 463 | F—F | 155 |
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| C—Cl | 328 | N—Br | 243 | | | Br—F | 237 |
| C—Br | 276 | | | S—H | 339 | Br—Cl | 218 |
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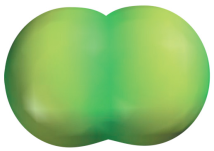
| C—S | 259 | H—F | 567 | S—Cl | 253 | | |
| | | H—Cl | 431 | S—Br | 218 | I—Cl | 208 |
| Si—H | 323 | H—Br | 366 | S—S | 266 | I—Br | 175 |
| Si—Si | 226 | H—I | 299 | | | I—I | 151 |
| Si—C | 301 | | | | | | |
| Si—O | 368 | | | | | | |
| Si—Cl | 464 | | | | | | |

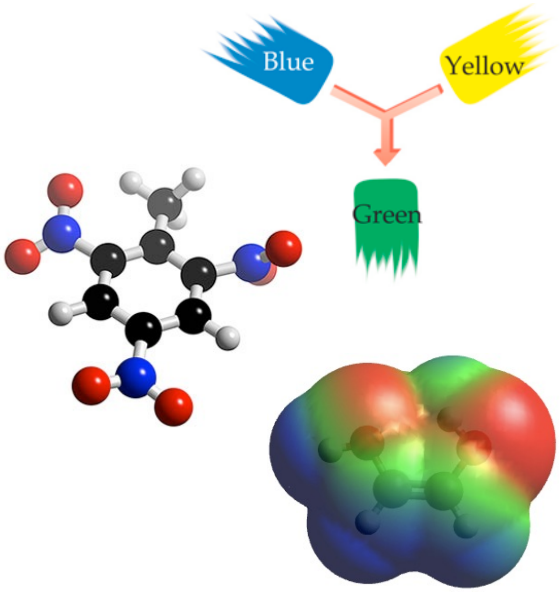
**Multiple Bonds**

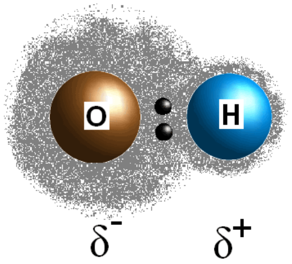
| | | | | | |
|---|---|---|---|---|---|
| C═C | 614 | N═N | 418 | $O_2$ | 495 |
| C≡C | 839 | N≡N | 941 | | |
| C═N | 615 | N═O | 607 | S═O | 523 |
| C≡N | 891 | | | S═S | 418 |
| C═O | 799 | | | | |
| C≡O | 1072 | | | | |

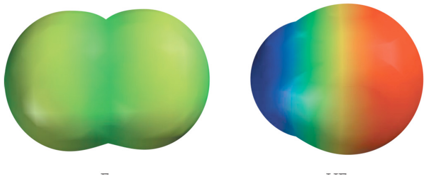


# Electronegativity

- Bond Polarity
  - Covalent bonds
    - electron affinity
    - polar covalent bonds
  - Electronegativity
    - Pauling values
    - bond polarity, ΔEN
      - covalent, ΔEN = 0-0.4
      - polar covalent, ΔEN = 0.4-2.0
      - ionic, ΔEN = 2.0+
  - Dipole moment
    - μ = qr
    - percent ionic character
- Writing Lewis Structures
  - Five Steps.
    - Take stock.
    - Draw a skeleton.
    - Distribute Electrons.
    - Push Electrons.
    - Evaluate Result.
- Resonance & Formal Charge
  - What formal charge is not
  - How to calculate formal charge
  - Formal Charge indicates the best possible structure
  - Resonance
- Exceptions to the Octet Rule
  - Odd Electron Systems
  - That prefer less than 8
  - Expanded Octets (more than 8)
- Bond Thermodynamics
  - What multiple bonds mean.
  - Bond Lengths
  - Bond Energies
    - Enthalpy of Reactions







# Questions?