Chapter 7

Covalent Bonds and Molecular Structure

Bonding Patterns

- Place the following formulas into two groups.
  - ♦ NaCl
  - ♦ P_4O_{10}
  - ♦ SF_6
  - ♦ $MgCl_2$
  - ♦ CoF_3
  - ♦ NH_3
  - ♦ OF_2
- How would you label or classify your groups?

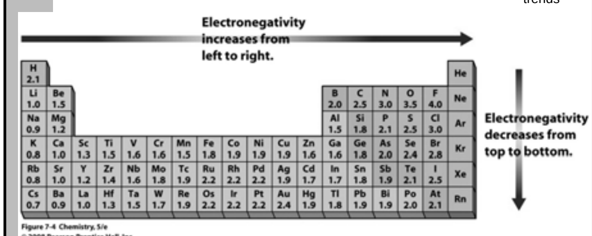
Differences in Covalent Bonds

- **Covalent bond: a bond that results from the sharing of electrons between atoms.**
  - ♦ Atoms don't always share electrons equally
- ***Electronegativity***: the ability of an atom in a molecule to attract e^- to itself. What other atomic property does this remind you of?

Electronegativity Diff.

Trends in Electronegativity

electronegativity trends



Polar or Nonpolar?

- Nonpolar covalent bonds have no e-neg difference (F_2, CH); polar covalent bonds (HF) have small differences; ionic bonds have large differences(LiF). **The greater the difference in electronegativities, the more ionic a bond is.**

F_2 HF LiF

- Red = high electron density; Blue = low electron density; Green = in between

Bonding

- Identify the type of bond (ionic, polar covalent, nonpolar covalent) holding atoms together in the following compounds.
- NaCl
- H_2
- PCl_3
- H_2O
- $CaBr_2$
- CH_4
- $NaNO_3$
- Problems 7.1, 7.2, 7.3

Electronegativities			
H	**2.1**	**N**	**3.0**
Na	**0.9**	**O**	**3.5**
Ca	**1.0**	**Cl**	**3.0**
P	**2.1**	**Br**	**2.8**
C	**2.5**	**F**	**4.0**

Group Work

- Identify the type(s) of bonds (ionic, polar covalent, nonpolar covalent) holding ALL atoms together in the following compounds:
- $MgCl_2$
- NCl_3
- $MgCO_3$
- Cl_2

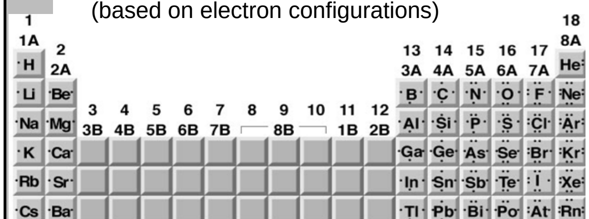
Group Work Answers

- $MgCl_2$ ionic
- NCl_3 polar covalent
- $MgCO_3$ ionic AND polar covalent
- Cl_2 nonpolar covalent

Lewis Dot Symbols

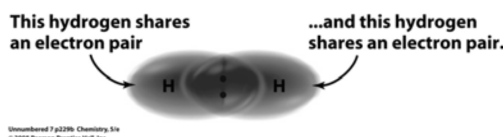
Lewis_symbols

- Can use ***Lewis Dot Symbols*** to represent the numbers of valence electrons for each atom (based on electron configurations)



Electron-Dot Structures

- Used to show how electrons are shared between nonmetals in a covalent bond. Use **valence electrons** to give each atom an octet, with a few exceptions (e.g., H).



Electron-Dot Structures

Lewis Symbol.exe

- Procedure for drawing structures:
  1) Draw an atomic skeleton (first atom is usually in the center)
  2) Count total valence electrons
     - Add or subtract electrons for polyatomic ions
  3) Place electron pairs between bonded atoms
  4) Place remaining electrons on the outside atoms, then the central atom
  5) Shift electrons, as necessary, to make multiple bonds

Single Bonds

- Single bond represented as H:H or H-H
- F_2: 14 valence electrons total

  :F:F: :F - F:

- ***Each atom is trying to get an octet*.**

Once you count valence electrons, you don't care how many electrons each atom brings….

- **Satisfy the octet rule and # of valence electrons**

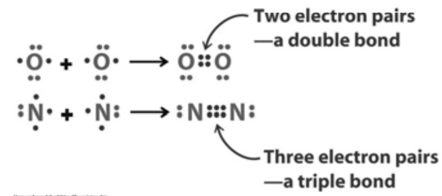
Electron-Dot Structures

1) How many total valence electrons?
2) Does every atom have an octet?

- **H only gets one bond; halogens <u>usually</u> only form single bonds.**
- **Draw structures for the following:**
  - ♦ CH_4, NH_3, H_2O, CCl_2F_2, $SOCl_2$, NH_4^+, SO_4^{2-}
- Worked Ex. 7.1, 7.2; Problems 7.4, 7.5

Multiple Bonds

- What do you do if there are too many electrons in the Lewis Dot Structure?
- Draw Lewis Structures for O_2 and N_2.



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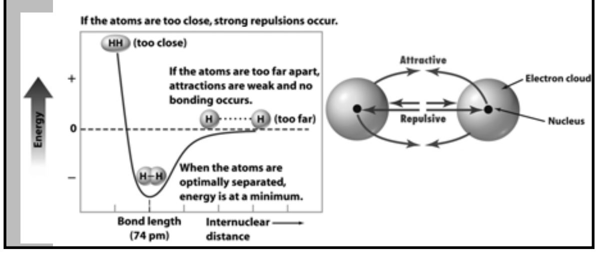
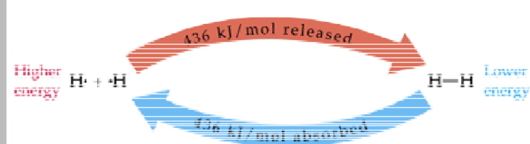
Covalent Bond

- There is an optimum distance between atoms in a covalent bond. This is the bond length: calculated by adding the radii of two atoms.



Strengths of Covalent Bonds

- Closer nuclei result in a stronger bond. Shorter bond = stronger bond.
- Energy is required (absorbed) to break a bond. Energy is given off (released) when a bond is formed.



Comparison of Bonds

- What type of bond (single, double, or triple) do you predict to be the strongest? The weakest? Why?
- What type of bond do you predict to be the shortest? The longest? Why?

Bond strength

- Bond energy (bond strength):
  - ♦Single bond < double bond < triple bond

Bond length

- Bond length (distance between atom nuclei)
  - ♦Single bond > double bond > triple bond
- Bond strength and bond length are inversely related

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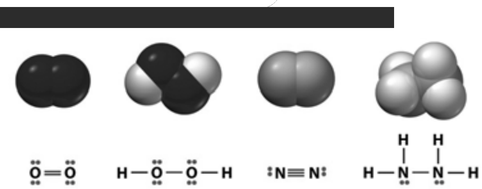
Comparison of Bonds



	$O=O$	$H-O-O-H$	$N\equiv N$	H_2N-NH_2
Bond length:	121 pm	148 pm	110 pm	145 pm
Bond strength:	498 kJ/mol	213 kJ/mol	945 kJ/mol	275 kJ/mol

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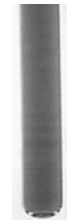
Group Work

- Draw Lewis Structures for the following substances:
- CO_2
- CO
- HCN
- SO_3^{2-}
- Worked Ex. 7.3, 7.4; Problems 7.6, 7.7

Exceptions to the Octet Rule



- Odd-Electron Molecules
  - ♦ Draw a Lewis structure for NO and NO_2
  - ♦ Why does NO_2 combine with itself to form N_2O_4?
- Incomplete Octets
  - ♦ Draw structures for $BeCl_2$, BH_3, BF_3, $AlCl_3$

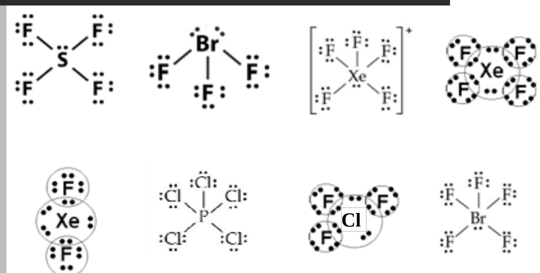
Exceptions to the Octet Rule

- What do you do if there are too many electrons?
- Draw Lewis Structures for the following:

SF_4	BrF_3	XeF_5^+	XeF_4
XeF_2	PCl_5	ClF_3	BrF_5

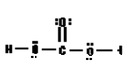
- When do we find expanded octets? (Hint: what shells (rows) are the central atoms in?)
- Worked Ex. 7.6 – 7.8; Problems 7.9 – 7.11

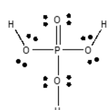
Exceptions to the Octet Rule



Electron-Dot Structures: Oxyacids and Carbon Chains

- Draw structures for:
  - ♦ H_2SO_4
  - ♦ H_3PO_4
  - ♦ H_2CO_3





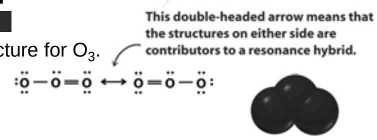
- Carbon always gets 4 electron pairs!
  - ♦ C_2H_6
  - ♦ $CH_3CH_2CH_2CH_3$
  - ♦ CH_2CHCN

The Concept of Resonance

- Sometimes a single Lewis structure doesn't accurately represent bonds. Sometimes multiple structures are needed to adequately show how electrons are shared.
  - ♦ Examples: O_3, SO_3, NO_3^-, CO_3^{2-}
- Example: nectarines. They are a combination of a peach and plum but you have to use both fruits to describe it accurately. Same with resonance structures. No one structure is accurate – we have to draw multiple structures.

The Concept of Resonance

- Draw the structure for O_3.



- Expect O – O bond (148 pm) to be longer than O = O bond (121 pm)
- Experimental evidence shows both bonds are 128 pm long
- ***Resonance structures***: two or more Lewis structures used for a single molecule that cannot be represented accurately by only one Lewis structure (a blend of two structures)

Resonance

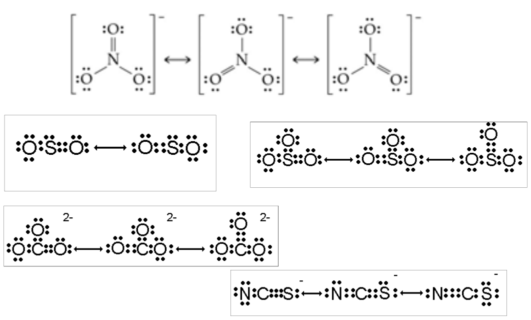
- How many different valid Lewis formulas can you draw for the following molecules or ions?

  NO_3^- SO_2 SO_3

  CO_3^{2-} NCS^-

- Worked Ex. 7.9, Problems 7.12 – 7.14

Resonance



Molecular Shapes: The VSEPR Model

- In your groups, draw (or find in your notes) Lewis Structures for the following molecules:
- CH_4
- NH_3
- H_2O
- BF_3
- SO_2
- CO_2
- PCl_5
- SF_6

Molecular Shapes: The VSEPR Model

- Valence-Shell Electron-Pair Repulsion
- Electron pairs (or groups of pairs) try to avoid one another because of repulsions between like-charged particles
- Regions where electrons are likely to be found are called electron domains:
  - ♦ Lone electron pairs
  - ♦ Single, double, and triple bonds
- Electron domains occur as far apart as possible
- Electronic geometry vs. molecular geometry

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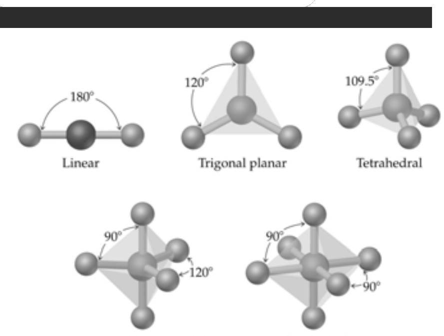
candiceVSEPR.exe

Five Fundamental Geometries



VSEPR Theory

- Use **A, B, E** notation: A = central atom; B = # outer atoms; E = # lone e^- pairs
  - ♦ CH_4 = AB_4, NH_3 = AB_3E, H_2O = AB_2E_2
- Can predict the angles between electron domains (charge clouds):
- 2 domains - linear (180º)
- 3 domains - trigonal planar (120º)
- 4 domains - tetrahedral (109.5º)
- 5 domains - trigonal bipyramidal (90º & 120º)
- 6 domains - octahedral (90º)
- Worked Ex. 7.11; Problems 7.17, 7.19

VSEPR

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Molecular Geometries

- A = central atom; B = # outer atoms; E = # lone e^- pairs

Electronic Geometry	Molecular Geom.	Molecular Geom.
AB_2 Linear		
AB_3 Trigonal Planar	**AB_2E Bent**	
AB_4 Tetrahedral	**AB_3E Trigonal Pyramidal**	**AB_2E_2 Bent**
AB_5 Trig. Bipyramidal	AB_4E See-Saw	AB_3E_2 T-Shaped
AB_6 Octahedral	AB_5E Square Pyramid	AB_4E_2 Square Planar

What are the molecular geometries of the following molecules?

- CO_2
- SO_2
- BF_3
- CH_4
- NH_4^+
- CCl_4
- NH_3
- H_2O
- SF_2
- $COCl_2$
- PCl_5
- OF_2
- ClO_4^-
- SF_6
- CS_2
- BiF_5
- $AlCl_4^-$
- ClO_2^-
- AsH_3

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Molecular Shapes

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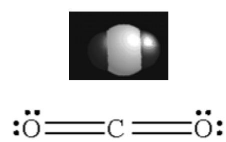
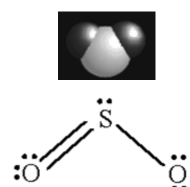
- Why don't CO_2 and SO_2 have the same geometry?



Carbon dioxide



Sulfur dioxide

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Valence Bond Theory

- Lewis structures and VSEPR give information about the shapes of molecules and the distributions of electrons. They don't explain ***why*** a bond forms.
- Valence-bond theory considers both bond formation and molecular shape
- Looks at how electrons are shared in a covalent bond
- VB theory considers the atomic orbitals occupied by the valence electrons

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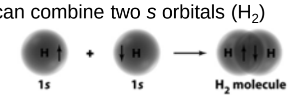
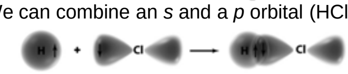
Creating Bonds

Sigma.exe

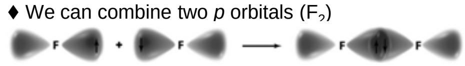
- Half-filled orbitals overlap so that 2 electrons can share space and form a covalent bond.
  - ♦ We can combine two *s* orbitals (H_2)



  - ♦ We can combine an *s* and a *p* orbital (HCl)



  - ♦ We can combine two *p* orbitals (F_2)



Examples to Use

- Before we discuss this process, draw Lewis Structures and determine molecular geometries for the following:
- CH_4
- BF_3
- $BeCl_2$
- PCl_5
- SF_6
- CH_2CH_2
- C_2H_2

Valence Bond Theory: Hybridization

- Combine these concepts:
- Electron configurations
  - ♦ Valence electrons (short-hand notation)
- Orbitals
  - ♦ s: spherical
  - ♦ p: dumb-bell shaped
  - ♦ Reminder: An orbital only holds two electrons
- Lewis Dot Structures
- VSEPR

Bond Formation

Liger: lion + tiger

geep

Zeedonk: zebra + donkey

- <u>Hybrids</u> In chemistry, covalent bonds are created by making orbitals equivalent in energy. This is done by combining or mixing atomic orbitals to create new, or hybrid, orbitals.
- This is the basis of ***Valence Bond Theory***: using atoms' valence electrons to explain how bonds form.

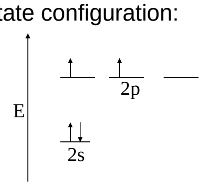
Hybridization in Methane

- Methane: CH_4
- Lewis Dot Structure?
- Carbon is central atom
- Electron configuration of carbon?
  - ♦ [He] $2s^2$ $2p^2$
- VSEPR shape?
  - ♦ Tetrahedral - indicates that all bonds are equal

Rasmol CH_4

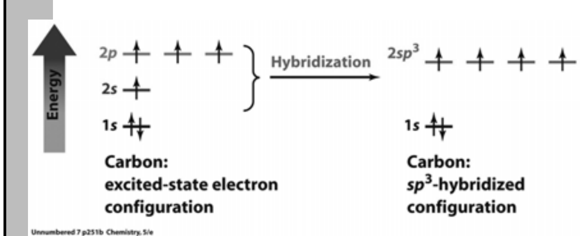
Hybridization in Methane

- Need 4 equivalent orbitals to form the 4 single (σ) bonds (based on VSEPR and experiments)
- Ground state configuration:



sp^3 formation

Carbon Hybridization



sp^3 Hybridization

- Combine one *s* orbital and three *p* orbitals → four hybridized orbitals (sp^3)

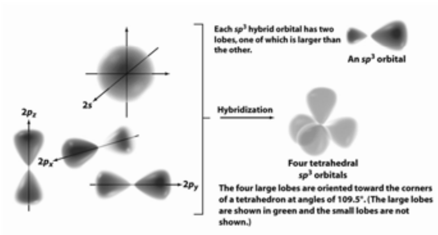


Figure 7-6 Chemistry, 5/e
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Sigma – C + H

Hybridization in Boron Trifluoride

- Boron trifluoride: BF_3
- Lewis Dot Structure?
- Boron is central atom
- Electron configuration of boron?
  - [He] $2s^2$ $2p^1$
- VSEPR shape?
  - Trigonal planar

sp^2 hybridization Rasmol BF_3

Hybridization in Beryllium Chloride

- Beryllium chloride: $BeCl_2$
- Lewis Dot Structure?
- Beryllium is central atom
- Electron configuration of beryllium?
  - [He] $2s^2$
- VSEPR shape?
  - Linear

sp hybridization Rasmol $BeCl_2$

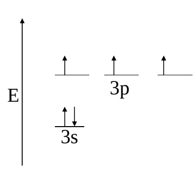
Hybridization in Phosphorus Pentachloride

- Phosphorus pentachloride: PCl_5
- Lewis Dot Structure?
- Phosphorus is central atom
- Electron configuration of phosphorus?
  - [Ne] $3s^2$ $3p^3$
- VSEPR shape?
  - Trigonal bipyramidal

Rasmol PCl5

Hybridization in Phosphorus Pentachloride

- How many single bonds in PCl_5?
- Where does the 5th orbital come from?
  - Expanded octet
  - sp^3d



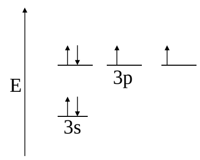
Hybridization in Sulfur Hexafluoride

- Sulfur Hexafluoride: SF_6
- Lewis Dot Structure?
- Sulfur is central atom
- Electron configuration of sulfur?
  - [Ne] $3s^2$ $3p^4$
- VSEPR shape?
  - Octahedral
- Problems 7.20 – 7.22

Rasmol SF6

Hybridization in Sulfur Hexafluoride

- Need 6 equivalent orbitals to form the 6 single bonds.
- Where does the 6^{th} orbital come from?
  - Expanded octet
  - sp^3d^2

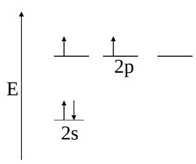


Hybridization in Multiple Bonds: Ethylene

- Ethylene: CH_2CH_2
- Lewis Dot Structure?
- Carbon is central atom
- Electron configuration of carbon?
  - [He] $2s^2$ $2p^2$
- VSEPR shape?
  - Trigonal planar

Hybridization in Ethylene

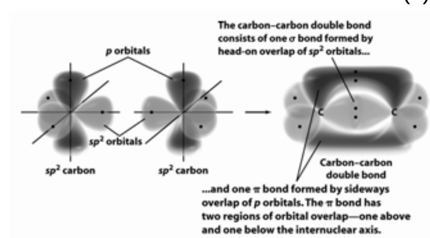
- How many **single** bonds in CH_2CH_2?
- Need 3 equivalent orbitals to form the 3 single bonds around one carbon atom.



sp^2 hybridization

Hybridization in Ethylene

- sp^2 hybridization accounts for single (σ) bonds, but what about the unhybridized 2*p* orbital?
- That orbital contributes to the double (π) bond.



Sigma bond

Pi bond

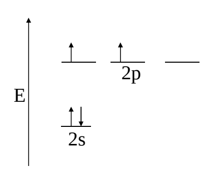
Hybridization in Acetylene

- Acetylene: HCCH
- Lewis Dot Structure?
- Carbon is central atom
- Electron configuration of carbon?
  - [He] $2s^2$ $2p^2$
- VSEPR shape?
  - Linear

Rasmol HCN

Hybridization in Acetylene

- How many **single** bonds in HCCH?
- Need 2 equivalent orbitals to form the 2 single bonds around 1 carbon atom.

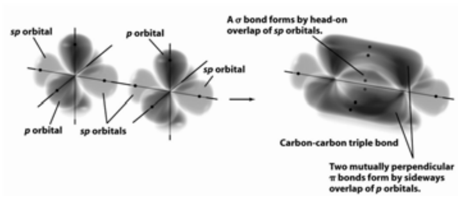


Aorbs.exe

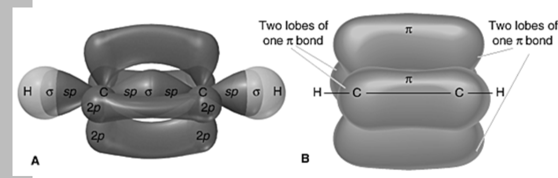
sp hybridization

Hybridization in Acetylene

- sp hybridization accounts for single (σ) bonds, but what about the unhybridized 2p orbitals?
- Those 2 unhybridized 2p orbitals help make the two π bonds.



Hybrid Orbitals in a Triple Bond



- What does the hybridization for N_2 look like?
- Worked Ex. 7.12; Problems 7.23 – 7.25

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Group work

- Determine the hybridization of the central atoms in your group quiz molecules:
- $POCl_3$
- BF_3
- NO_2^-
- PCl_5
- CO_3^{2-}

Summary

- According to Valence Bond Theory, covalent bonds form when:
  - there are two electrons in each orbital; one electron from each atom
  - these two orbitals “overlap”
- The number of hybridized orbitals equals the number of atomic orbitals that are combined.
  - sp → 2 orbitals combined ($BeCl_2$ and HCN)
  - sp^2 → 3 orbitals combined (BF_3 and CH_2O)
  - sp^3 → 4 orbitals combined (CH_4)
  - sp^3d → 5 orbitals combined (PCl_5)
  - sp^3d^2 → 6 orbitals combined (SF_6)

Summary

- **The number of hybridized orbitals equals the number of *__electron domains__* (including lone e^- pairs) around a central atom (starting with s)**
  - **sp, sp^2, sp^3, sp^3d, sp^3d^2**
- A single bond has 1 σ bond (the same goes for a lone pair of electrons)
- A double bond has 1 σ bond and 1 π bond
- A triple bond has 1 σ bond and 2 π bonds
- Unhybridized *p* orbitals participate in π bonding (to make double and triple bonds)