Chpt 8 Bonding Genral Concepts

Bonding I

Chemical Bonds

- **The forces that hold a group of atoms together so that they can function as a group.**

Bond Energy

- The amount of energy needed to break a chemical bond.

Ionic Bonds

- Metal + Non-metal
- High Δelectronegativity
  - > 2.0 * (other definitions exist)
- Opposite charges attract so Coulomb's Law applies
    - $F = \frac{k_e Q_1 Q_2}{r^2}$ where F is the force of attraction between two point sources.
  - $E = (2.31 \times 10^{-19}\ \mathrm{J{\bullet}nm})\,(Q_1 Q_2/r)$
    - E is energy, Q_1 and Q_2 are the respective charges and r is radius or bond length.
    -

Ionic Bonds

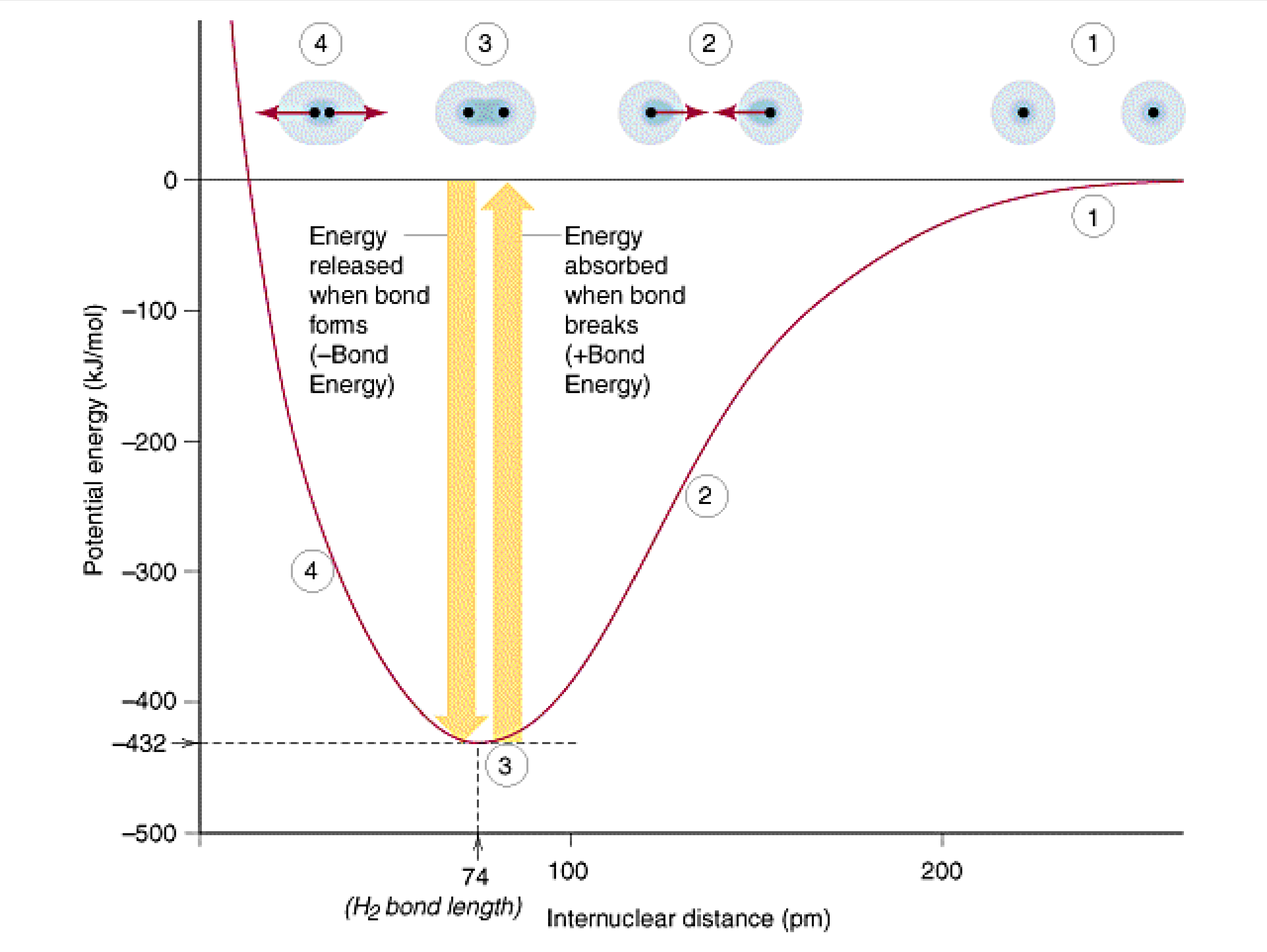
- Solving for Lattice Energy
- $E = (2.31 \times 10^{-19}\ J \bullet nm)\ (Q_1 Q_2 / r)$
- E is lattice energy, Q_1 and Q_2 are the respective charges and r is bond length.

- At 0.276 nm (2.76 Å) bond length for example in NaCl, $E = -8.37 \times 10^{-19}$ J. Negative energies represent attractions. Positive signs would be repulsion
  - E smaller as r increases.
  - Bond is a low energy configuration (large - #s).

Ionic vs Covalent substances

- Molecular substances
  - Non conductors
  - Low melting point
  - Low solubilities in H_2O
- Ionic substances
  - Conduct when dissolved or molten
  - High melting points
  - High solubilities in H_2O

Bond length vs Energy



Bond length

- 1) A bond will form if the energy of the aggregate is lower than that of the separated atoms.
- 2) The bond length is the distance at which system has minimal energy.
- 3) At this distance electrons are simutaneously attracted to both protons, yet not too close to repel each other

Covalent bonds

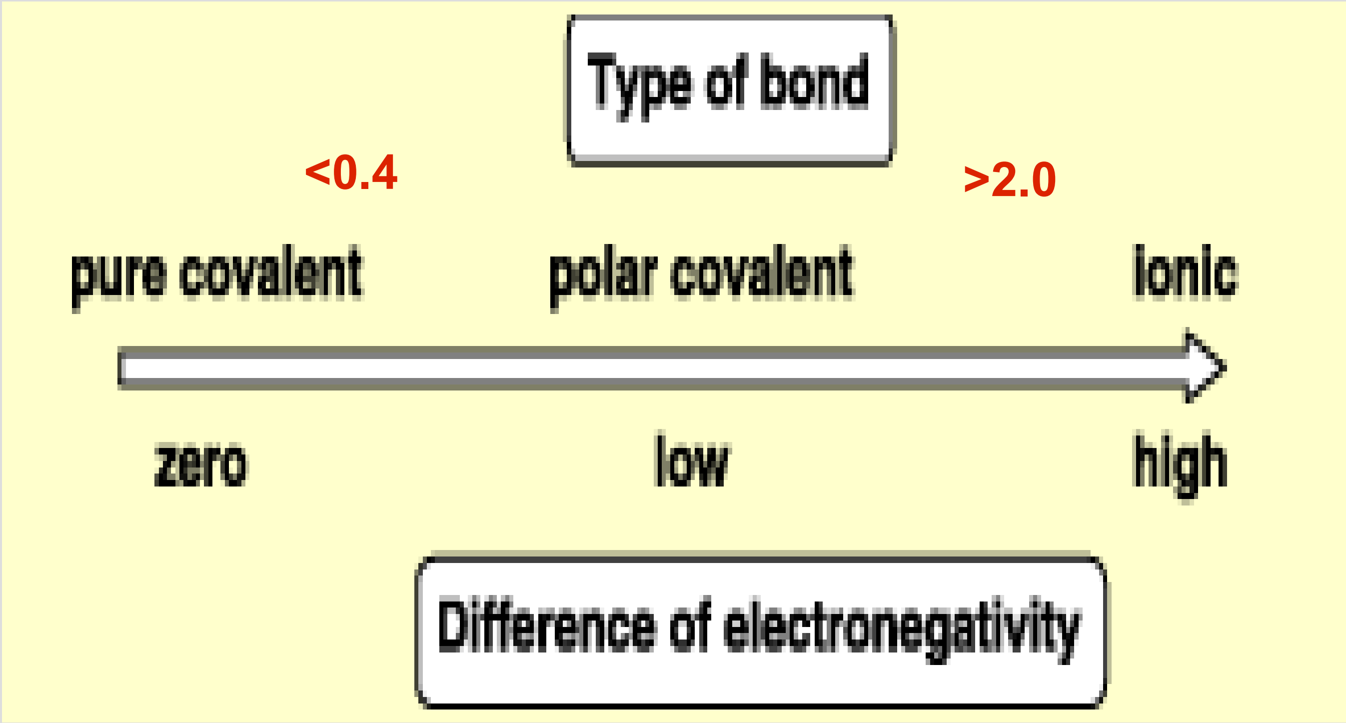
- **Bonds in which electrons are shared are called covalent.**
- **They result in molecular compounds.**

Electronegativity

- Differences in electronegativity control the type of bond between atoms.
-
  - The ability of an atom in a molecule to attract shared electrons to itself.
  - Greediness for electrons
    - Best friend
    - Older brother
    - Lunch room bully

Electronegativity

- Electronegativity difference controls type of bond between two atoms

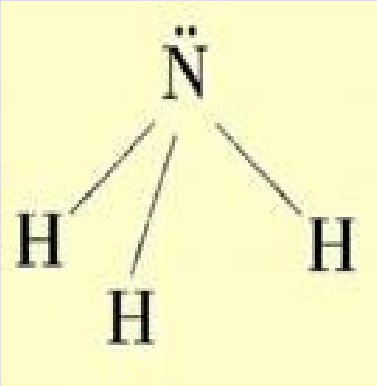


Electronegativity

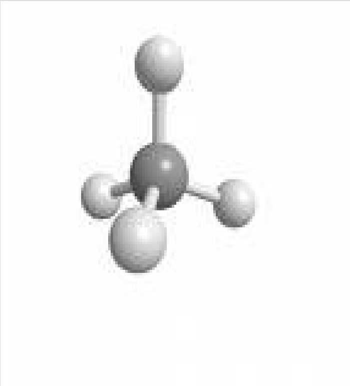
- Polar molecules must meet two criteria
  - 1. polar covalent bonds must be present.
  - 2. a net dipole moment must be present.
    - Dipoles must not cancel each other.
    - Non-symmetric arrangement.

Are these molecules polar?

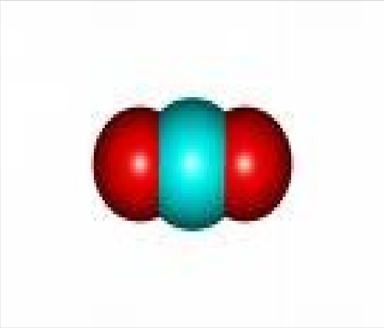
ammonia



methane



Carbon dioxide



Ionic compounds

- Electronegativity values > 2.0
- Dissolve and yeild ions in solution
- Conduct electricity if molten or dissolved.
- Really only exist in solid state only

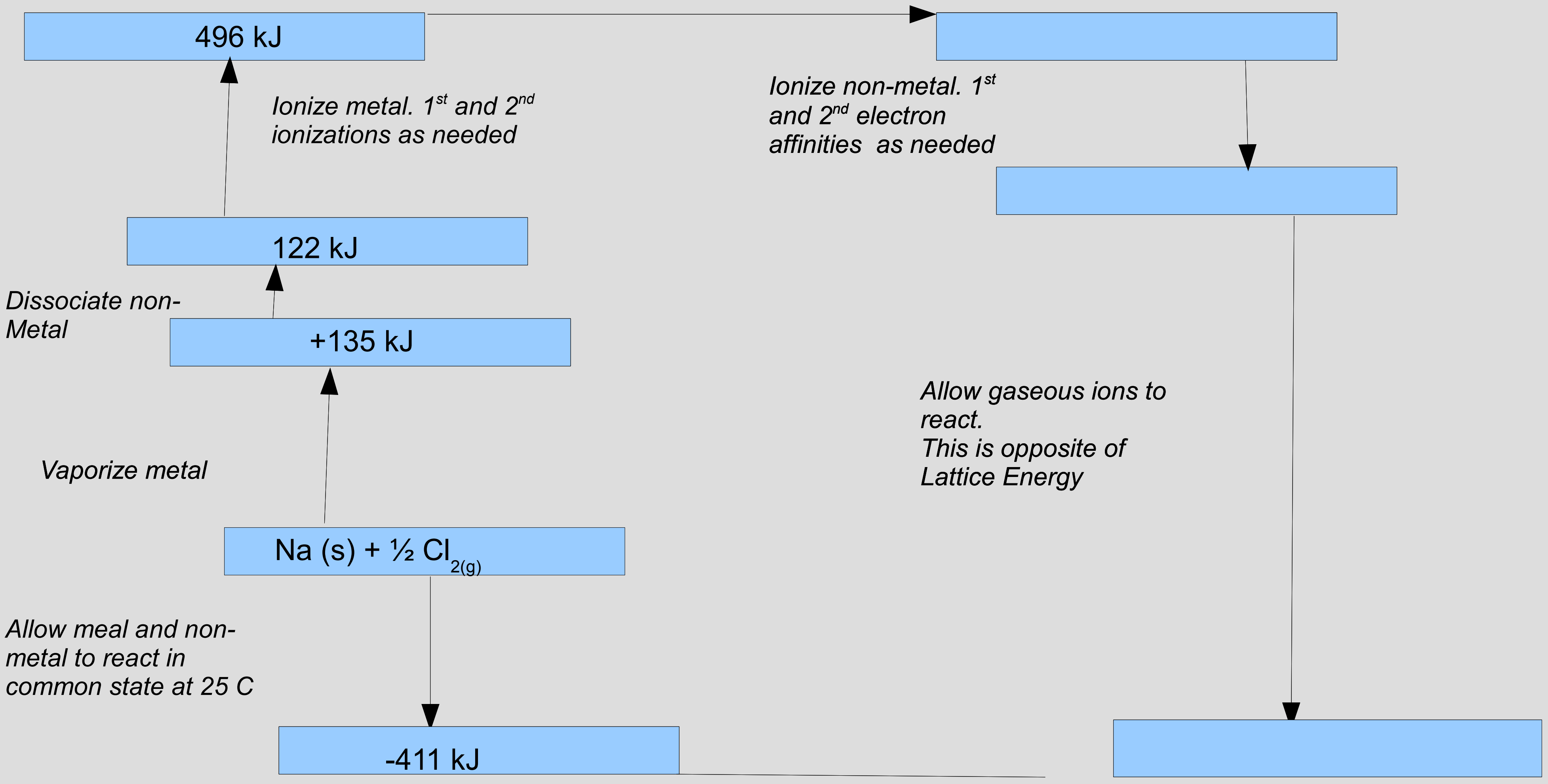
Ionic Compounds

- 3-d array of ions closely packed so as to minimize the + +, and - - repulsions and maximize the + - attractions. Electrons are transferred from metal to non-metal so both become isoelectric with nearest noble gas. Use criss-cross to predict formulas.

Lattice Energy

- Energy change when gaseous ions combine to form ionic solid. This is always exothermic
- $M^+(g) + X^-(g) \rightarrow MX(s)$
- Older textbooks define lattice energy as the amount of energy required to convert 1 mole of ionic substance into gaseous ions. Endothermic or + kJ

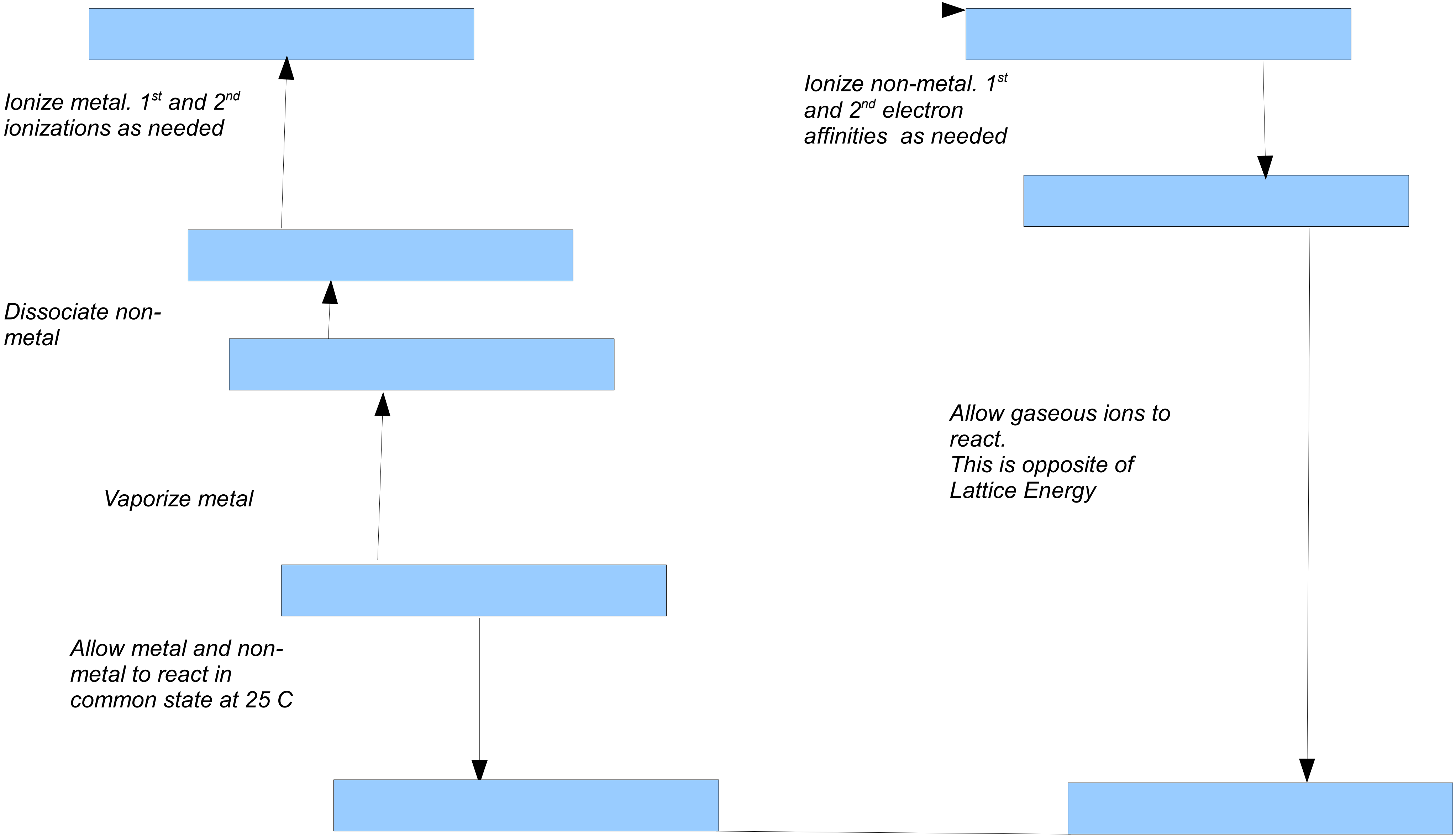
Lattice Energy (The steps)



Lattice Energy (The steps)

- Sublimation of solids to gases
- Ionization of cation (IE_1 and/or IE_2)
- Disassociation of anion (if diatomic wimp)
- Electron affinity for anion (making it an ion)
- Heat of formation (bringing it all together)

Born- Haber cycle Template ionic solids



Building a crystal from scratch

- Calculating Lattice energy
- Balance the equation: $Li + ½\, Br_2 \rightarrow LiBr$
- Break into steps — How much energy
  - *1. $Li(s) \rightarrow Li(g)$* — *$E = 161$ kJ*
  - *2. $Li(g) \rightarrow Li^{+}(g) + e^{-}$* — *$E = 520$ kJ*
  - *3. $½\, Br_2(l) \rightarrow 1/2 Br_2\,(g)$* — *$E = 8$ kJ*
  - *4. $½\, Br_2\,(g) \rightarrow Br\,(g)$* — *$E = 95$ kJ*
  - *5. $Br(g) + e^{-} \rightarrow Br^{-}(g)$* — *$E = -324$ kJ*
  - *6. $Li + ½\, Br_2 \rightarrow LiBr$* — *$E = +351$ kJ*
  - *$U =$* — *811 kJ*

Covalent Chemical Bonds

- *What is a chemical bond? ... Energy !!! ;)*
- *It takes 1652 kJ/mole to break CH_4 apart so on average a C-H bond consists of 413 kJ/mole of energy*
- *What is the bond energy associated with C-Cl if chloromethane takes 1578 kJ/mole to break apart into its elements?*

Bond Energy and Enthalpy

- Since bonds store (are) energy, adding up the energies of breaking old bonds and making new bonds works well to give us the Enthalpy of reaction.
- $\Delta H_{rxn} = \Sigma D_{\text{(breaking)}} - \Sigma D_{\text{(making)}}$
- *Somewhat counter-intuitive: breaking bonds takes energy. Making bonds releases energy*

Heat of Formation from bond Energy

- *What is ΔH_{rxn} for the reaction $H_2 + F_2$ 2HF*
- $\Delta H_{rxn} = (D_{H\text{-}H} + D_{F\text{-}F}) - 2(D_{H\text{-}F})$
- $\Delta H_{rxn} = (1 \text{ mol} \times 432 \text{ kJ/mol} + 1 \text{ mol} \times 154 \text{ kJ/mol})$
- – (2 mol x 565 kJ/mol)
- -544 kJ/mol
- Checking against standard table of ΔH˚ 2mol x – 271 kJ/mol = -542 kJ/mol (so we are close enough).

Harder Example (Try on your own)

- *What is ΔH_{rxn} for forming icky nasty ozone destroying Freon 12 from methane, chlorine and fluorine?*
- *1. Balance reaction:*
- $CH_4 + 2Cl_2 + 2F_2 \rightarrow CF_2Cl_2 + 2\ HF + 2\ HCl$

Bond energies

- *2. Get bond energies from table (- = "bond")*
  - C-H 413 kJ/mole
  - Cl-Cl 239 kJ/mole
  - F-F 154 kJ/mole
  - C-F 485 kJ/mole
  - C-Cl 339 kJ/mole
  - H-F 565 kJ/mole
  - H-Cl 427 kJ/mole

Example cont'd

- *1. $\Delta H_{rxn} = \Sigma D_{\text{(breaking)}} - \Sigma D_{\text{(making)}}$*
- *2. Energy in breaking bonds subtotal*
- (4 mol C-H x 413kJ/mol) + (2 mol Cl-Cl x 239 kJ/mol) + (2 mole F-F x 154 kJ/mol) = 2438 kJ

Continued

- *1. Energy in making bonds subtotal*
- 2mol C-F x 485 kJ/mol + 2mol C-Cl x 339kJ/mol + 2 mol H-F x 565 kJ/mol + 2 mol H-Cl x 427 kJ/mol = 3632 kJ
- 2. $\Delta H_{rxn} = \Sigma D_{(breaking)} – \Sigma D_{(making)}$
- $\Delta H_{rxn} = 2438\ kJ – 3632\ kJ = - 1194\ kJ$

  (exothermic)

A reminder on sign convention

- Energy breaking bonds: (+) energy
  - as energy is required to be supplied to break bond.
- Energy making bonds: (-) energy
  - As bonds are energy lows they release energy to the environment.

- $\Delta H_{rxn} = \Sigma D_{(breaking)} + - \Sigma D_{(making)}$

Lewis Dot Diagrams

- Total number of valence electrons
    - From compound formula and column on Per. Table
- ABA or central atom
- 2 electrons to form a bond
- 8 electrons per non-metal
    - Double and Triple bond as needed
- OK to short metals

Exceptions

- *Central atom can exceed an octet*
- *3rd row elements often exceed octet*
- *Boron (can be electron deficient)*
- *Sulfur (and other elements from 3rd period) can exceed octet.*
  - *They have unfilled 3d orbitals with nearly the same energy level to store extra e's*

Try some of these

- PCl_5
-
-
- $BeCl_2$
-
-
- I_3^-

Formal Charge

- Odd numbers of electrons (How do they bond if Lewis structures require 2e- per bond?)
- Lewis structures and assigning oxidation numbers assign all electrons to the more electronegative species.
- Exaggerated charges.
-
- Enter Formal Charge.

Formal Charge

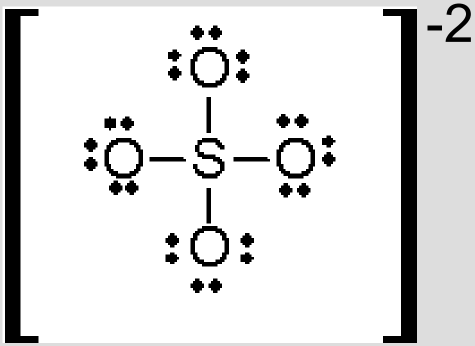
- *Formal charge (trying to decide which wrong structure is right)*
- ***Key***
- *Formal charge =* ***# of valence electrons of free atom − # of electrons assigned when in a molecule*****.**

Formal Charge

- *Determine number of valence electrons in free neutral atom (column on PT)*
- *Determine number of electrons belonging to atom in a molecule*
  - *Lone pairs of electrons belong to the atom*
  - *Shared electrons are* ***<u>divided</u>*** *between atoms in the molecule.*
  - *Sum of formal charges must equal charge on species (ion or molecule)*

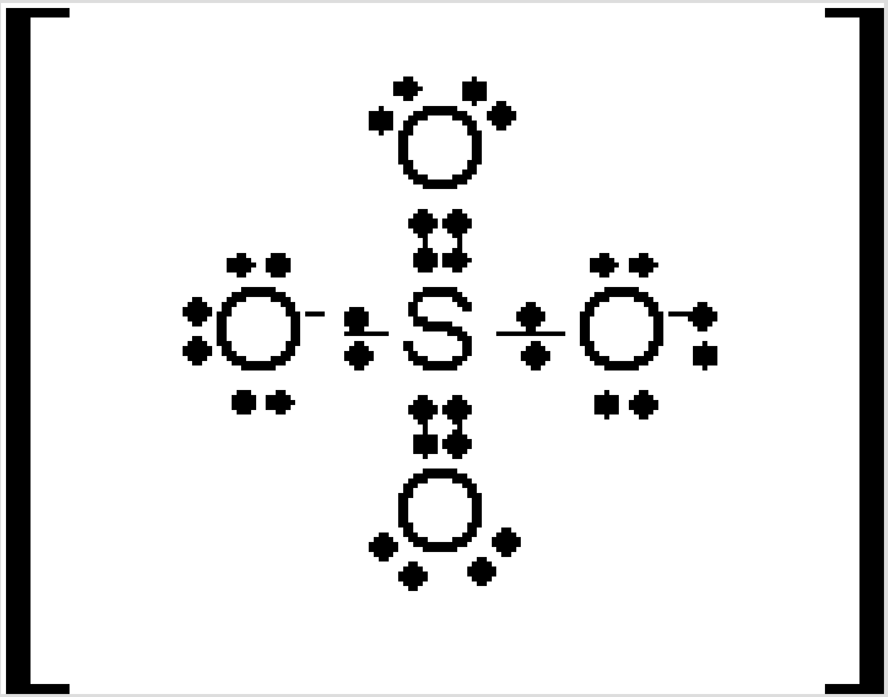
Example

- *1. SO_4^{-2} 32 total electrons*
- *2. Lewis dot diagram*
- Obeys octet rule, every body happy….?



- Calculate formal charges. S 6 ve – 4 be = 2
- O 6 ve – (6 lps + 1 be) = -1
- Central atom too positive, O too negative.

Formal Charge



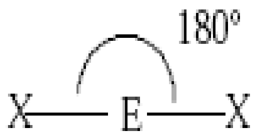
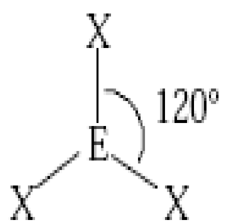
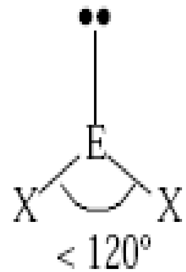
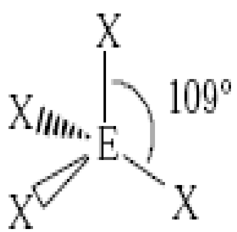
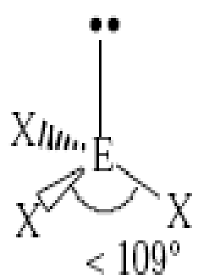
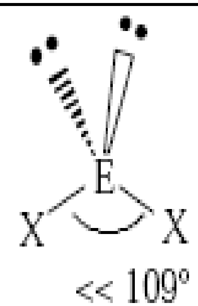
Better !!! :)

- DB O's 4 + 1/2(4)=6
- 6-6= 0 FC
- SB O's 6+1/2(2)= 7
- 6-7 = -1 FC
- S 0 + 1/2(12)= 6
- 6-6 = 0 FC
- More things closer to zero.
- Neg FC with >En element
- FC adds to charge

Formal Charge

- So this must be a plausible structure even though S now has 12 electrons!
- In violation of the octet rule.
- But it is a 3 row element!

VSEPR Geometries

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 **Linear**				
3	 **Trigonal Planar**	 **Bent or Angular**			
4	 **Tetrahedral**	 **Trigonal Pyramid**	 **Bent or Angular**		

VSEPR Geometries

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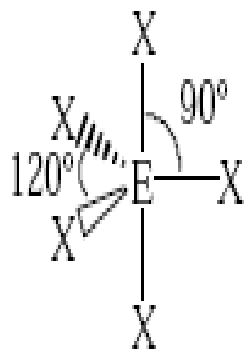
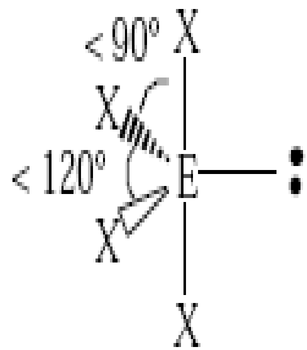
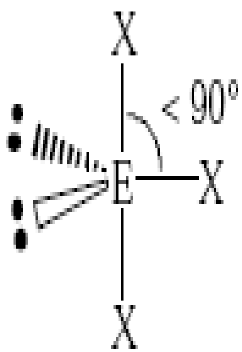
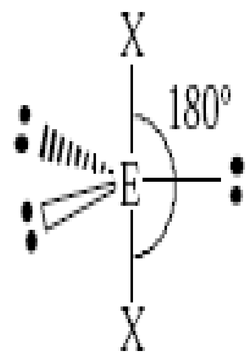
0 lone pair</th><th>1 lone pair</th><th>2 lone pairs</th><th>3 lone pairs</th><th>4 lone pairs</th></tr>
<tr><td>5</td><td>
Trigonal Bipyramid</td><td>
Sawhorse or Seesaw</td><td>
T-shape</td><td>
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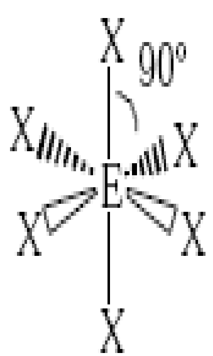
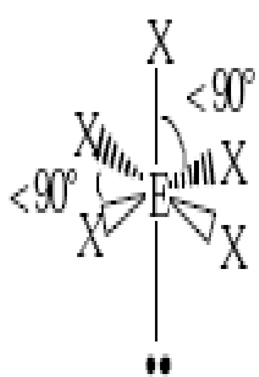
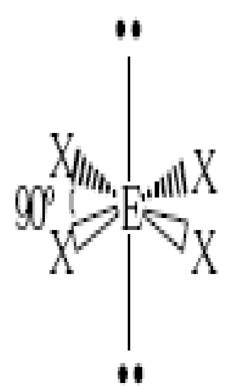
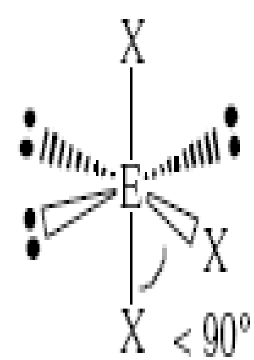
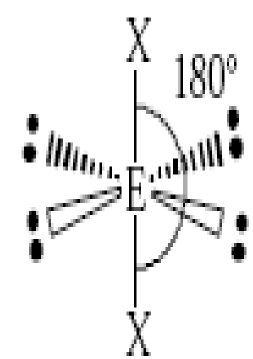
<tr><td>6</td><td>
Octahedral</td><td>
Square Pyramid</td><td>
Square Planar</td><td>
T-shape</td><td>
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