# CHEM 115

## Lewis Structures → VSEPR and Valence Bond Theory

Lecture 25
Prof. Sevian

## Agenda for Lectures 25 and 26

- Using bond enthalpies to estimate enthalpy of reaction
- Lewis structures when expanded octets are possible
- Molecular dipoles
- Valence shell electron pair repulsion theory (VSEPR)
- Return Exam 3 at end of Lecture 25

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- Valence bond theory
  - Hybridization of atomic orbitals to prepare for bonding
    - Single, double and triple bonding
    - $\sigma$ and $\pi$ bonding orbitals
  - Predicting bond angles
  - Refrain molecular dipoles
- Molecular orbital theory
- Give out “individualized academic prescriptions” at end of Lecture 26

# Announcements

***Reminders:***

- Final Exam has been scheduled for:

  Tuesday, May 19
  3:00-6:00 PM
  Lipke Auditorium (S-2-003A), which is our regular classroom

  - Final exam is comprehensive (covers the whole semester)
  - Official ACS exam
  - 70 questions, all multiple-choice
  - There will be some questions on topics that we haven't covered (e.g., gas laws) - these will be extra credit if you get them right, and no penalty if you get them wrong, so it's to your advantage to guess

# Using bond enthalpies to estimate enthalpy change during a reaction

- Breaking bonds costs energy (hint for remembering: think of sticks)
- When bonds form, energy is released (bonded atoms are more stable)

| | | | |
|---|---|---|---|
| **Matter balance** | Some molecules that have bonds in them | → | Some different molecules that have bonds in them |
| ***Energy balance*** | *Break these bonds (put energy in)* | → | *Form new bonds (energy is released)* |

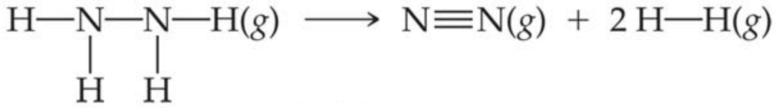
***Estimate of energy change***

$$\Delta H_{rxn} = \sum bonds\ broken - \sum bonds\ \ formed$$

## Example

*Exercise on p. 332*

Estimate $\Delta H$ for the reaction



Bonds to break (endothermic):

four N-H bonds @ 391 kJ/mol

one N-N bond @ 163 kJ/mol

Energy input = +1727 kJ

Bonds to form (exothermic):

one N≡N bond @ 941 kJ/mol

two H-H bonds @ 436 kJ/mol

Energy released = -1813 kJ

$$\Delta H^o_{rxn} = \sum bonds\ broken - \sum bonds\ \ formed = 1727 - 1813\text{ kJ} = -86\text{ kJ}$$

Comparison to $\Delta H^o_f$ method:

$$\Delta H^o_{rxn} = \sum_{products} \Delta H^o_f - \sum_{reactants} \Delta H^o_f$$

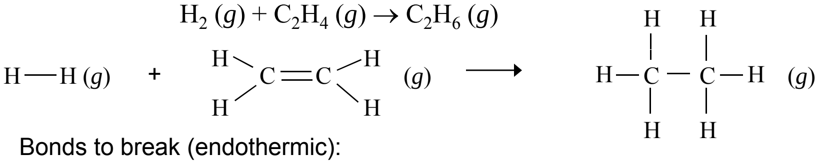
$$\Delta H^o_{rxn} = \left[1 \cdot \Delta H^o_f(\text{N}_2(g)) + 2 \cdot \Delta H^o_f(\text{H}_2(g))\right] - \left[1 \cdot \Delta H^o_f(\text{N}_2\text{H}_4(g))\right]$$

= [1(0) + 2(0)] – [1(-95.40)] kJ = +95.40 kJ

## Another example

Use bond enthalpies to estimate the enthalpy change for the reaction of hydrogen with ethene. Then calculate the standard enthalpy change using heats of formation.

$$\text{H}_2\,(g) + \text{C}_2\text{H}_4\,(g) \rightarrow \text{C}_2\text{H}_6\,(g)$$



Bonds to break (endothermic):

one H-H bond @ 436 kJ/mol

four C-H bonds @ 413 kJ/mol

\+ one C=C bond @ 614 kJ/mol

Energy input = +2702 kJ

Bonds to form (exothermic):

one C-C bond @ 348 kJ/mol

\+ six C-H bonds @ 413 kJ/mol

Energy released = -2826 kJ

$$\Delta H^o_{rxn} = \sum bonds\ broken - \sum bonds\ \ formed = 2702 - 2826\text{ kJ} = -124\text{ kJ}$$

Comparison to $\Delta H^o_f$ method:

$$\Delta H^o_{rxn} = \sum_{products} \Delta H^o_f - \sum_{reactants} \Delta H^o_f$$

$$\Delta H^o_{rxn} = \left[1 \cdot \Delta H^o_f(\text{C}_2\text{H}_6(g))\right] - \left[1 \cdot \Delta H^o_f(\text{H}_2(g)) + 1 \cdot \Delta H^o_f(\text{C}_2\text{H}_4(g))\right]$$

= [1(-84.68)] – [1(0)+1(+52.30)] kJ = -136.98 kJ

## Clicker question #1

Clicker questions 1, 2 and 3 refer to the following reaction:

$$N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$$

What are the bonds broken?

(A) One N-N bond and 3 H-H bonds
(B) One N=N bond and 3 H-H bonds
(C) One N≡N bond and 3 H-H bonds
(D) Two N-H bonds
(E) Six N-H bonds

## Clicker question #2

$$N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$$

What are the bonds formed?

(A) One N-N bond and 3 H-H bonds
(B) One N=N bond and 3 H-H bonds
(C) One N≡N bond and 3 H-H bonds
(D) Two N-H bonds
(E) Six N-H bonds

## Clicker question #3

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)$$

| Bond | Bond Enthalpy (kJ/mol) |
|---|---|
| N≡N | 941 |
| H–H | 436 |
| N–H | 391 |

Given the data in the table above, which expression below is an estimate of $\Delta H$ for the reaction shown?

(A) $\Delta H \approx \left[(941)+3(436)\right]-\left[6(391)\right] kJ$

(B) $\Delta H \approx \left[(941)+3(436)\right]-\left[2(391)\right] kJ$

(C) $\Delta H \approx \left[2(941)+6(436)\right]-\left[6(391)\right] kJ$

(D) $\Delta H \approx \left[(941)+(436)\right]-\left[(391)\right] kJ$

## Theories that predict molecular structures

- Lewis structures (electron dot) model
  - Electrons in pairs, either bonding or nonbonding
  - Only octets can form on simple atoms
  - Expanded octets are possible on elements in *n*=3 and higher
  - Electron pair geometry predicts molecular shape
    - Atoms are visible, nonbonding electron pairs are invisible
    - By combining molecular shape with bond polarity, you can predict whether a whole molecule is polar or not
- VSEPR theory
  - Bonds are squeezed together by nonbonding pairs
- Valence bond theory
  - Hybridization of different combinations of *s*, *p* and *d* atomic orbitals accounts for electron pair geometry, i.e., explains how bond angles arise
  - Single bonds are always $\sigma$ type, orbitals overlap directly on axis of bond
  - Second and third bonds are always $\pi$ type, off axis by atomic *p*-orbital overlap (i.e., to make $\pi$ bonds in molecules, must reserve some atomic *p*-orbitals and not hybridize them)

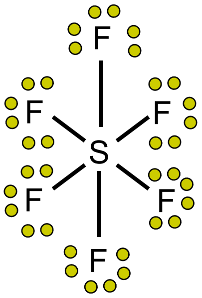
# Exceptions to Octet Rule

1. Less than an octet on an atom
   - Only happens with Group 3A elements (such as boron) because these elements have 3 valence electrons so they make 3 bonds (not 4)
   - Examples: $BF_3$, $B(OH)_3$
2. Odd number of electrons
   - Impossible for all electrons to be paired
   - Lone electron usually resides on atom with lowest electron affinity (which is usually central atom)
   - Called “free radicals”
   - Very reactive because electrons are more stable in pairs
   - Examples: NO (11 valence electrons), $NO_2$ (17 valence electrons)
3. More than an octet on an atom
   - Can happen if valence electrons are in *n*=3 level and higher because *d*-orbitals can be used for bonding

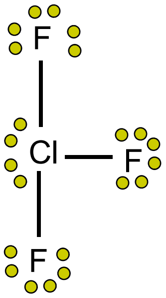
# Examples of more than an octet on the <u>central atom</u>

Only elements in periods 3 and higher (e.g., S, Cl) can do this.

$SF_6$ ㊽



$ClF_3$ ㉘



## Practice using Lewis structures model to predict stable molecular structures

a) $CCl_4$
b) $NF_3$
c) $SF_4$
d) $Cl_3^-$
e) $XeF_4$

*Note: The most important reason for practicing doing this with small molecules is so that you can understand bond angles in large molecules, because this is what determines secondary and tertiary structures of large molecules, as well as lots of other interesting properties.*

- Draw the Lewis structures
- How many locations for electron pairs make up the electron domain geometry around the central atom
- Identify the shape of the molecule or ion by imagining that you can't see the lone pairs of electrons, you can only see where atoms are
- Determine bond angles

## Clicker question #4

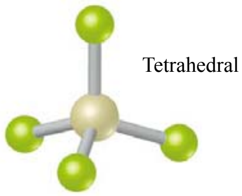
How many electron pairs surround P in phosphorus trifluoride?

(A) 1 pair
(B) 2 pairs
(C) 3 pairs
(D) 4 pairs
(E) 5 pairs

## Clicker question #5

Which is the shape of the phosphorus trifluoride molecule?

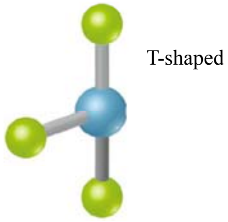
(A)



(C)

(B)

(D)



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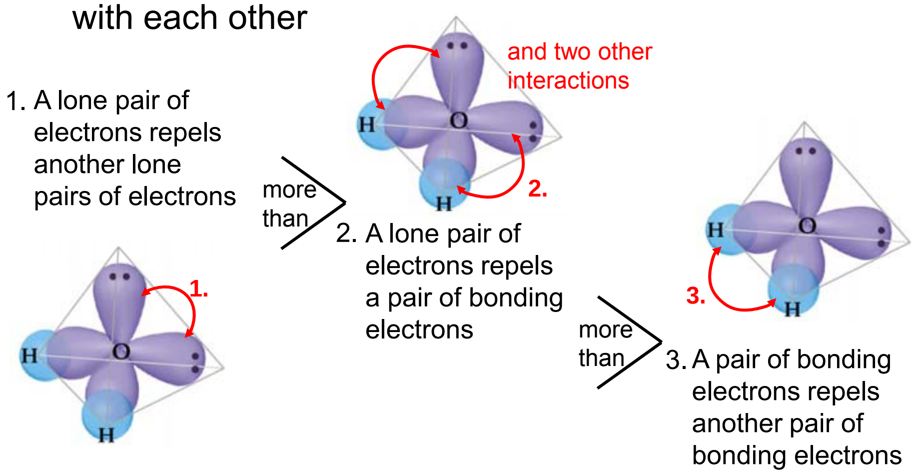
## A place where the Lewis Structure model breaks down

- Bond angles predicted by Lewis structure theory are a good first approximation, but they are often not quite correct
- A modification to address this: Valence shell electron pair repulsion (VSEPR) theory
  - Distinguishes between non-bonding pairs of electrons (lone pairs belonging to a single atom), and bonding pairs of electrons (pairs of electrons that are shared by two atoms)
  - Because non-bonding pairs are more confined in space, they have greater charge density, and can repel bonding pairs a little bit

# VSEPR

How pairs of electrons around a central atom interact with each other



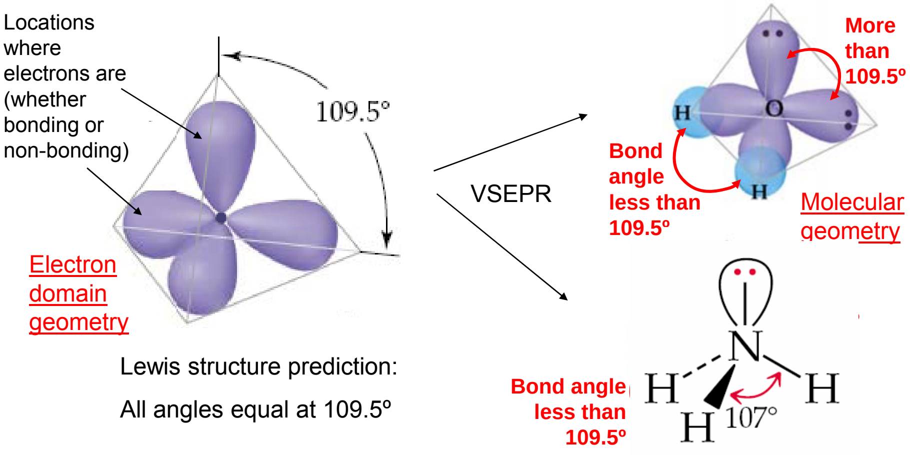
1. A lone pair of electrons repels another lone pairs of electrons

2. A lone pair of electrons repels a pair of bonding electrons

3. A pair of bonding electrons repels another pair of bonding electrons

# VSEPR results

- Some bond angles are smaller than Lewis structure predicts
- Some bond angles are larger than Lewis structure predicts

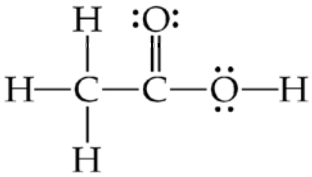


Lewis structure prediction:

All angles equal at 109.5°

## Clicker question #6

What is the C-O-H bond angle in $CH_3COOH$ (acetic acid)?



(A) 180°

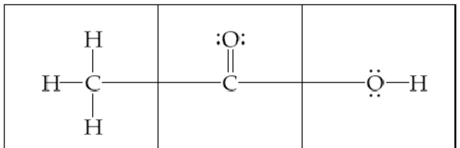
(B) About 120°

(C) About 109.5°

(D) A little larger than 109.5°

(E) A little smaller than 109.5°

## Why predicting bond angles is important



| | | | |
|---|---|---|---|
| Number of electron domains | 4 | 3 | 4 |
| Electron-domain geometry | Tetrahedral | Trigonal planar | Tetrahedral |
| Predicted bond angles | 109.5° | 120° | 109.5° |
| | H-C-H<br>H-C-C<br>bond angles | C-C-O<br>O-C-O<br>bond angles | C-O-H<br>bond angle a little less than 109.5° |

Being able to predict bond angles is important for:

- Predicting sites and strengths of polar regions of large molecules
- Understanding/predicting secondary and tertiary structures
  - Protein folding, enzyme lock-and-key mechanisms

# How do bond polarities sum to determine molecular polarity?

A molecule is a dipole:

1. If it has at least one bond in it that is polar covalent

<u>and</u>

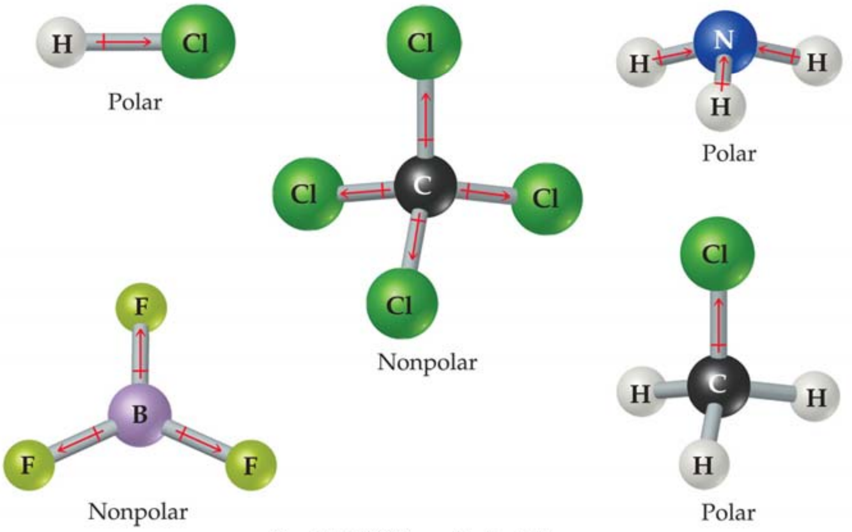
2. If the bond dipoles do not cancel each other out (cancellation happens when bond dipoles are symmetrically located)

Remember how to determine whether a bond is a dipole?

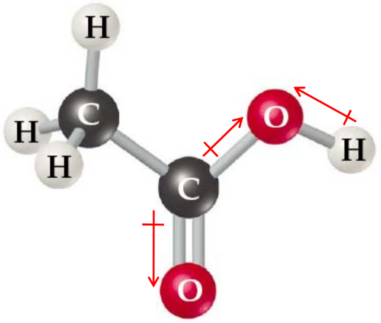
Difference in electronegativities of the two atoms in the bond

- No difference: perfectly covalent
- Some difference (as between non-metals): polar covalent
- Very different (as between a metal and a non-metal): ionic

# These are some molecules that contain polar bonds, but not all of the molecules are polar



## Molecular dipole example



Dipole moment of the molecule is the vector sum of the three bond dipoles:

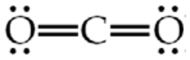
1.74 D

- The strength of a molecule’s dipole explains many properties of the compound, such as:
  - How high (or low) the melting and boiling points are
  - How well the compound can dissolve in polar or nonpolar solvents
  - How reactive the compound is, and where its reactivity sites are

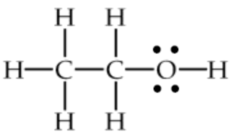
## Clicker question #7

Which of the following molecules would be expected to have the largest molecular dipole moment?

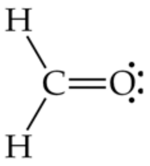
(A) $CO_2$



(C) $C_2H_5OH$



(B) $CH_2O$



(D) $CH_4$