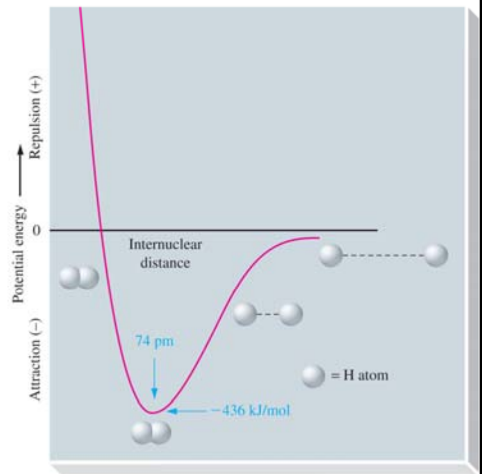
Chemical Bonding and Molecular Structure

What are bonds? Why do bonds form?

Valence Electrons:

- Number and distribution of valence e- determines reactivity
- Main Group Elements (s and p block):
- Transition Metals (d block):
- EXAMPLES: Bromine and Iron



Bonding: Ionic vs Covalent Two Extremes

<u>Ionic Bonding</u>:

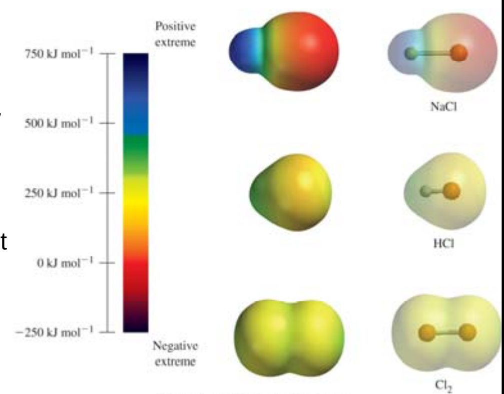
- Electrostatic attraction
  - Discreet charges… “transferred” electrons
- Modeled using Coulomb’s Law

$$F = \frac{Q_1Q_2}{\varepsilon r^2}$$

Q = charge
r = separation
ε = dielectric constant

<u>Covalent Bonding</u>:

- Also an electrostatic attraction
  - No charge separation… “shared” electrons



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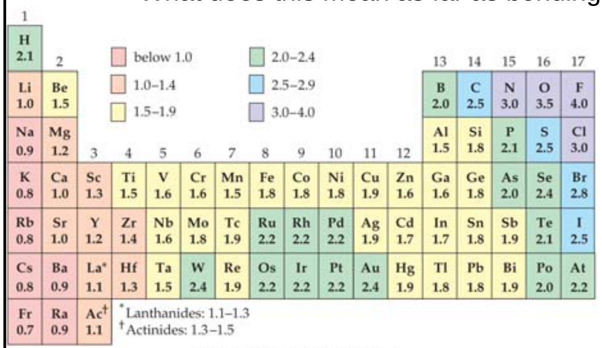
Electronegativity: Essential in understanding bonding and predicting structure.

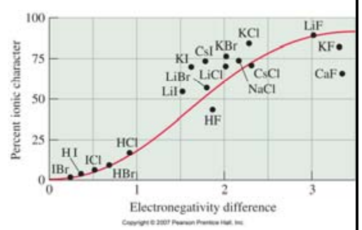
Electronegativity: ability of an atom in a bond (molecule) to attract electrons to itself

- Trends in electronegativity
- Related to Ionization Energy and Electron Affinity

$$EN \propto (IE - EA)$$

- What does this mean as far as bonding is concerned?





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Bonding Models

- Attempts to explain real life (shape, reactivity, properties). Sometimes they work better than others. REAL LIFE WINS!

Using Lewis Dot Structures to Model Molecules

- Localized electron bonding model
  - Valence electron bookkeeping
- Primary goal in bond formation:
- Representing bonding using Lewis structures has two key features:
  1.
  2.
- Best suited for s and p block compounds
  - Particularly up to Ne

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Guidelines for Drawing Lewis Structures

Underlying criteria: "Octet Rule": Kind of like the Pirate Code

General Scheme: (CH_2Cl_2 and CO_2 as examples)

1. Determine arrangement of atoms (skeletal structure)…HOW?
   - Central vs peripheral (terminal) atoms
2. Determine total # of valence e^-…HOW?
3. Draw single bonds between central atom and each peripheral atom
4. Distribute remaining e- as lone pairs around peripheral atoms until all have an octet
5. Add multiple bonds to central atom if necessary until all atoms have filled octets.
6. Double-check that all e- have been used and that all atoms have filled octets!

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Guidelines for Drawing Lewis Structures

Formal Charge (FC)

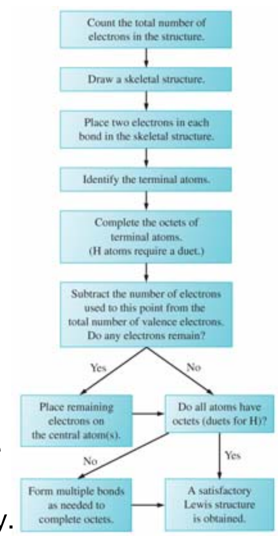
- Calculated for a **specific** atom in a molecule

  FC = group # - [# of e- in lone pairs + 1/2(# of bonding e-]
- IMPORTANT! The sum of all the FC for a species or ion MUST equal the net charge on the species!

Example: Calculate the FC on each atom in CN-:

FC can help when drawing Lewis Structures

1. FC on each atom should be as small as possible
2. (-) FC should appear on the most electronegative atoms, (+) FC on least electronegative.
3. FC of the same sign on adjacent atoms is unlikely.



Things to Keep in Mind

Molecules are THREE DIMENSIONAL and real life wins!

- Not everything satisfies the octet rule!
  - Hydrogen is different! (so is boron)
  - Some atoms an “expand their octets”
  - Odd electron species exist! (NO, for example)
  - Transition metals and the octet rule.
- Carbon forms four bonds…usually.
- Isoelectronic Species (i.e. NO^+, N_2, CO, CN^-)
- Resonance (Section 10.5)

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Bonding, Lewis Structures, and Molecular Shape

Valence Shell Electron Pair Repulsion (VSEPR) model:

- Bonding and lone pairs of electrons repel each other and try to get as far apart as possible

What shapes would we predict? AX_n or AX_nE_m models. **(It all starts with Table 10.1)**

- X = terminal atoms, E = unshared electron pairs on central atom.
- Suggestion: think of “things” around the central atom.
- Those “things” want to get as far apart in space as possible.
- Unshared pairs take up more room than bonding pairs.
- *Electron-pair geometry* may be different than *molecular geometry*

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Bonding, Lewis Structures, and Molecular Shape

Case 1: No lone pairs around central atoms

- (don't worry about lone pairs on peripheral atoms)
- Electron-pair and molecular geometry are the same.

Case 2: Lone pairs on central atom:

- Two things to remember
  1. Lone pairs occupy space (*more space than bonding pairs*)
  2. Lone pairs repel electrons
- BUT: You predict shape by predicting electron-pair geometry and converting to molecular geometry.
  - Electron-pair and molecular geometry may (and typically are) different.

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Bonding, Lewis Structures, and Molecular Shape

- Families evolve based on total number of "Things" around central atom (n + m)
  - *A multiple bond counts as one "Thing"*
- # Things = 2

TABLE 10.1 Molecular Geometry as a Function of Electron-Group Geometry

VSEPR Basic Molecular Configurations models

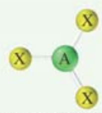
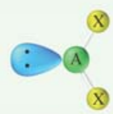
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
2	linear	0	AX_2	 (linear)	180°	$BeCl_2$	

[a]For a discussion of the structure of SO_2, see page 402.
[b]For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

Bonding, Lewis Structures, and Molecular Shape

- # Things = 3

TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
3	trigonal-planar	0	AX_3	 (trigonal planar)	120°	BF_3	
	trigonal-planar	1	AX_2E	 (bent)	120°	SO_2[a]	

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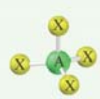
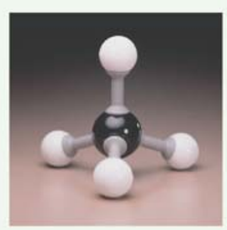
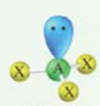
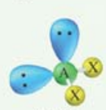
Bonding, Lewis Structures, and Molecular Shape

- # Things = 4

ued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
4	tetrahedral	0	AX_4	 (tetrahedral)	109.5°	CH_4	
	tetrahedral	1	AX_3E	 (trigonal-pyramidal)	109.5°	NH_3	
	tetrahedral	2	AX_2E_2	 (bent)	109.5°	OH_2	

Bonding, Lewis Structures, and Molecular Shape

- # Things = 5

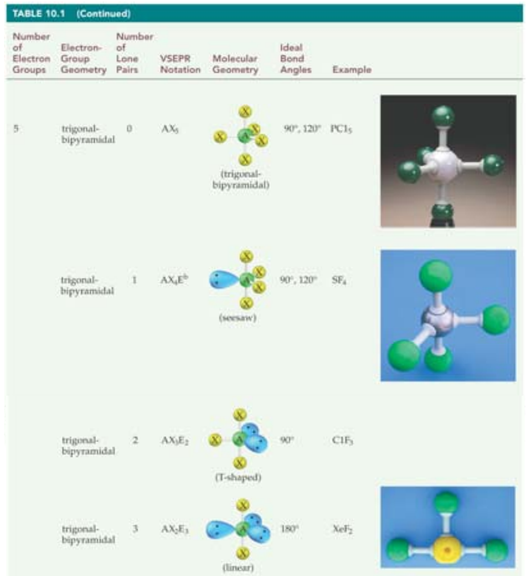


TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
5	trigonal-bipyramidal	0	AX_5	(trigonal-bipyramidal)	90°, 120°	PCl_5
	trigonal-bipyramidal	1	AX_4E^b	(seesaw)	90°, 120°	SF_4
	trigonal-bipyramidal	2	AX_3E_2	(T-shaped)	90°	ClF_3
	trigonal-bipyramidal	3	AX_2E_3	(linear)	180°	XeF_2

Bonding, Lewis Structures, and Molecular Shape

- # Things = 6

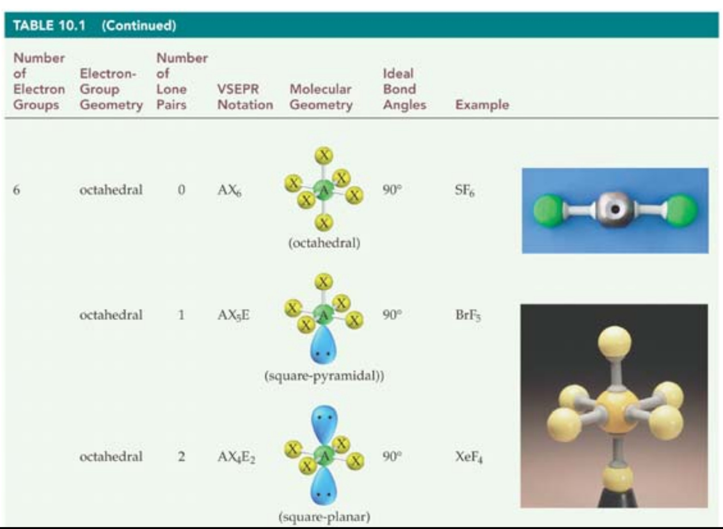


TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
6	octahedral	0	AX_6	(octahedral)	90°	SF_6
	octahedral	1	AX_5E	(square-pyramidal))	90°	BrF_5
	octahedral	2	AX_4E_2	(square-planar)	90°	XeF_4

Bond and Molecular Polarity

Polar bonds result from unequal sharing of electrons

- Due to electronegativity differences
- Produced bond dipoles.

Just as bonds can be polar, molecules can also be polar

- Molecular polarity plays major role in:
  - solubility (like dissolves like),
  - reactivity (biochemical interactions)

Molecular polarity is determined by polarity and *orientation* of bonds in the molecule

- Need structure first!

Examples: H_2O, CO_2, CCl_4

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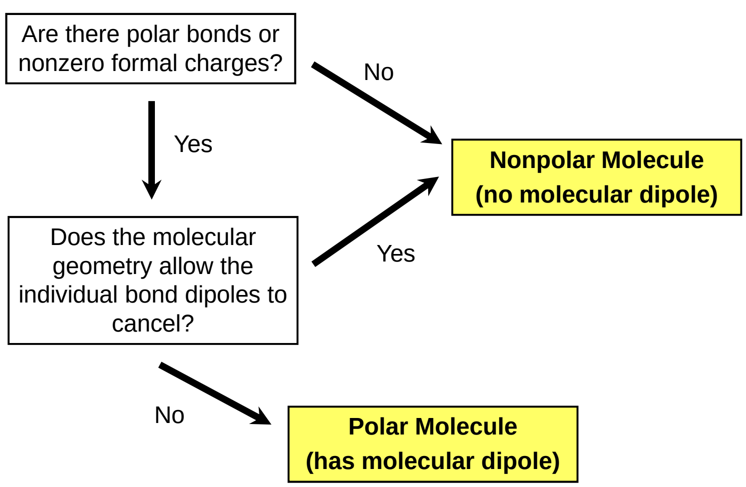
Predicting Molecular Polarity



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Bond Characteristics

Bond Order:

Bond Length (Table 10.2):

TABLE 10.2 Some Average Bond Lengths[a]

Bond	Bond Length, pm	Bond	Bond Length, pm	Bond	Bond Length, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—Cl	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

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Bond Characteristics

Bond Strength (Bond Dissociation Energy, Table 10.3): Useful in predicting thermodynamics

- Bond breaking: _______________ energy
- Bond formation: _______________ energy

TABLE 10.3 Some Average Bond Energies[a]

Bond	Bond Energy, kJ/mol	Bond	Bond Energy kJ/mol	Bond	Bond Energy kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736[b]	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
				Br—Br	193
				I—I	151

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Calculating ΔH^o_{rxn} for gas phase reactions:

- Why Gas Phase?

	$CH_4(g) + 2\ O_2(g) \rightarrow\ CO_2(g)\ + 2\ H_2O(g)$
Lewis Structure	
Bonds Broken	
Bonds Formed	
Energies (kJ)	

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

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Isomers

Isomers: different compounds with same molecular formula

Stereoisomers: isomers where connections are same, but arrangement in space different

Constitutional Isomers: isomers where atoms are connected differently

Enantiomers: stereoisomers that are mirror images

Diastereomers: stereoisomers that are not mirror images

EXAMPLE: $C_2H_2Cl_2$ has 3 possible structures, only 2 are diastereomers

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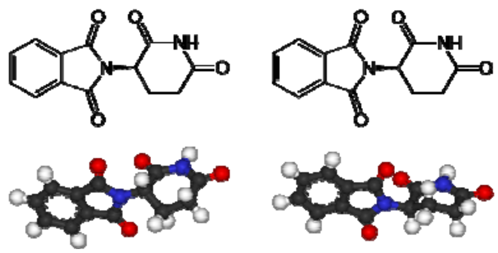
Enantiomers

Molecules that have Enantiomers are Chiral

- Amino Acids are one Enantiomer
- Some bacteria use the amino acids of the other chirality to trick their hosts

Enantiomers have similar physical properties (nearly identical)

- Interact differently with polarized light
- May have dramatically different reactivity
  - Thalidomide



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