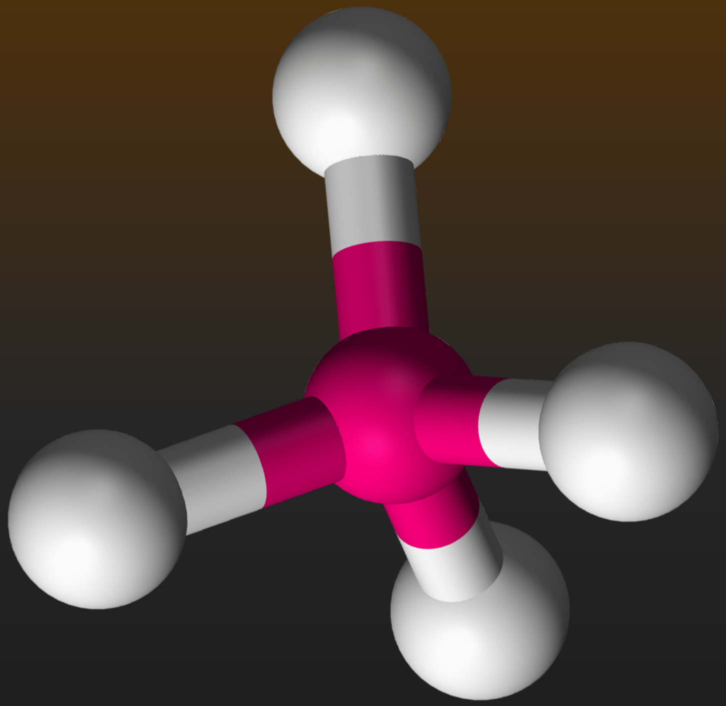
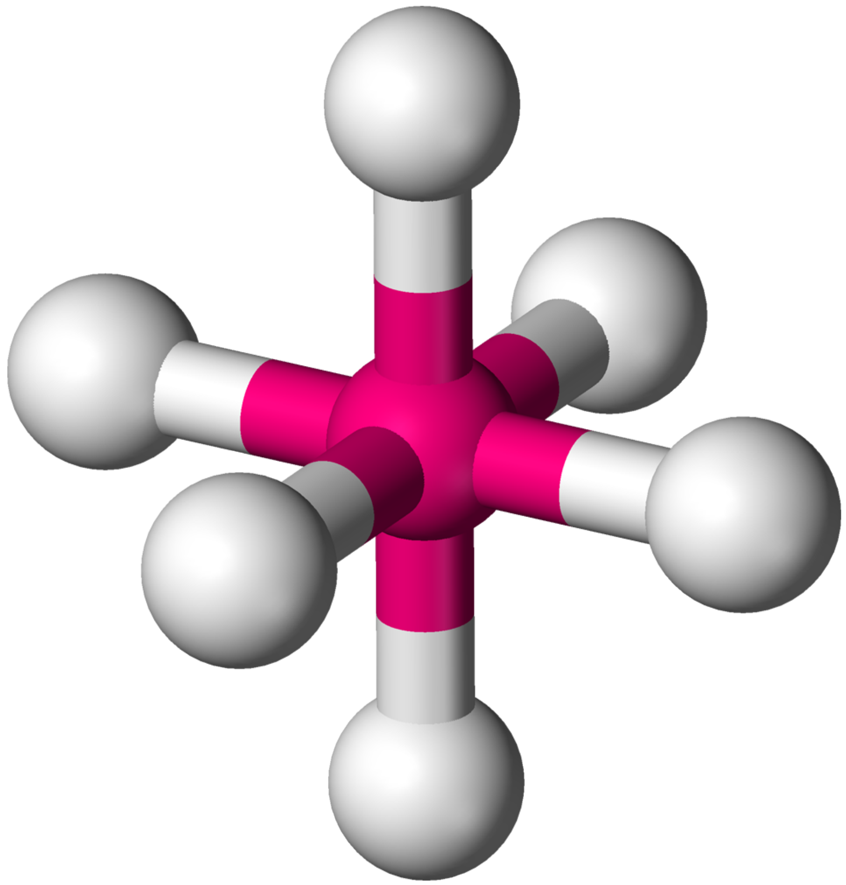


Unit 3 Review 1

INTRODUCTION TO BONDING, LEWIS STRUCTURES, RESONANCE

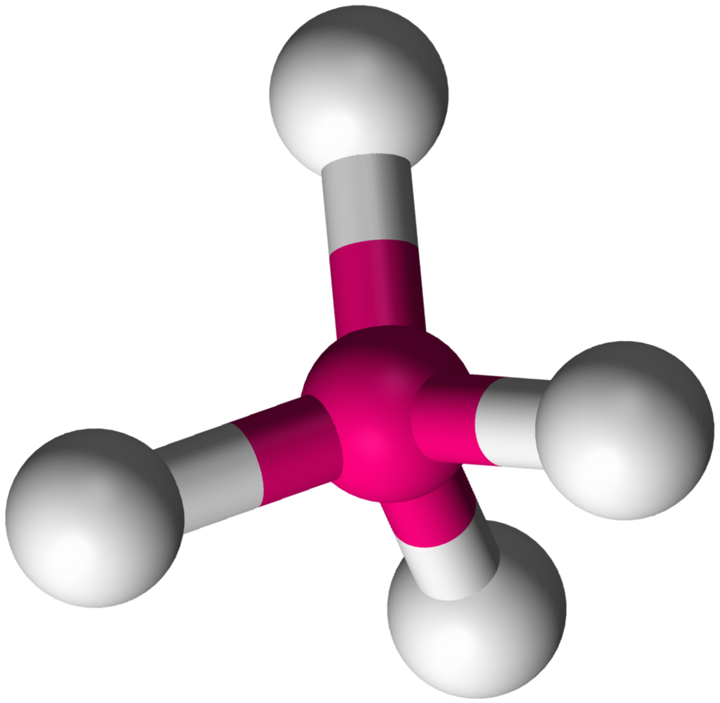
Overview of Unit 3

- Understand and quantify ionic bonds
- Understand and quantify covalent bonds
- Understand electronegativity and polarity in covalent bonds
- Draw Lewis Structures
- Understand complex topics on covalent compounds: formal charge, resonance, and Lewis Structure exceptions
- VSEPR Theory: apply 2D Lewis Structures to 3D electronic and molecular geometries
- Apply your knowledge of polarity to 3D geometries to determine overall molecular polarity



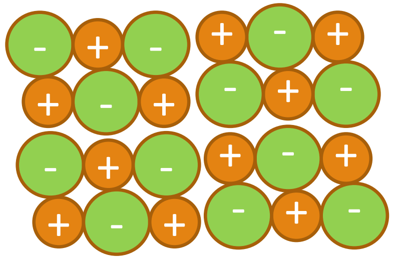
Goals for Today

- Ionic Compounds
  - Basic definitions
  - Lattice energy
- Covalent Compounds
  - Basic definitions
  - Lewis Structures
    - Basic to advanced
  - Introduction to Resonance
  - Expanded, Incomplete Octet

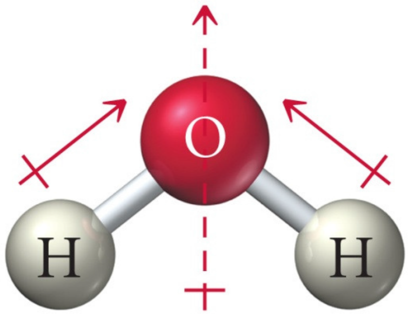


Ionic vs. Covalent Bonds

- Ionic bonds are the electrostatic interaction between discrete fully positive and fully negative charges.
  - Ionic bonds are quantified by lattice energy
  - Ionic compounds are almost always a metal (+) and nonmetal (-)
  - The ions can be elements or polyatomic ions (which are, themselves, covalent compounds)
  - Results in an alternating lattice of positive and negative charges



- Covalent bonds are the sharing of electrons between two species
  - Covalent bonds are quantified by bond length, bond strength, bond order, and polarity (Δen)
  - Covalent bonds result from the electrostatic interaction between partial charges (∂^+, ∂^-)
  - Results in molecules



Is lattice energy positive or negative?

- Depends on how you're measuring it. But use the absolute value.
- **Lattice energy indicates the amount of energy necessary to overcome the negative potential energy binding the charges of an ionic compound**

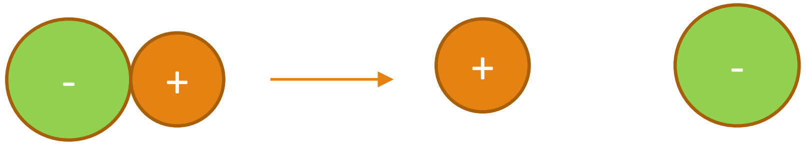
Lattice Energy

- Lattice Energy: is directly proportional to the charges of the ions (q_1 and q_2) and inversely proportional to the size of the ions (r)

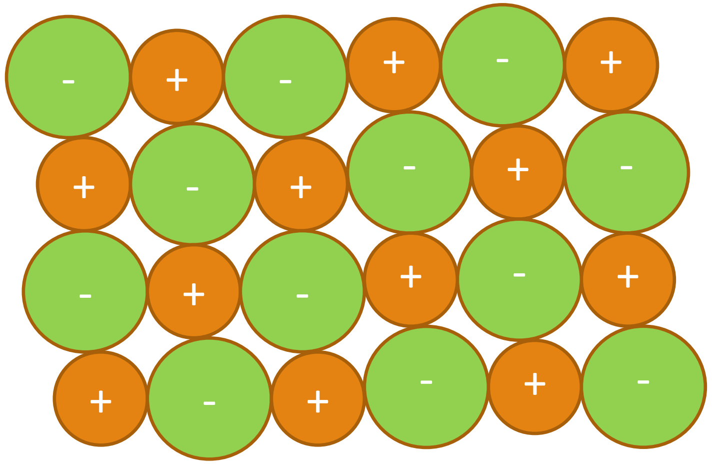
$$\Delta H_{lattice} \propto \frac{q_1 q_2}{r}$$

- This describes the energy required for the following reaction:

$$NaCl \rightarrow Na^{+} + Cl^{-}$$



+ Energy



When Ranking Lattice Energies:

1. Prioritize **charge first**
2. If two ionic compounds have the same charge, the **smaller one will have a higher energy**
3. Polyatomic ions are **big**

Lattice Energy: Conceptual Questions

- Which has the higher lattice energy?

$NaCl$ *vs.* $CaBr_2$

Lattice Energy: Conceptual Questions

- Which has the higher lattice energy?

$MgBr_2$ *vs.* $CaCO_3$

Lattice Energy: Conceptual Questions

- Which has the higher lattice energy?

MgO *vs.* $CaSO_4$

Lattice Energy: Challenge Question

List the following in terms of decreasing ionization energy:

LiF, MgO, Na_2S, LiBr, $MgSO_4$, NH_4Br

$\overset{+1\ -1}{LiF}$, $\overset{+2\ -2}{MgO}$, $\overset{+1\ -2}{Na_2S}$, $\overset{+1\ -1}{LiBr}$, $\overset{+2\ -2}{MgSO_4}$, $\overset{+1\ -1}{NH_4Br}$

Lowest

Highest Charge, smallest radius: MgO

$MgSO_4$

Na_2S

LiF

$LiBr$

NH_4Br

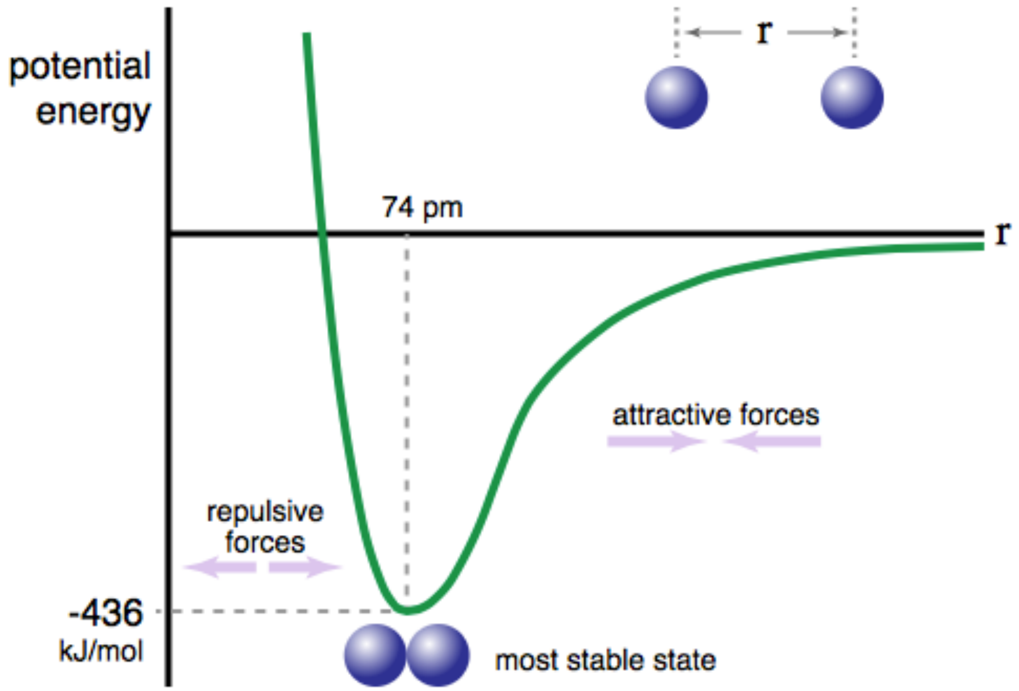
Covalent Bond Definitions

- Bond strength: the energy required to break a covalent bond (also known as Bond Dissociation Enthalpy)
- Bond order: a measurement of the average number of chemical bonds between two atoms in a species
  - This gets more detailed as time goes on; for now, think of single, double, and triple bonds
- Bond length: the distance between atoms in a bond
- Electronegativity: a measurement of the electron-withdrawing nature of an element in a bond. Leads to unequal sharing of electrons in a covalent bond, or polarity.
- Resonance: multiple acceptable Lewis Structures are available for a given compound, meaning that the compound actually exists as the average of all acceptable structures
- Delocalized electrons: in the case of resonance, electrons are not confined to a single bond. Instead they "resonate" over multiple bonds. We call this delocalization.

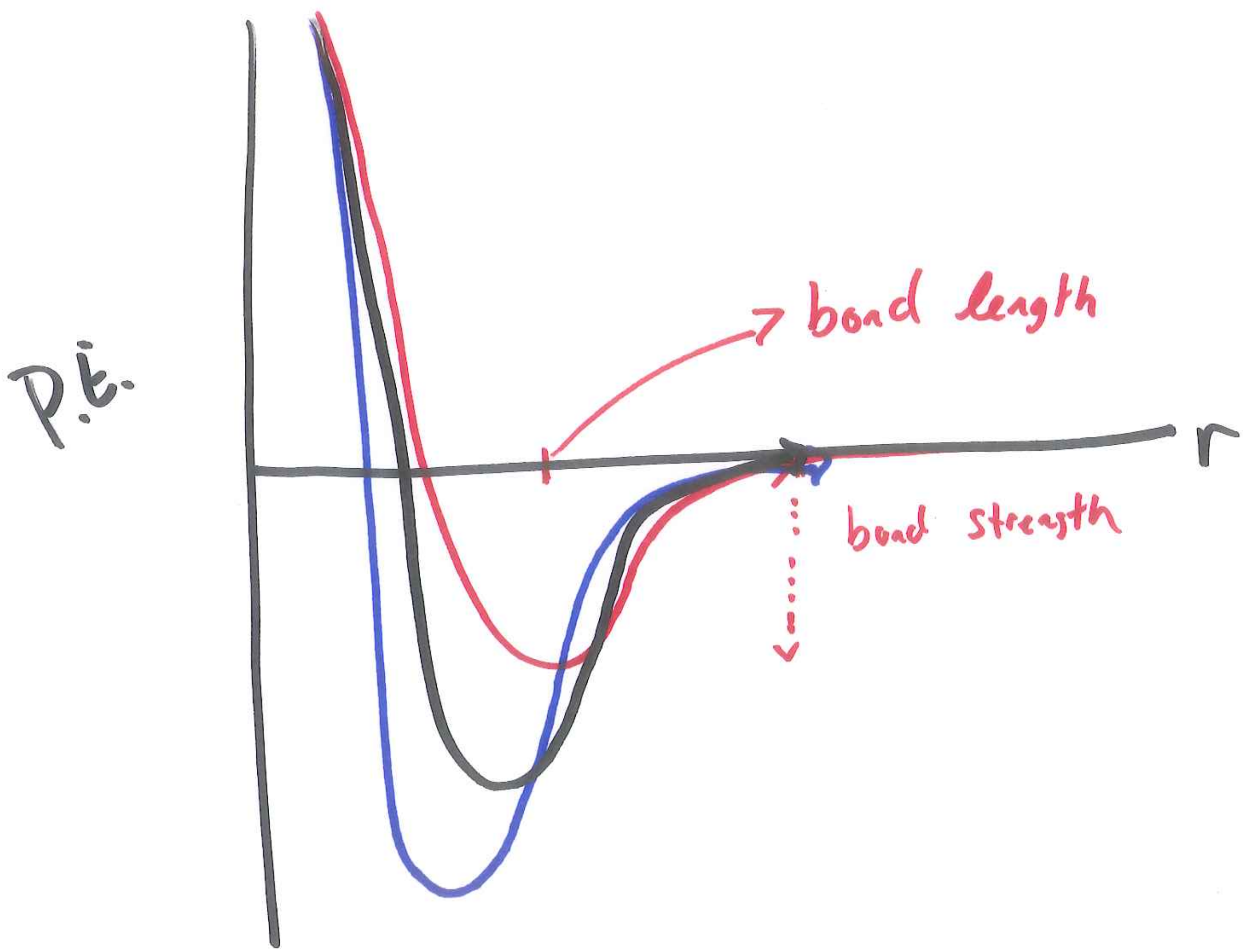
Note: bond strength and order are both indicators of stability. Higher bond order means a higher bond strength, which also correlates inversely with bond length.

Covalent Bond Strength and Stability

- Bond strength: the energy required to break a covalent bond (also known as Bond Dissociation Enthalpy)
- Bond order: a measurement of the average number of chemical bonds between two atoms in a species
- Bond length: the distance between atoms in a bond
- **KEY: stronger bonds are shorter; higher order bonds are stronger (and thus shorter)**



Notice how when a covalent bond gets just right, your potential energy is minimized just like lattice energy!



= $C-C$ bond

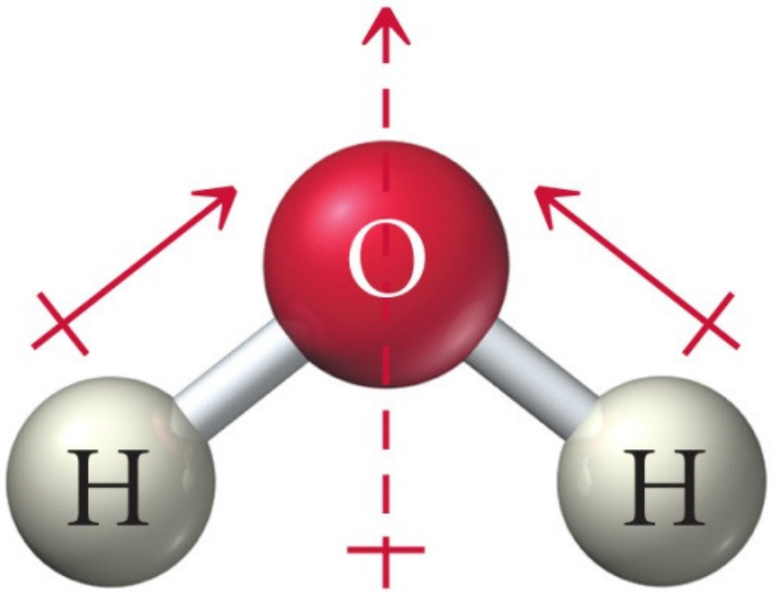
= $C=C$ bond

= $C\equiv C$ bond

Shortest bond length,
Highest bond strength,
Most (-) P.E.

Polarity and Electronegativity

- Polarity is the word we use when electrons are unevenly shared in a covalent bond, thus creating a partial positive pole and a partial negative pole.
- **An atom with a high electronegativity has a high electron-withdrawing nature.** In a covalent bond, this atom will carry a partial negative.
- **An atom with a low electronegativity has a high electron-donating nature.** In a covalent bond, this atom will carry a partial positive.



Notable polar bonds include: C-N, C-O, C-F, C-Cl, C-Br, N-H, O-H, H-F, H-Cl, H-Br

Notable *mostly* nonpolar bonds include: diatomics, C-C, C-H (debatable), C-S, S-H (debatable), B-H

Q: Draw the structure for cyanide. What is the formal charge around the carbon and nitrogen?

Lewis Structures

- Lewis structures are the main form of drawing molecules. There are two important equations to know when drawing Lewis Structures:

$$S = N - A$$

- The number of shared electrons is equal to the total electrons **needed** to fill the valence (2 for hydrogen, 8 for other non-exception elements) minus the electrons **available** (valence electrons). Account for positive charge by subtracting from available; account for negative charge by adding to available.
- **You can then calculate the number of bonds by dividing the shared electrons by two (bonds = S/2)**

$$FC = \text{Valence} - (\text{lone electrons} + \text{bonds})$$

- **The formal charge of any atom in a molecule is equal to the the valence electrons of the atom (as seen on the periodic table) minus the "things it's touching" in the Lewis structure (the lone electrons and the number of bonds)**

$$FC = \text{Valence} - (\text{"things it's touching"})$$

CN^{-}

$S = N - A$

C: 8×1 C: 4×1 $(-) \times 1 = 1$

N: 8×1 N: 5×1

$16e^- - 10e = 6e^-$ shared $/$ $2\ e^-/\text{bond}$

3 bonds

$[:C \equiv N:]^{-1}$

$FC_{carbon} = 4e^- - 5 = -1$

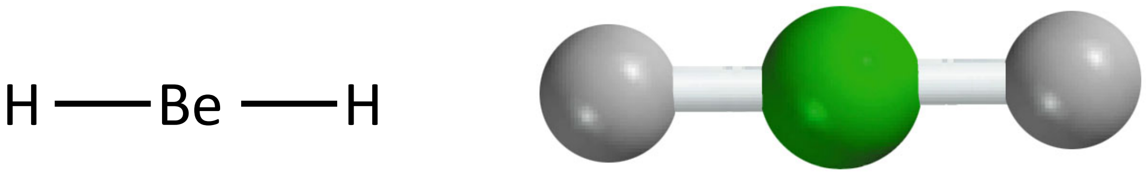
$FC_{nitrogen} = 5e^- - 5 = 0$

$FC_{CN^-} = -1$

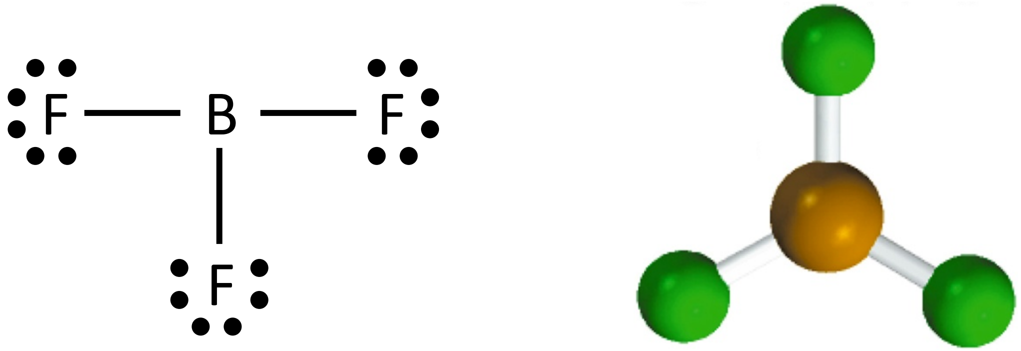
Incomplete Octet

Exam Tip: there are only a few good examples of the incomplete octet: BeX_2 and BX_3, where X is either Hydrogen or a Halogen.

- The octet rule will also be useless for central atoms with fewer than 4 valence electrons (ex: **Boron** and **Beryllium**).
- Beryllium (Be) is satisfied making **2 bonds** (4 valence e^-).
- Boron is satisfied making **3 bonds** (6 valence e^-)
- Boron and beryllium don't have many valence electrons and they have low electronegativies, so we consider them to be **electron-poor** elements with little desire to fill their octets.



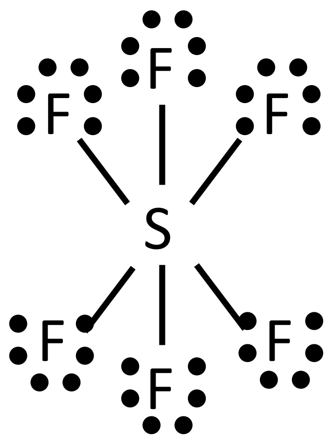
Be (2 e^-) + 2H (1e^-) = 4 total e^-



B (3 e^-) + 3F (7e^-) = 24 total e^-

Solving For Lewis Structure Exceptions

1. Find the number of electrons **available** (valence electrons plus the charges – subtract for positive charge, add for negative).
2. Add your bonds create the lowest possible formal charges possible.*
3. Add lone pairs to your peripheral atoms
4. If you have any electrons left based on your **available** electrons from step 1, add them to your central atom.
5. **Confirm your molecule's structure by checking the formal charge**



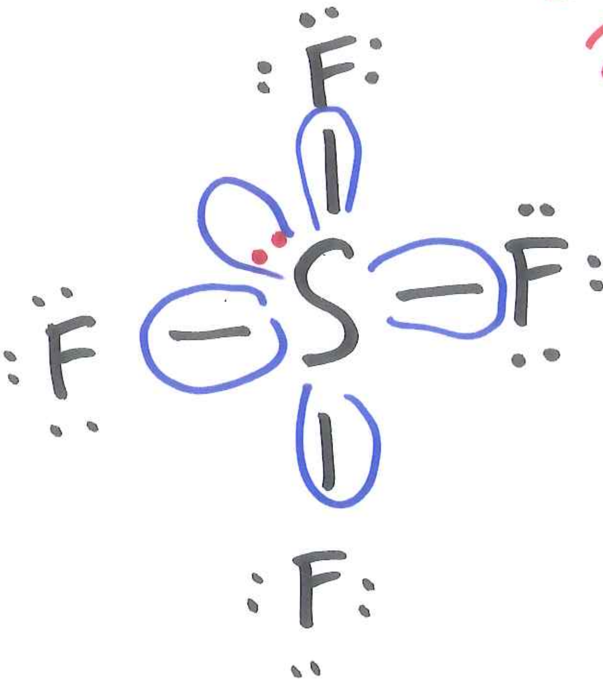
*By this I mean be smart about adding your bonds. The more you practice, the easier this step will be to make a sensible first-attempt at a structure (use the chart in the next slide if necessary)

SF_4 Available: $6 + 4(7)$

$34e^-$

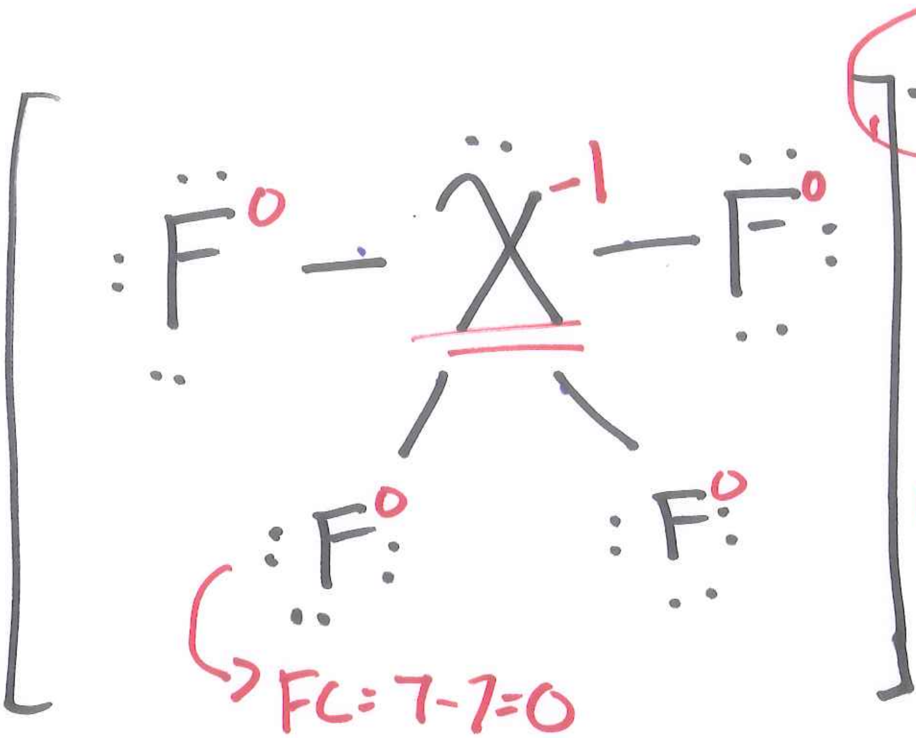
$32e^-$

$2e^-$



$10e^-$ is OK

$FC = 6 - 6 = \varnothing$



-1

What is X?

~~a)~~ C

b) N

c) P

~~d)~~ S

Group # = Valence

FC = valence e^- − ("things its touching")

$-1 = \underline{\quad\quad} - 6$

→ 5 valence e^-

Lewis Structure Formal Charge Foundations

Element	-1 Charge	Neutral	+1 Charge
Hydrogen	x	1 bond	x
Carbon*	3 bonds, 1 LP (rare)	4 bonds	x
Nitrogen	2 bonds, 2 LP (rare)	3 bonds, 1 LP	4 bonds
Oxygen	1 bond, 3 LP	2 bonds, 2 LP	3 bonds, 1 LP
Halogens**	x	1 bond, 3 LP	x

This chart represents a "best guess" to draw out simple Lewis Structures. The formal charges are calculated based on a full octet and no exceptions.
*Carbon almost always has four bonds. Some notable exceptions are CO, CN^-, CNO^-
**Represents halogens are a peripheral atom, not a central atom. In other words, this applies to the fluorine in ClF_3 but not the chlorine.

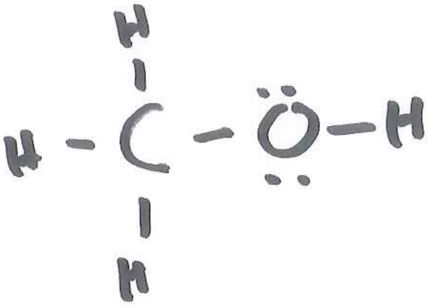
1) CO_2

2) CO

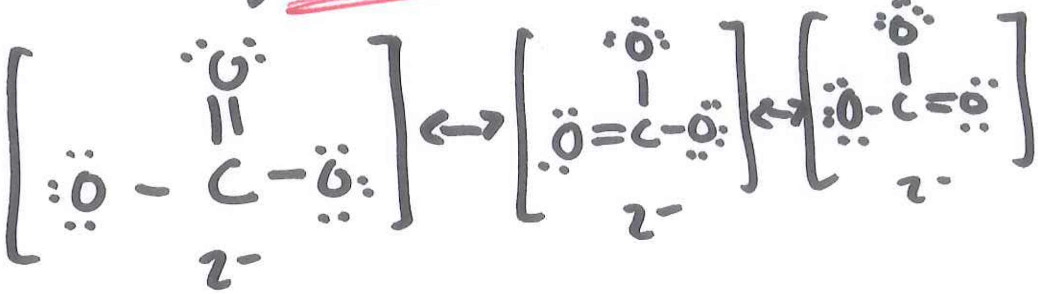
FC = 0

4 - 5 = -1, 6 - 5 = 1

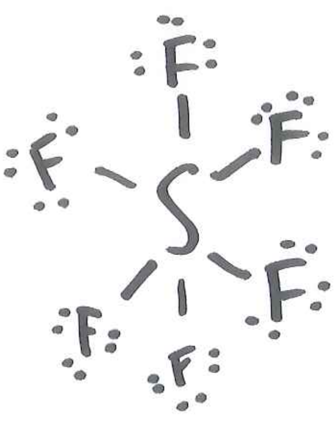
3) CH_3OH



4) CO_3^{2-}



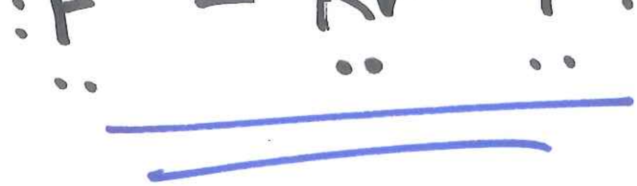
5) SF_6



6) KrF_2

Available = 8 + 2(7)

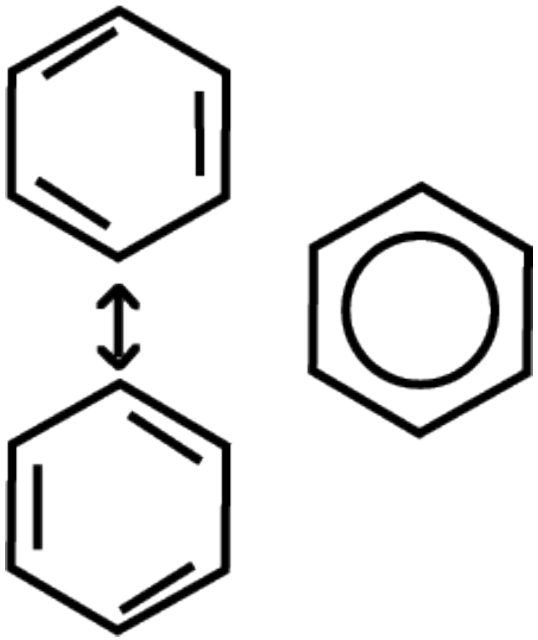
$22e^-$



Extra Slides

Resonance

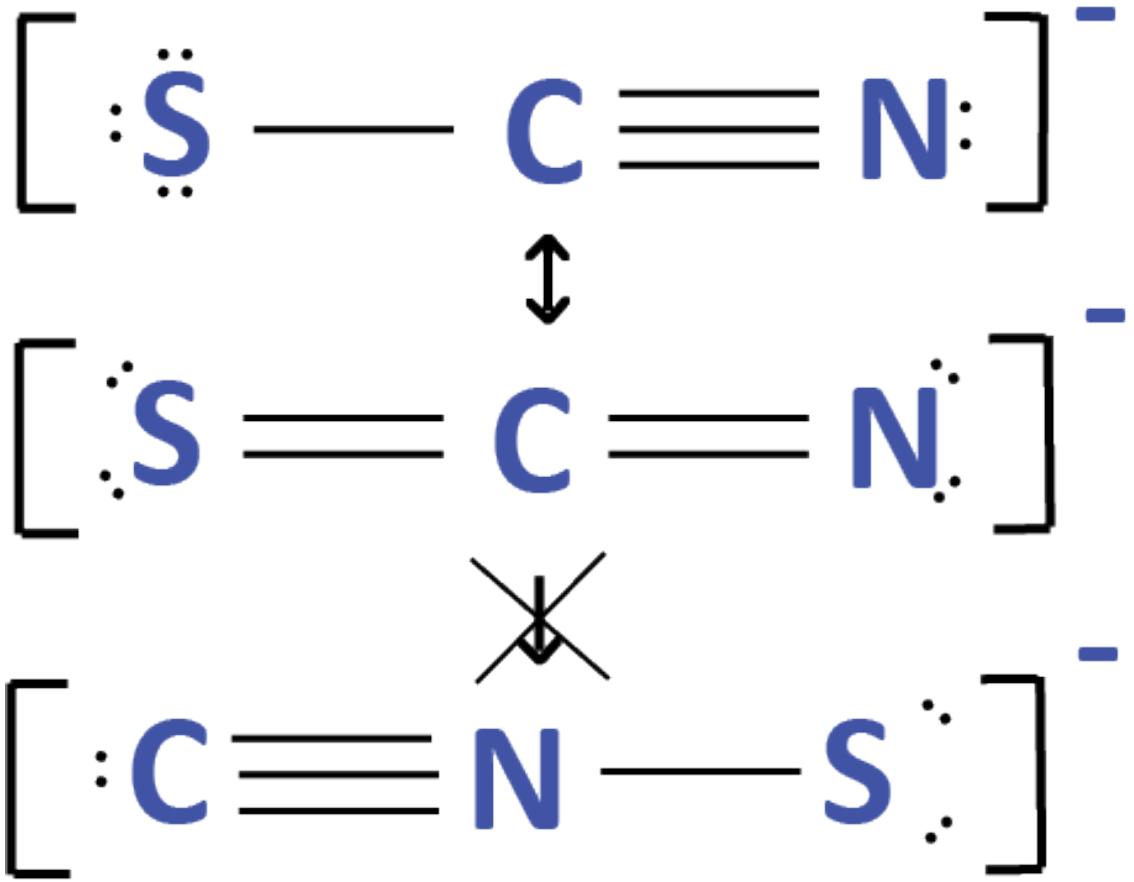
- Resonance occurs whenever a structure has multiple acceptable Lewis Structures.
- The science behind this is that the electrons do not exist in a single place, nor do they "flicker" back and forth between the bonds. Instead, electrons are delocalized and their average charge is spread out over among multiple bonds



We call either the top or bottom drawings of Benzene "acceptable" structures. However, only the drawing on the right shows the actual delocalization of electrons **(a perfect average of the acceptable structures)**

Resonance

- What constitutes an "acceptable" Lewis Structure?
  - The negative charge is placed on only the electronegative atoms and minimized on your central atom (generally)
  - Any individual charge does not exceed +/- 1 (generally)
  - Put your charges on as few atoms as possible
  - **Your structure accurately reflects the number of available electrons in your atoms**



Challenge Question

Earlier we drew three structures with carbon and oxygen: carbon dioxide, carbon monoxide, and carbonate. Which molecule/ion has the least stable bonds?

Resonance

Which of the three Lewis structures is the most important for the fulminate ion (CNO^-)? Select all of the correct answers.