Chapter 8

Bonding

What is a Bond?

- A force that holds atoms together.
- Why?
- We will look at it in terms of energy.
- Bond energy- the energy required to break a bond.
- Why are compounds formed?
- Because it gives the system the lowest energy.

Ionic Bonding

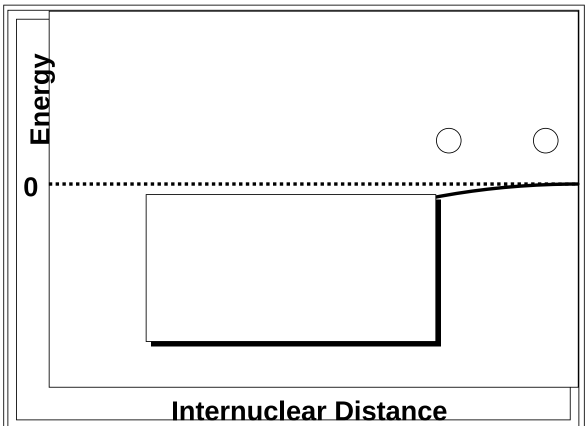
- An atom with a low ionization energy reacts with an atom with high electron affinity.
- A metal and a non metal
- The electron moves.
- Opposite charges hold the atoms together.

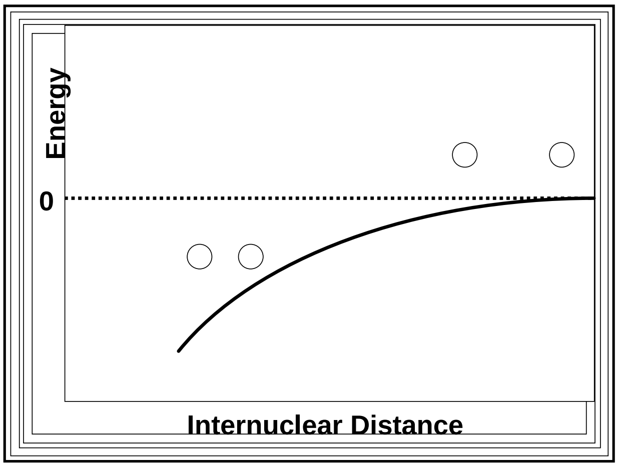
Coulomb's Law

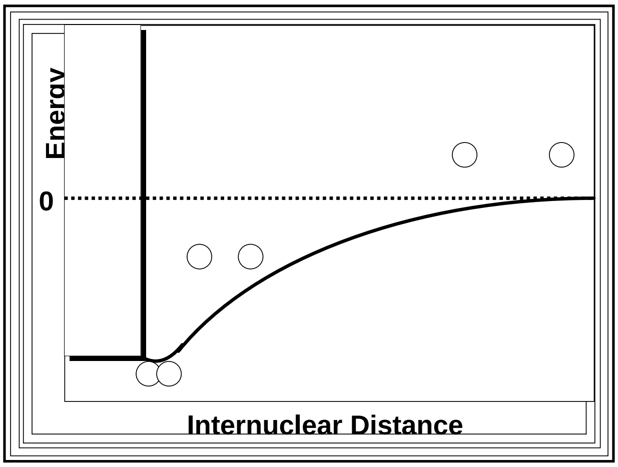
- E= 2.31 x 10^{-19} J · nm(Q_1Q_2)/r
- Q is the charge.
- r is the distance between the centers.
- If charges are opposite, E is negative
- exothermic
- Same charge, positive E, requires energy to bring them together.

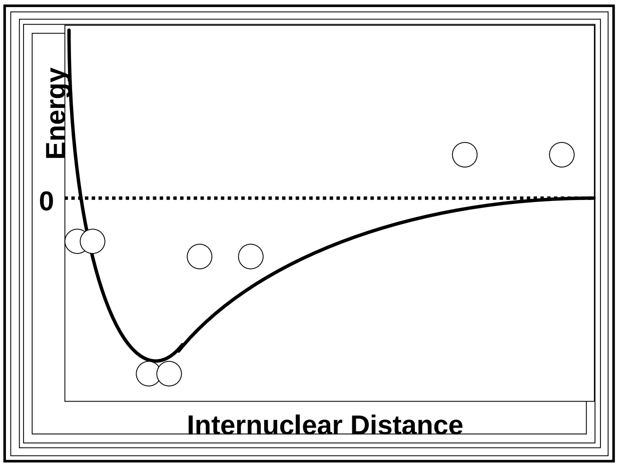
What about covalent compounds?

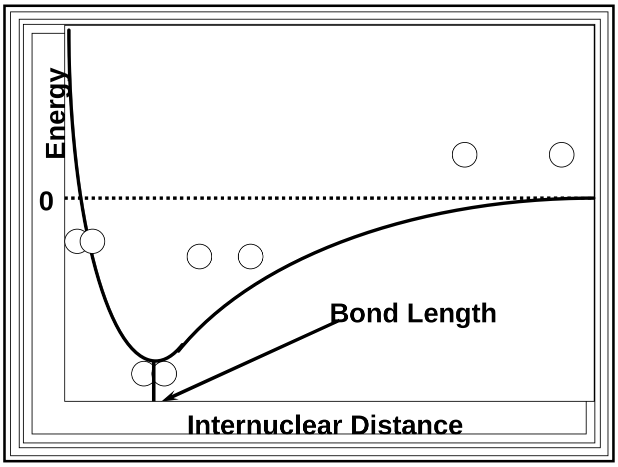
- The electrons in each atom are attracted to the nucleus of the other.
- The electrons repel each other,
- The nuclei repel each other.
- The reach a distance with the lowest possible energy.
- The distance between is the bond length.

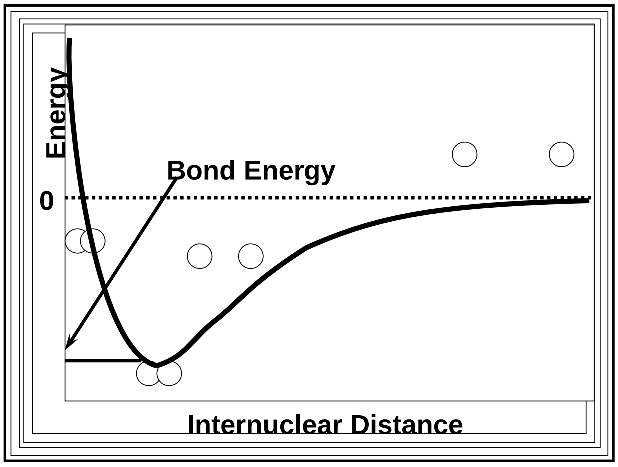








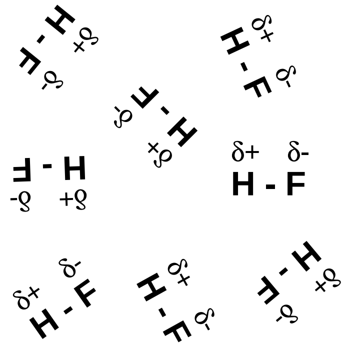


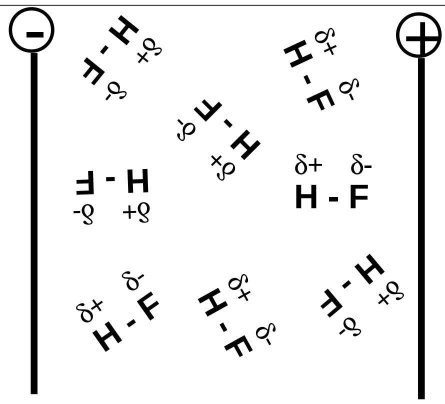


Covalent Bonding

- Electrons are shared by atoms.
- These are two extremes.
- In between are polar covalent bonds.
- The electrons are not shared evenly.
- One end is slightly positive, the other negative.
- Indicated using small delta δ.

δ+ δ-
H - F



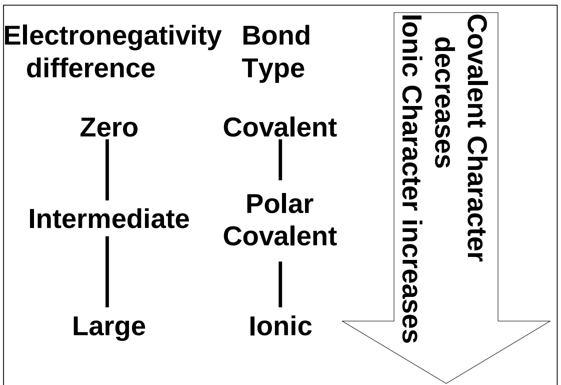


Electronegativity

- The ability of an electron to attract shared electrons to itself.
- Pauling method
- Imaginary molecule HX
- Expected H-X energy =
$$\frac{\text{H-H energy} + \text{X-X energy}}{2}$$
- $\Delta = (\text{H-X})_{\text{actual}} - (\text{H-X})_{\text{expected}}$

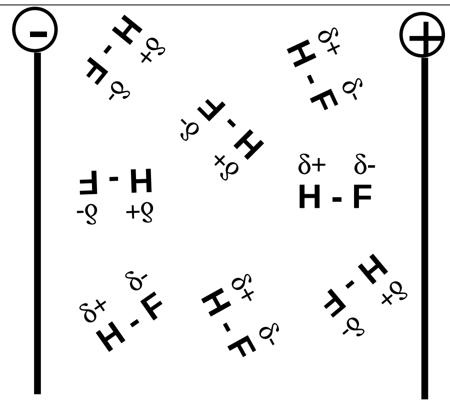
Electronegativity

- Δ is known for almost every element
- Gives us relative electronegativities of all elements.
- Tends to increase left to right.
- decreases as you go down a group.
- Most noble gases aren’t discussed.
- Difference in electronegativity between atoms tells us how polar the bond is.

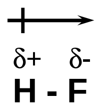


Dipole Moments

- A molecule with a center of negative charge and a center of positive charge is dipolar (two poles),
- or has a dipole moment.
- Center of charge doesn't have to be on an atom.
- Will line up in the presence of an electric field.



How It is drawn

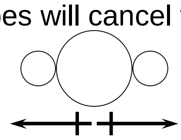


Which Molecules Have Dipoles?

- Any two atom molecule with a polar bond.
- With three or more atoms there are two considerations.
  1) There must be a polar bond.
  2) Geometry can't cancel it out.

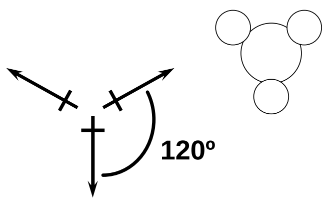
Geometry and polarity

- Three shapes will cancel them out.
- Linear



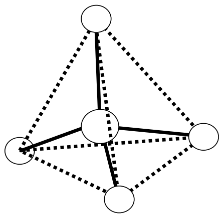
Geometry and polarity

- Three shapes will cancel them out.
- Planar triangles



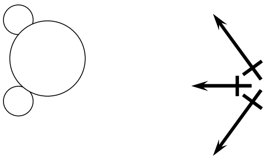
Geometry and polarity

- Three shapes will cancel them out.
- Tetrahedral



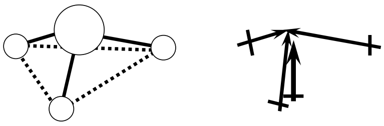
Geometry and polarity

- Others don't cancel
- Bent



Geometry and polarity

- Others don't cancel
- Trigonal Pyramidal



Ions

- Atoms tend to react to form noble gas configuration.
- Metals lose electrons to form cations
- Nonmetals can share electrons in covalent bonds.
  - When two non-metals react.(more later)
- Or they can gain electrons to form anions.

Ionic Compounds

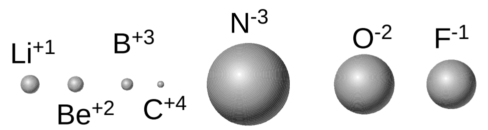
- We mean the solid crystal.
- Ions align themselves to maximize attractions between opposite charges,
- and to minimize repulsion between like ions.
- Can stabilize ions that would be unstable as a gas.
- React to achieve noble gas configuration

Size of ions

- Ion size increases down a group.
- Cations are smaller than the atoms they came from.
- Anions are larger.
- across a row they get smaller, and then suddenly larger.
- First half are cations.
- Second half are anions.

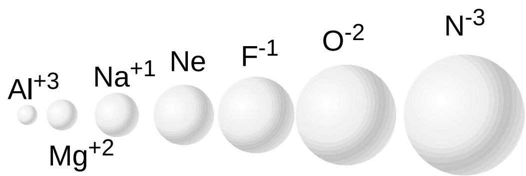
Periodic Trends

- Across the period nuclear charge increases so they get smaller.
- Energy level changes between anions and cations.



Size of Isoelectronic ions

- Positive ions have more protons so they are smaller.



Forming Ionic Compounds

- **Lattice energy - the energy associated with making a solid ionic compound from its gaseous ions.**
- $M^+(g) + X^-(g) \rightarrow MX(s)$
- **This is the energy that "pays" for making ionic compounds.**
- **Energy is a state function so we can get from reactants to products in a round about way.**

$Na(s) + ½F_2(g) \rightarrow NaF(s)$

- First sublime Na — $Na(s) \rightarrow Na(g)$, $\Delta H = 109$ kJ/mol
- Ionize Na(g) — $Na(g) \rightarrow Na^+(g) + e^-$, $\Delta H = 495$ kJ/mol
- Break F-F Bond — $½F_2(g) \rightarrow F(g)$, $\Delta H = 77$ kJ/mol
- Add electron to F — $F(g) + e^- \rightarrow F^-(g)$, $\Delta H = -328$ kJ/mol

$Na(s) + ½F_2(g) \rightarrow NaF(s)$

- Lattice energy

$Na^+(g) + F^-(g) \rightarrow NaF(s)$

$\Delta H = -928$ kJ/mol

Calculating Lattice Energy

- Lattice Energy = $k(Q_1Q_2 / r)$
- k is a constant that depends on the structure of the crystal.
- Q's are charges.
- r is internuclear distance.
- Lattice energy is with smaller ions
- Lattice energy is greater with more highly charged ions.

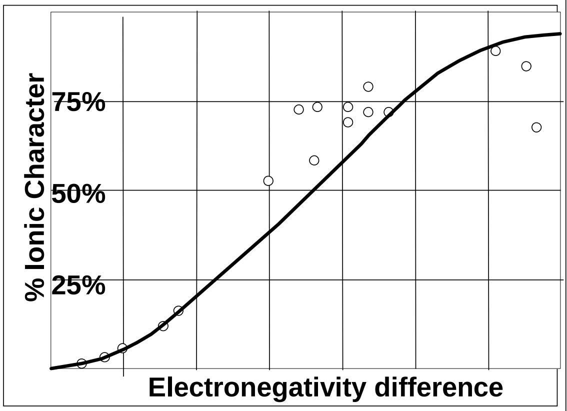
Calculating Lattice Energy

- This bigger lattice energy “pays” for the extra ionization energy.
- Also “pays” for unfavorable electron affinity.
- $O^{2-}(g)$ is unstable, but will form as part of a crystal

Bonding

Partial Ionic Character

- There are probably no totally ionic bonds between individual atoms.
- Calculate % ionic character.
- Compare measured dipole of X-Y bonds to the calculated dipole of X^+Y^- the completely ionic case.
- $\% \text{ dipole} = \frac{\text{Measured X-Y}}{\text{Calculated } X^+Y^-} \times 100$
- In the gas phase.



How do we deal with it?

- If bonds can’t be ionic, what are ionic compounds?
- And what about polyatomic ions?
- An ionic compound will be defined as any substance that conducts electricity when melted.
- Also use the generic term salt.

The Covalent Bond

- The forces that causes a group of atoms to behave as a unit.
- Why?
- Due to the tendency of atoms to achieve the lowest energy state.
- It takes 1652 kJ to dissociate a mole of CH_4 into its ions
- Since each hydrogen is hooked to the carbon, we get the average energy = 413 kJ/mol

- CH_3Cl has 3 C-H, and 1 C - Cl
- the C-Cl bond is 339 kJ/mol
- The bond is a human invention.
- It is a method of explaining the energy change associated with forming molecules.
- Bonds don't exist in nature, but are useful.
- We have a model of a bond.

What is a Model?

- Explains how nature operates.
- Derived from observations.
- It simplifies them and categorizes the information.
- A model must be sensible, but it has limitations.

Properties of a Model

- A human inventions, not a blown up picture of nature.
- Models can be wrong, because they are based on speculations and oversimplification.
- Become more complicated with age.
- You must understand the assumptions in the model, and look for weaknesses.
- We learn more when the model is wrong than when it is right.

Covalent Bond Energies

- We made some simplifications in describing the bond energy of CH_4
- Each C-H bond has a different energy.
- $CH_4 \rightarrow CH_3 + H$ $\Delta H = 435$ kJ/mol
- $CH_3 \rightarrow CH_2 + H$ $\Delta H = 453$ kJ/mol
- $CH_2 \rightarrow CH + H$ $\Delta H = 425$ kJ/mol
- $CH \rightarrow C + H$ $\Delta H = 339$ kJ/mol
- Each bond is sensitive to its environment.

Averages

- There is a table of the averages of different types of bonds pg. 365
- single bond- one pair of electrons is shared.
- double bond- two pair of electrons are shared.
- triple bond- three pair of electrons are shared.
- More bonds, more bond energy, but shorter bond length.

Using Bond Energies

- We can estimate ΔH for a reaction.
- It takes energy to break bonds, and end up with atoms (+).
- We get energy when we use atoms to form bonds (-).
- If we add up the energy it took to break the bonds, and subtract the energy we get from forming the bonds we get the ΔH.
- Energy and Enthalpy are state functions.

Find the energy for this

$2\ CH_2 = CHCH_3 + 2NH_3 + O_2$

$\rightarrow 2\ CH_2 = CHC \equiv N + 6\ H_2O$

C-H 413 kJ/mol	**O-H 467 kJ/mol**
C=C 614kJ/mol	**O=O 495 kJ/mol**
N-H 391 kJ/mol	**C≡N 891 kJ/mol**
C-C 347 kJ/mol	

Localized Electron Model

- Simple model, easily applied.
- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.
- Three Parts

1) Valence electrons using Lewis structures
2) Prediction of geometry using VSEPR
3) Description of the types of orbitals (Chapt 9)

Lewis Structure

- Shows how the valence electrons are arranged.
- One dot for each valence electron.
- A stable compound has all its atoms with a noble gas configuration.
- Hydrogen follows the duet rule.
- The rest follow the octet rule.
- Bonding pair is the one between the symbols.

Rules

- Sum the valence electrons.
- Use a pair to form a bond between each pair of atoms.
- Arrange the rest to fulfill the octet rule (except for H and the duet).
- H_2O
- A line can be used instead of a pair.

Quiz Answers

1. D
2. B
3. A
4. D
5. C
6. E
7. D
8. E
9. E

A useful equation

- (happy-have) / 2 = bonds
- CO_2 C is central atom
- $POCl_3$ P is central atom
- SO_4^{2-} S is central atom
- SO_3^{2-} S is central atom
- PO_4^{3-} P is central atom
- SCl_2 S is central atom

Exceptions to the octet

- BH_3
- Be and B often do not achieve octet
- Have less than an octet, for electron deficient molecules.
- SF_6
- Third row and larger elements can exceed the octet
- Use 3d orbitals?
- I_3^-

Exceptions to the octet

- When we must exceed the octet, extra electrons go on central atom.
- (Happy – have)/2 won't work
- ClF_3
- XeO_3
- ICl_4^-
- $BeCl_2$

Resonance

- Sometimes there is more than one valid structure for an molecule or ion.
- NO_3^-
- Use double arrows to indicate it is the "average" of the structures.
- It doesn't switch between them.
- NO_2^-
- Localized electron model is based on pairs of electrons, doesn't deal with odd numbers.

Formal Charge

- For molecules and polyatomic ions that exceed the octet there are several different structures.
- Use charges on atoms to help decide which.
- Trying to use the oxidation numbers to put charges on atoms in molecules doesn't work.

Formal Charge

- The difference between the number of valence electrons on the free atom and that assigned in the molecule or ion.
- We count half the electrons in each bond as "belonging" to the atom.
- SO_4^{-2}
- Molecules try to achieve as low a formal charge as possible.
- Negative formal charges should be on electronegative elements.

Examples

- XeO_3
- NO_4^{3-}
- SO_2Cl_2

VSEPR

- Lewis structures tell us how the atoms are connected to each other.
- They don't tell us anything about shape.
- The shape of a molecule can greatly affect its properties.
- Valence Shell Electron Pair Repulsion Theory allows us to predict geometry

VSEPR

- Molecules take a shape that puts electron pairs as far away from each other as possible.
- Have to draw the Lewis structure to determine electron pairs.
- bonding
- nonbonding lone pair
- Lone pair take more space.
- Multiple bonds count as one pair.

VSEPR

- The number of pairs determines
  - bond angles
  - underlying structure
- The number of atoms determines
  - actual shape

VSEPR

Electron pairs	Bond Angles	Underlying Shape
2	180°	Linear
3	120°	Trigonal Planar
4	109.5°	Tetrahedral
5	90°& 120°	Trigonal Bipyramidal
6	90°	Octagonal

Actual shape

Electron Pairs	Bonding Pairs	Non-Bonding Pairs	Shape
2	2	0	linear
3	3	0	trigonal planar
3	2	1	bent
4	4	0	tetrahedral
4	3	1	trigonal pyramidal
4	2	2	bent

Actual Shape

Electron Pairs	Bonding Pairs	Non-Bonding Pairs	Shape
5	5	0	trigonal bipyrimidal
5	4	1	See-saw
5	3	2	T-shaped
5	2	3	linear

Actual Shape

Electron Pairs	Bonding Pairs	Non-Bonding Pairs	Shape
6	6	0	Octahedral
6	5	1	Square Pyramidal
6	4	2	Square Planar
6	3	3	T-shaped
6	2	1	linear

Examples

- SiF_4
- SeF_4
- KrF_4
- BF_3
- PF_3
- BrF_3

No central atom

- Can predict the geometry of each angle.
- build it piece by piece.

How well does it work?

- Does an outstanding job for such a simple model.
- Predictions are almost always accurate.
- Like all simple models, it has exceptions.
- Doesn't deal with odd electrons

Polar molecules

- Must have polar bonds
- Must not be symmetrical
- Symmetrical shapes include
  - Linear
  - Trigonal planar
  - Tetrahedral
  - Trigonal bipyrimidal
  - Octahedral
  - Square planar