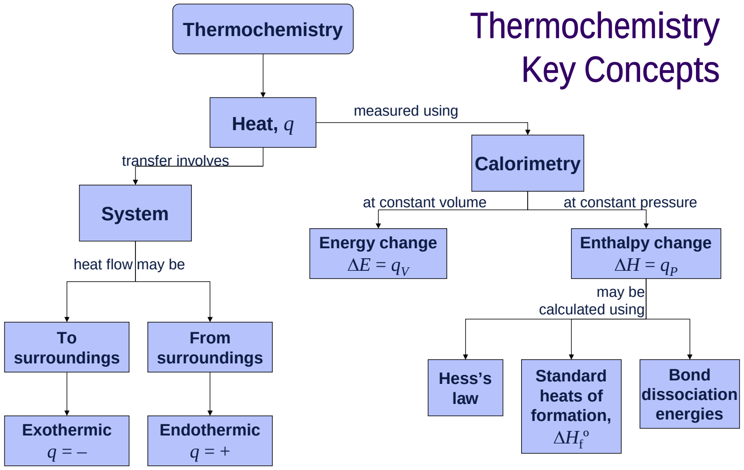
CHEM 115
Course Review, Second Half

Lecture Slides
May 10, 2007
Prof. Sevian

Agenda

- Thermochemistry (ch. 5)
- Electronic structure of atoms (ch. 6)
- Periodic properties (ch. 7)
- Chemical bonding basics (ch. 8)
- Molecular geometry and bonding theories (ch. 9)

Thermochemistry Key Concepts



Adapted from McMurray & Fay, 2001

More to come: entropy (S), entropy change (ΔS), free energy change (ΔG), spontaneity, etc.

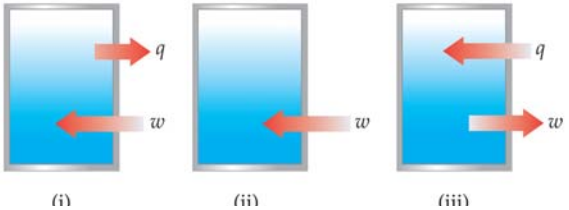
Map of chapter 5

- Energy in chemistry
  - Kinetic and potential energy changes as heat energy is added to a pure substance
- First law of thermodynamics
  - Transfer of energy and the Law of Conservation of Energy
  - Endothermic vs. exothermic changes
  - Enthalpy
- Measuring heat energy (enthalpy) changes (ΔH) in the laboratory
  - Heat energy and heat capacity of a material
  - Calorimetry technique
- Using laboratory measurements to calculate ΔH for reactions we can't measure in the lab

Energy content or Internal energy, *E*

- Sum of the kinetic and potential energies of all the particles in the system
- Can change in only two ways:
  - When heat (*q*) is transferred to the system (from the surroundings) or vice versa
  - When work (*w*) is done on the system (by the surroundings) or vice versa

For the systems below, describe what is happening to $\Delta E = q + w$



Energy

- Energy can be converted from one form to another
- Energy transfer occurs in such a way that the total energy of the universe remains constant (First Law of Thermodynamics)
- Energy transfer occurs in such a way that matter and energy become more dispersed, that is, more spread out (Second Law of Thermodynamics)
- Let's consider how energy transfer happens when we are concerned only with thermal energy (a.k.a., heat)

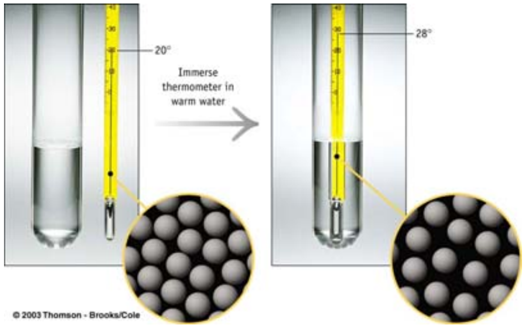
Heat Transfer

- Thermal energy
  http://www.colorado.edu/physics/2000/bec/temperature.html
- Transfer of thermal energy from one location to another
  http://jersey.uoregon.edu/vlab/Thermodynamics/therm1a.html

  When thermal energy is transferred, it always transfers from a location with more thermal energy to a location with less thermal energy. Energy continues to transfer until thermal equilibrium is established. (Energy gets more spread out.) Simply: hot to cold.
- To understand more about thermodynamic equilibrium, try all 7 "thought experiments" at
  http://jersey.uoregon.edu/vlab/Thermodynamics/index.html

Temperature

- A measurement made using an instrument called a thermometer
- How it works:



- So, what does temperature measure?

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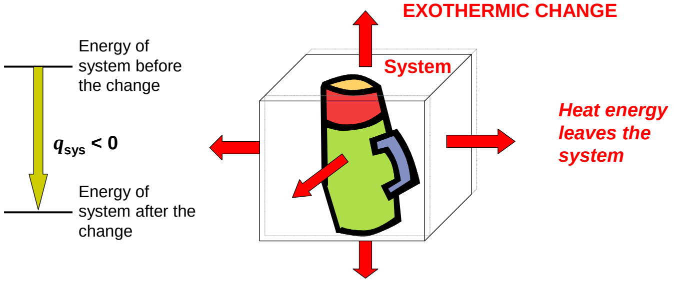
Relative vs. Absolute Temperature Scales

- Relative temperature (linear) scale measures temperature of an object relative to two points
  - Coldest and warmest temperatures at which humans can typically survive → Fahrenheit scale is relative
  - Freezing and boiling points of water → Celsius scale is relative
- Absolute temperature (linear) scale measures absolute motion of particles → Kelvin scale is absolute
  - Absolute zero temperature is a point of reference for disorder: there is no disorder at zero (Third Law of Thermodynamics)
  - Convenience: the size of 1 ºC is equal to the size of 1 K

What happens to a SYSTEM when heat transfer occurs?

- As coffee eventually cools, heat energy is transferred to the air around the thermos and the counter beneath it.
- System: Particles in the coffee slow down their motion.
- Surroundings: Particles in the air, and particles in the counter, speed up their motion.

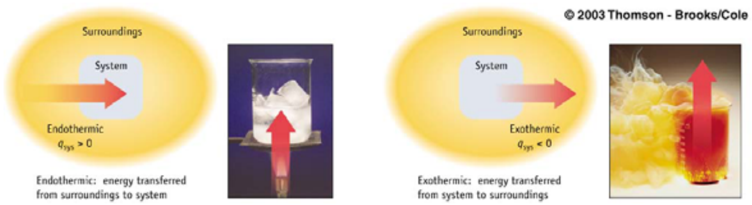


Conservation of Energy

- When heat energy enters or leaves matter, energy is conserved.
- This means energy has to come from somewhere, and it has to go somewhere. It can be accounted for.
- Particle level: energy can go into or come out of the system, thereby increasing or decreasing the energy in the particles
  - Kinetic energy: motion of particles (translation, vibration, rotation) in solid, liquid and gas states
  - Potential energy: electron states in atoms or within bonds

Endothermic vs. Exothermic

Endothermic	Exothermic
Example: ice melting	Example: fire burning
Heat enters system	Heat exits system
System gains energy	System loses energy
$q_{sys} > 0$	$q_{sys} < 0$



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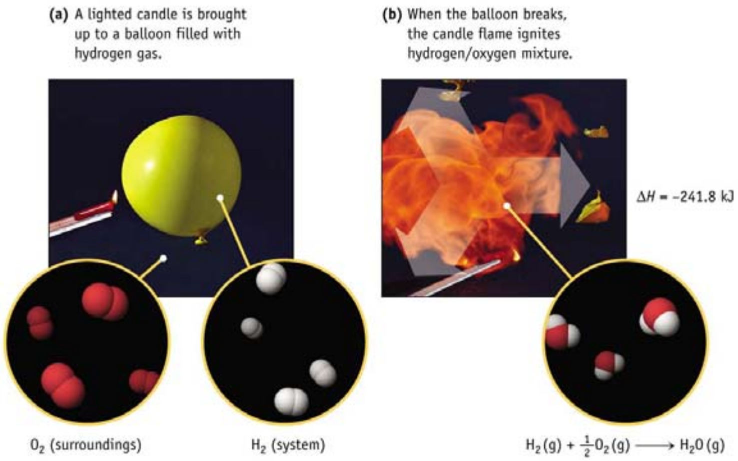

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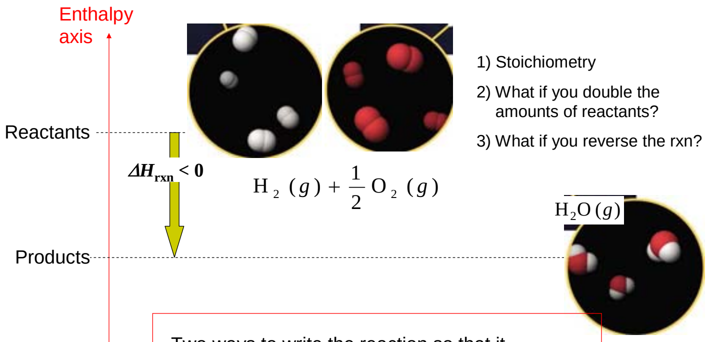
Enthalpy Change



1) Stoichiometry

2) What if you double the amounts of reactants?

3) What if you reverse the rxn?

Two ways to write the reaction so that it includes enthalpy information

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g) + 241.8\,kJ$$

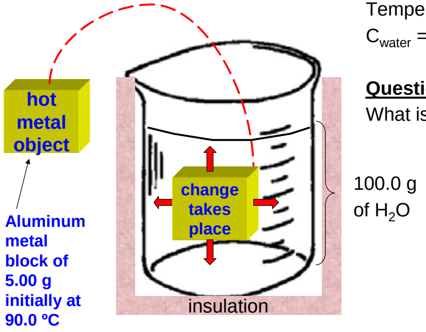
$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g) \qquad \Delta H = -241.8\,kJ$$

Important things to know about state functions like Δ*H* and Δ*E*

1. The delta (Δ) always means change from initial to final, calculated as "final minus initial."
   $\Delta H_{rxn} = H\text{ (products)} - H\text{ (reactants)}$
   Therefore, when Δ*H* is positive, it means the products were higher than the reactants
2. Reversing a reaction means changing the sign of the state function, since products and reactants are switched.
3. ΔH_{rxn} can be given in two ways: as kJ or as kJ/mol. If it is given in kJ, then it depends on the amount of reactant.
4. The physical states of the chemicals in the reaction matter.
   $2\ H_2\,(g)\ +\ O_2\,(g)\ \rightarrow\ 2\ H_2O\,(l) \qquad \Delta H_{rxn} = -571.66\text{ kJ}$
   $2\ H_2\,(g)\ +\ O_2\,(g)\ \rightarrow\ 2\ H_2O\,(g) \qquad \Delta H_{rxn} = -483.64\text{ kJ}$
5. State functions don't depend on the path***

A hot metal block placed in cold water

Measuring heat transferred from a system



Beaker image: core.ecu.edu/chem/chemlab/ equipment/ebeaker.htm

Given information

Initial temperature of Al block = 90.00ºC

Mass of Al block = 5.00 g

Mass of water = 100.0 g

Temperature of water before = 23.00ºC

Temperature of both after = 23.71ºC

C_{water} = 4.184 J/g·K

Question:

What is the heat capacity of Al?

Problem Solving Strategy

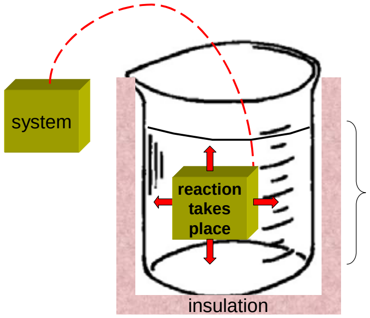
$q_w = m_w C_w \Delta T_w$

where $\Delta T_w = temp\ change\ of\ H_2O$

q_{sys} *is opposite of* q_w

Calorimetry is the same idea

Measuring heat transferred from a system



100.0 g of H_2O

Problem Solving Strategy

$q_w = m_w C_w \Delta T_w$

where ΔT_w = *temp change of* H_2O

q_{sys} *is opposite of* q_w

Given information

Mass of water = 100.0 g

Temperature of water before = 23.3ºC

Temperature of water after = 47.3ºC

C_{water} = 4.184 J/g·K

The confusing part is that once the change takes place, the system and the water are mixed together, and the heat energy gets distributed throughout the mixture

Beaker image: core.ecu.edu/chem/chemlab/ equipment/ebeaker.htm

Calorimetry problems

- Water is something we know a lot of very accurate data about
- Measure heat changes that get transferred to water by a (reaction) system
- Calculate amount of heat that water received from or gave to a system
- If the calorimeter is insulated, then all heat that enters (or leaves) the water must have come from (or gone to) the system being studied
- Figure out things about the system that you didn't know before

Heat transfer measurement and enthalpy of reaction

- Systems can either lose or gain heat during a change
  - Exothermic: heat flows out to surroundings
  - Endothermic: heat flows in to system
- Heat changes can be measured using calorimetry
  - Typical calorimetry uses liquid water as the surroundings
  - Liquid water either absorbs heat from the system (T_{water} increases) or gives heat to the system (T_{water} decreases)
  - If calorimeter is well insulated then $q_{water} = -q_{system}$, and $q_{water} = m_{water} C_{water} \Delta T_{water}$ (where C_{water} is slope of line for liquid region)
- Under typical laboratory conditions (constant pressure), heat change is equal to enthalpy change
- Enthalpy change (ΔH) is a state function (path independent)
- Because of its path independence, enthalpy change can be calculated by several methods:
  - Hess's law
  - Standard heats of formation
  - Bond dissociation energies

Reversing the direction of a reaction

1) Formation of water

$H_2\ (g) + ½\ O_2\ (g) \rightarrow H_2O\ (l)$ ΔH = -285.83 kJ

http://jws-edcv.wiley.com/college/bcs/redesign/student/resource/0,12264,_0471150584_BKS_1907__10615_3446__,00.html

2) Electrolysis of water

$H_2O\ (l) \rightarrow H_2\ (g) + ½\ O_2\ (g)$ ΔH = +285.83 kJ

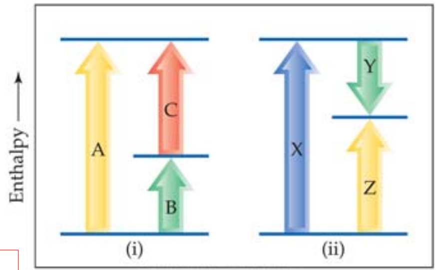
http://jchemed.chem.wisc.edu/JCESoft/CCA/samples/cca3ElecW02.html

More on Hess's Law

- Concept is simple, mathematics seems more complicated

How is ΔH_A related to ΔH_B and ΔH_C?

How is ΔH_X related to other enthalpy changes in the diagram?



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$$\boxed{\Delta H_A = \Delta H_B + \Delta H_C}$$

$$\boxed{\Delta H_X = \Delta H_Z + (-\Delta H_Y) = \Delta H_Z - \Delta H_Y}$$

- Hess's law says that ΔH_{rxn} for a given reaction is equal to products minus reactants of the heats of formation for the chemicals involved in the reaction

Summary of Hess's law

- A reaction and its reverse have equal magnitude, opposite sign ΔH values
  - If A → B has ΔH = 100 kJ, then B → A has ΔH = –100 kJ
- If you multiply a reaction by a factor, then you multiply the ΔH by the same factor
  - If A → B has ΔH = 100 kJ, then 2A → 2B has ΔH = 200 kJ
- When you add two reactions, you add the ΔH values
  - If A → B has ΔH = 100 kJ, and C → D has ΔH = 50 kJ, then A + C → B + D has ΔH = 100 + 50 kJ = 150 kJ

What is a heat of formation? What is a formation reaction?

- Standard heat (or enthalpy) of formation, ΔH_f^o, is the enthalpy of reaction associated with a formation reaction
- A formation reaction for a compound is a reaction that produces one mole of that compound from the pure elements in their standard states (p=1 atm, T=25°C)

Examples of formation reactions and their heats of formation:

Formation of sodium bicarbonate, $NaHCO_3$ (*s*):

$$\boxed{Na\,(s) + \frac{1}{2}H_2\,(g) + C(s) + \frac{3}{2}O_2\,(s)} \rightarrow NaHCO_3\,(s) \qquad \Delta H_f^o = -947.7\,{}^{kJ}\!/_{mol}$$

Formation of ethylene, C_2H_4 (*g*):

$$\boxed{2\,C(s) + 2\,H_2\,(g)} \rightarrow C_2H_4\,(g) \qquad \Delta H_f^o = +52.30\,{}^{kJ}\!/_{mol}$$

Using Heats of Formation to Calculate Enthalpies of Reaction

Standard enthalpies of formation

$$\Delta H_f^o[H_2O(l)] = -285.83\,{}^{kJ}\!/_{mol}$$
$$\Delta H_f^o[CO_2(g)] = -393.5\,{}^{kJ}\!/_{mol}$$
$$\Delta H_f^o[C_2H_5OH(l)] = -277.7\,{}^{kJ}\!/_{mol}$$

Example problem: Use standard enthalpies of formation to calculate the enthalpy of reaction for the combustion of ethanol, C_2H_5OH (*l*).

Solution: Start by writing the reaction

$$C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2\,CO_2\,(g) + 3\,H_2O\,(l) \qquad \Delta H_f^o = ?$$

Method 1: Write all the formation reactions for any non-elements at standard state. Then figure out how to arrange those reactions to sum to the overall reaction and do the same to the ΔH's.

Method 2: Use the equation

$$\boxed{\Delta H_{rxn}^o = \sum_{products} \Delta H_f^o - \sum_{reactants} \Delta H_f^o}$$

Using bond enthalpies to predict 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)*

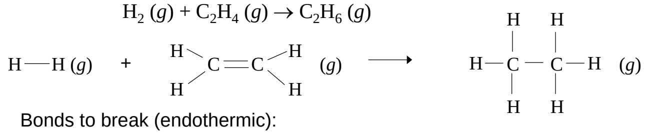
Estimate of energy change

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

Comparing ΔH_f^0 method with bond enthalpy method

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.

$$H_2\,(g) + C_2H_4\,(g) \rightarrow C_2H_6\,(g)$$



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 ΔH_f^o method:

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

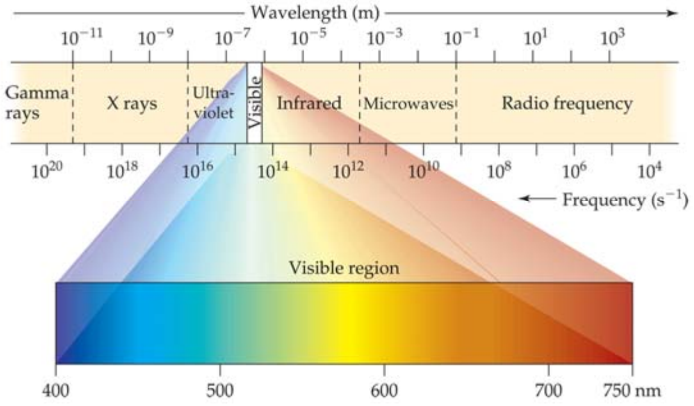
$$\Delta H^o_{rxn} = \left[1 \cdot \Delta H^o_f\left(C_2H_6(g)\right)\right] - \left[1 \cdot \Delta H^o_f\left(H_2(g)\right) + 1 \cdot \Delta H^o_f\left(C_2H_4(g)\right)\right]$$

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

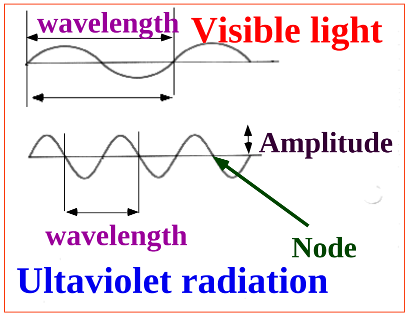
Properties of electromagnetic radiation (Ch. 6)

- Waves can be described by three interrelated measurements: wavelength, speed and frequency
  - These are related by $c = \lambda\nu$
- Energy of a wave is proportional to frequency
- Some properties of light are explained by wave behavior (e.g., diffraction)
- Other properties of light are explained by particle behavior (e.g., photoelectric effect)

Electromagnetic spectrum divided up based on frequency



How light waves differ from each other



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Compare visible and UV light:

Both are light, so they have the same velocity (speed of light, *c* = 3.0 x 10^8 m/s)

Wavelength

$\lambda_{\text{visible}} > \lambda_{\text{UV}}$

Frequency

$\nu_{\text{visible}} < \nu_{\text{UV}}$

Calculation of Light Properties

Red light has λ = 690 nm. What is its frequency?

Convert wavelength to standard SI units:

$$690\ nm \times \frac{10^{-9}\ m}{1\ nm} = 6.9 \times 10^{-7}\ m$$

Calculate frequency:

$$c = \lambda\nu \quad \therefore \quad \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ m/s}{6.9 \times 10^{-7}\ m} = 4.35 \times 10^{14}\ s^{-1} \text{ or } Hz$$

Spectroscopy

Macroscopic observations

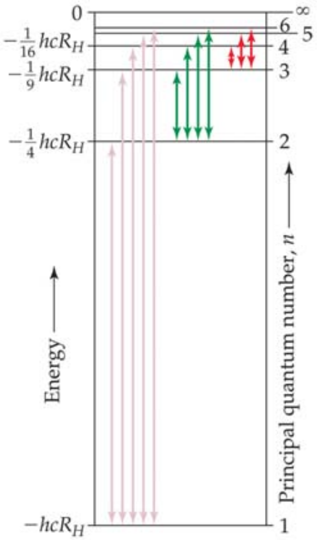
- When energy enters atoms, atoms give off light at discrete wavelengths (line **emission** spectrum)
- Line emission is fingerprint of an element (demonstrations in class)
- Entire periodic table at http://jersey.uoregon.edu/vlab/elements/Elements.html

Particle level explanation

- Electrons are so small that their quantum mechanical properties become important (Heisenberg uncertainty principle)
- Electrons can reside in various different quantum mechanical potential energy states, only one of which is the lowest energy ground state
- For a very nice, short summary explanation with helpful pictures, see http://www.avogadro.co.uk/light/bohr/spectra.htm

Symbolic representation (mathematical model)

Emission Spectrum of Hydrogen



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Bohr Theory

Bohr first thought to mathematically model electrons as in orbit around nucleus, and when "quantization postulate" applied, Bohr's model correctly predicts hydrogen spectrum that is experimentally seen

Rydberg equation:

$$\Delta E = -hcR_H\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

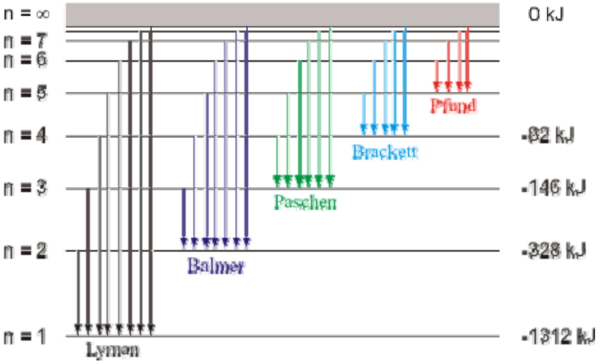
$$\text{where} \quad hcR_H = 2.18 \times 10^{-18}\ J$$

See equation 6.5, p. 226

Emission Spectrum of Hydrogen

$$\Delta E = -hcR_H\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

where $hcR_H = 1312\ {}^{kJ}/_{mol}$



See http://www.ktf-split.hr/glossary/image/emission_spectrum_of_hydrogen.gif

Using the Rydberg equation

Example:

Compare the *n*=3→*n*=2 transition with the *n*=4→*n*=3 transition.

$$\Delta E_{3\to 2} = -2.18\times 10^{-18}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)J$$
$$= -2.18\times 10^{-18}\left(\frac{1}{4} - \frac{1}{9}\right)J$$
$$= -3.03\times 10^{-19}\ J \text{ per atom}$$

Exothermic

Using N_A to convert to per mol:
Release of 182.2 kJ/mol

$$\Delta E_{4\to 3} = -2.18\times 10^{-18}\left(\frac{1}{3^2} - \frac{1}{4^2}\right)J$$
$$= -2.18\times 10^{-18}\left(\frac{1}{9} - \frac{1}{25}\right)J$$
$$= -1.55\times 10^{-19}\ J \text{ per atom}$$

Exothermic

Using N_A to convert to per mol:
Release of 93.3 kJ/mol

Where in the electromagnetic spectrum are these energies?

Converting energy to wavelength

- Energy equation

$$E = h\nu$$

- Wavelength equation

$$c = \lambda\nu \qquad \Rightarrow \qquad \nu = \frac{c}{\lambda}$$

- Substituting

$$E = h\nu = h\left(\frac{c}{\lambda}\right) = \frac{hc}{\lambda}$$

- Solving for wavelength

$$\lambda = \frac{hc}{E}$$

Example continued

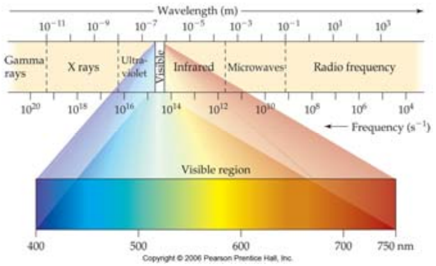
Where in the electromagnetic spectrum are these energies?

$$\lambda = \frac{hc}{E} = \frac{(6.63\times 10^{-34}\ J\cdot s)(3.00\times 10^{8}\ m\cdot s^{-1})}{3.03\times 10^{-19}\ J}$$
$$= 6.57\times 10^{-7}\ m\times \frac{1\ nm}{10^{-9}\ m} = 657\ nm$$

RED

$$\lambda = \frac{hc}{E} = \frac{hc}{1.55\times 10^{-19}\ J}$$
$$= 1.28\times 10^{-6}\ m\times \frac{1\ nm}{10^{-9}\ m} = 1280\ nm$$

Infra-RED



The Schrodinger equation and wave functions that obey it

$$H\psi_{nlm}(\theta,\phi,r)=E_n\psi_{nlm}(\theta,\phi,r)$$

where $H\,|\psi(t)\rangle = \mathrm{i}\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$

$$\psi_{nlm}(\theta,\phi,r)=\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]}}\,e^{-\rho/2}\rho^l L^{2l+1}_{n-l-1}(\rho)\cdot Y_{l,m}(\theta,\phi)$$

ψ_{nlm} are a set of functions that are mathematical solutions in three-dimensional space (radial coordinates θ, ϕ, r instead of Cartesian coordinates x, y, z) that depend on three quantum numbers n, l, m

a_o is the “Bohr radius” given by $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c\alpha}$

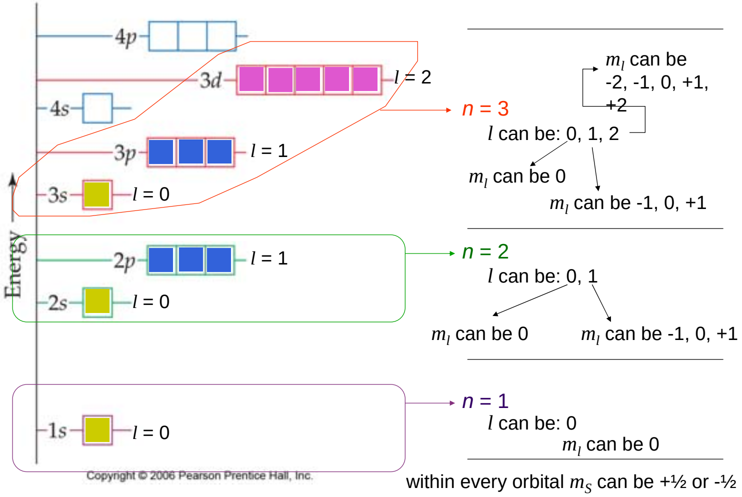
ρ, L and Y are just special functions that depend on the parameters shown

Four quantum numbers

Electrons are mathematical wave functions (orbitals) specified by:

1. Principal quantum number, n
    - Can take values 1, 2, 3, 4, …
    - Radial distance from the nucleus (shell #)
2. Azimuthal quantum number, l
    - Can take values up to but not including n value
    - Shape of orbital (when l=0 has *s*-shape, when l=1 has *p*-shape, when l=2 has *d*-shape, etc.)
3. Magnetic quantum number, m_l
    - Can take values ranging from –l up to +l
    - Orientation of the orbital
4. Spin quantum number, m_s
    - Can take one of two values (+½ or –½), does not depend on other quantum numbers

Summary of all 4 quantum numbers



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n = 3
l can be: 0, 1, 2
m_l can be -2, -1, 0, +1, +2
m_l can be 0
m_l can be -1, 0, +1

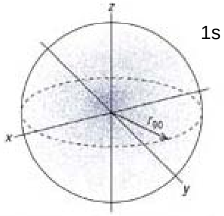
n = 2
l can be: 0, 1
m_l can be 0
m_l can be -1, 0, +1

n = 1
l can be: 0
m_l can be 0

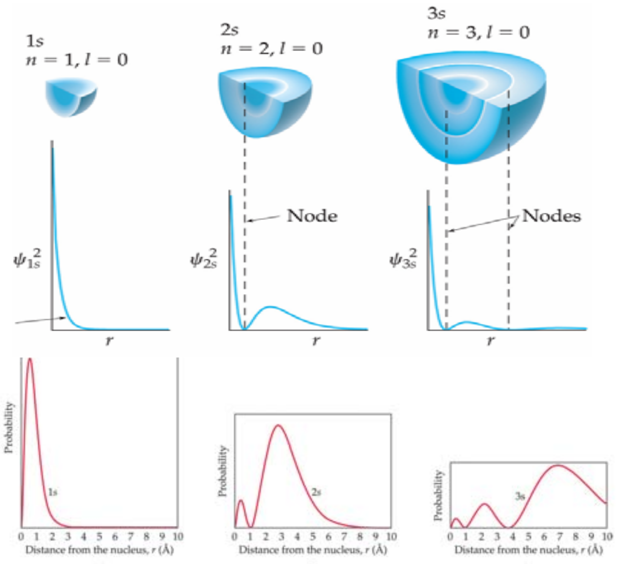
within every orbital m_s can be +½ or -½

What Orbitals Are

- Electron cloud pictures
- Probability density describing where electron is located
- Proportional to the square of the wave function with specific quantum numbers (wave function symbolized by Greek letter ψ)
- Think of a bird at a bird feeder, and a time-lapse photo

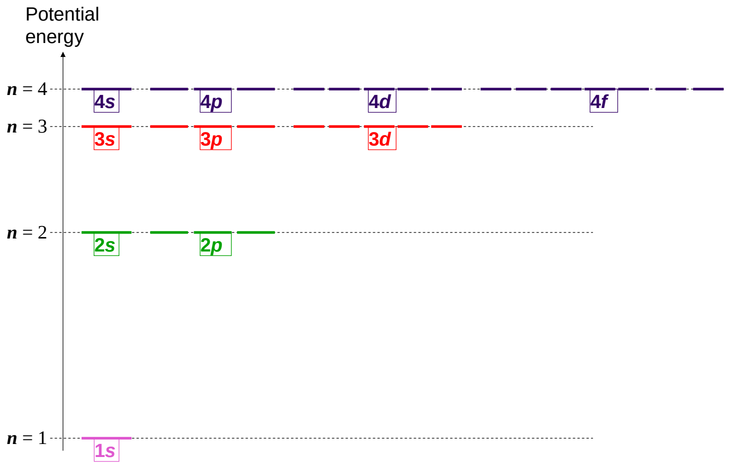


1s orbital
n = 1
l = 0
m_l = 0

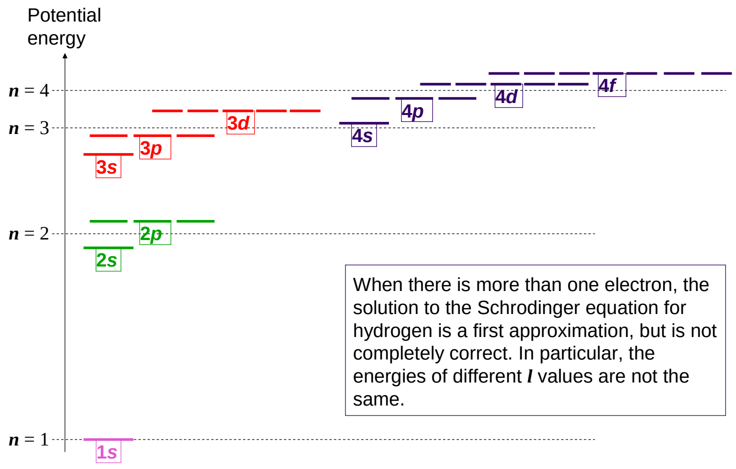


Orbital Energies in Hydrogen (Only)

How QM model simplifies to the Bohr model



Orbital Energies in Multielectron Atoms



When there is more than one electron, the solution to the Schrodinger equation for hydrogen is a first approximation, but is not completely correct. In particular, the energies of different ***l*** values are not the same.

The "game" of QM: What you need to know

- Study pp. 232-233 in the text to learn the rules
- Know the difference between s, p, d and f orbitals (these are "*l*" values of 0, 1, 2 and 3)
- Be able to tell which combinations of quantum numbers (n, l, m_l) are allowed and which combinations are not allowed
- Given a particular electron address, determine a set of quantum numbers (n, l, m_l) that correspond to it
- Given an atom with a specific number of electrons, determine the electronic "ground state" configuration

How to find ground state electron configuration for an element

1. Aufbau ("building up/assembly") principle

   Add electrons sequentially from lowest energy orbitals on upward.

2. Pauli exclusion principle

   Electrons are uniquely specified. If two electrons have the same first three quantum numbers (same orbital), then their fourth quantum number (m_l) must differ.

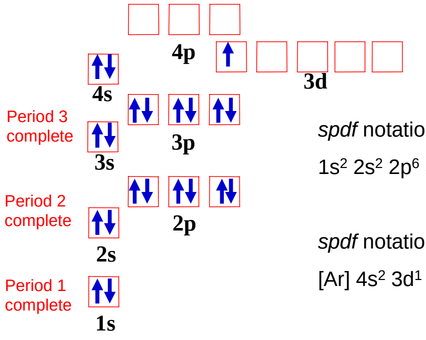
3. Hund's rule

   Electrons that are in the same subshell (same l value) tend to distribute so that they are in different orbitals (different m_l values) and have parallel spin (same m_s values).

Aufbau (Building) Elements

Scandium

Atomic number 21



Paramagnetic because it has one unpaired electron

spdf notation

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$

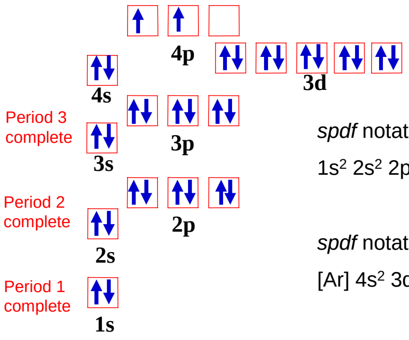
spdf notation written with noble gas core

$[Ar]\ 4s^2\ 3d^1$

Aufbau (Building) Elements

Germanium

Atomic number 32



Paramagnetic because it has two unpaired electrons

spdf notation

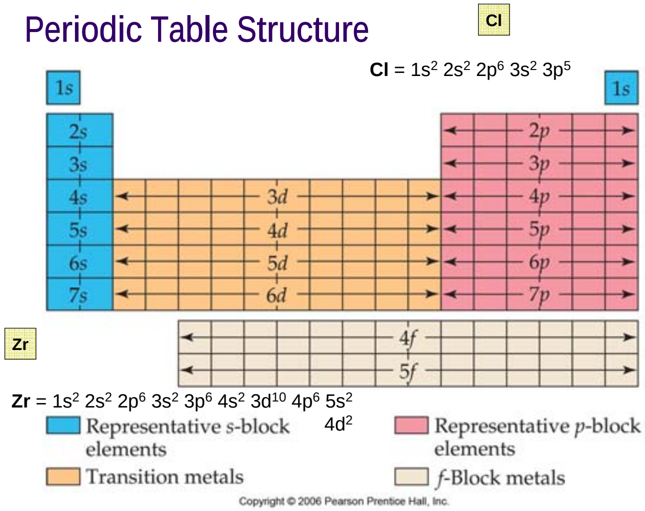
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$

spdf notation written with noble gas core

$[Ar]\ 4s^2\ 3d^{10}\ 4p^2$

Periodic Table Structure

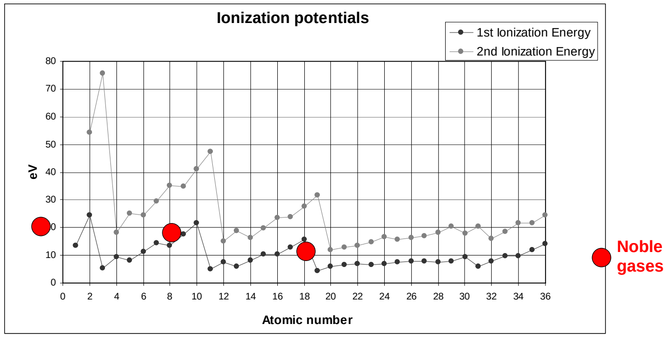
Cl = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$



Zr = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^2$

Ionization Energies of Elements

The energy required to remove the most weakly bound electron from an atom or ion.



Trend seen: **As atomic number increases, the first ionization energy of the noble gases**

Data from H. Sevian et al, Active Chemistry
or see Table 7.2, p. 271 of text

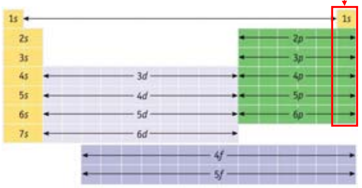
Comparing Noble Gas Group Elements

Pd	Elem	Electron Configuration
1	He	$1s^2$
2	Ne	$1s^2\ 2s^2\ 2p^6$
3	Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
4	Kr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$
5	Xe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6$

How does this explain the trend seen?

Trend: As atomic number increases, the first ionization energy of the noble gases decreases.

Explanation: This happens because the number of shells increases as you go down the group, so the most loosely bound electron is getting further away from the nucleus that is holding it on the atom. The further away the electron is from the nucleus,

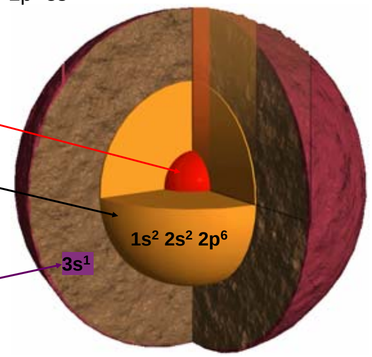


Example of core vs. valence: Sodium Atom

A neutral sodium atom has 11 protons and 11 electrons

Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$

(Note: not drawn to scale!)



Book calls this Z_{eff}

CORE

Net +1 charge

11 protons and some neutrons (charge: +11)

All complete inner shells of electrons (charge: -10)

VALENCE SHELL

Net -1 charge

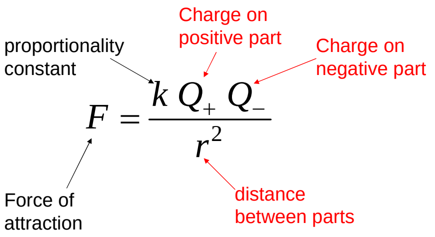
Outer electrons beyond all complete inner shells (charge: -1)

Image modified from http://www.badastronomy.com/bad/movies/thecore_review.html

Recall Coulomb's Law

Force of attraction (or repulsion):

- Increases when magnitudes of charges increase
- Decreases as distance between charges increases



$$F = \frac{k\,Q_+\,Q_-}{r^2}$$

proportionality constant

Charge on positive part

Charge on negative part

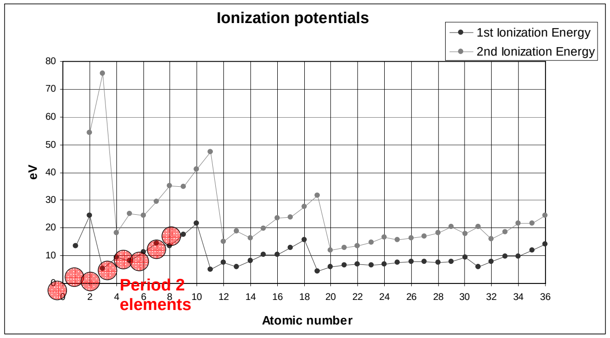
Force of attraction

distance between parts

To reason using Coulomb's law, you must talk about the magnitudes of the charges (Q_+ and Q_-) and the separation of the charges (r).

Ionization Energies of Elements

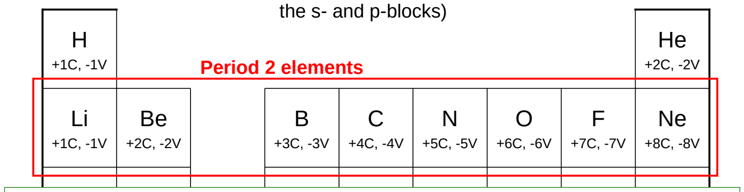
The energy required to remove the most weakly bound electron from an atom or ion.



Trend seen: **As atomic number increases, the first ionization energy of the period 2 elements increases.**

Core vs. Valence

An abbreviated periodic table (showing only the s- and p-blocks)



H +1C, -1V							He +2C, -2V
Li +1C, -1V	Be +2C, -2V	B +3C, -3V	C +4C, -4V	N +5C, -5V	O +6C, -6V	F +7C, -7V	Ne +8C, -8V

How does this explain the trend seen?

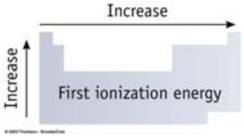
Trend: **As atomic number increases, the first ionization energy of the period 2 elements increases.**

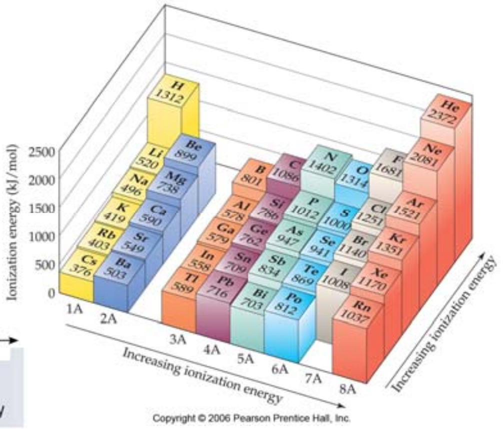
Explanation: **This happens because the core charge (Z_{eff}) increases as you go from left to right across a period. Since we are comparing the most loosely bound electron, which is sitting in the valence shell, and since the valence shell is the same for all the period 2 elements, then Z_{eff} increasing means the force of attraction holding the electron increases, resulting in larger ionization**

Summary of Ionization Energy Trends

Ionization energy generally:

- Increases across a period (row)
- Decreases down a group (column)





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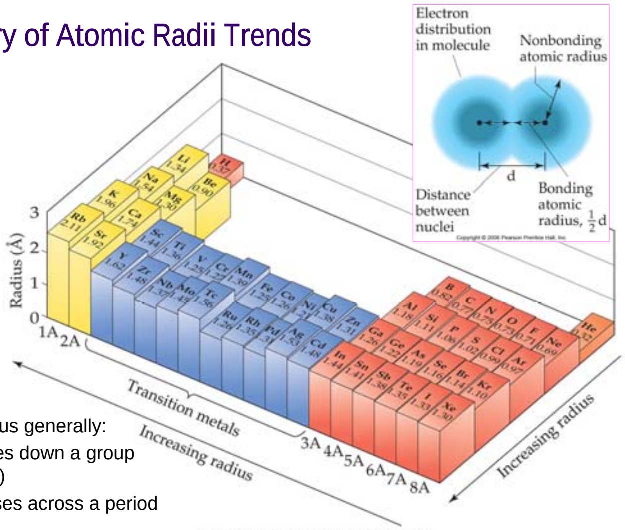
Summary of Atomic Radii Trends



Atomic radius generally:

- Increases down a group (column)
- Decreases across a period (row)

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Periods vs. Groups

Comparing two elements in the same period:

- Same number of complete shells, so size (radius) of cores is the same
- Different charges in nucleus, but same number of core electrons, leads to different core charge
- Different numbers of electrons in valence
- Arguments are usually based on Q_+ (core charge) and Q_- (valence charge) being different while distance between core and valence (r) is nearly the same

Comparing two elements in the same group:

- Different number of complete shells, so size (radius) of cores is different
- Core charges are the same because valence electrons same
- Arguments are usually based on distance between core and valence (r) being different while Q_+ and Q_- are the same

The big picture: The pattern of a Coulomb's law argument

1. Usually comparing one set of circumstances to a second set, to explain why one measure is larger or smaller than another
    - Neon atom vs. sodium atom with atomic radius
    - $MgCl_2$ vs. $CaCl_2$ with energy required to break the ionic bonds
2. For each set of circumstances, determine what the relevant attraction is between a Q_- and a Q_+
    - Attraction between outermost electron (-) and effective core charge (+) will affect atomic radius
    - Attraction between negatively charged ion (Cl^-) and positively charged ion (Mg^{2+} or Ca^{2+}) will determine strength of ionic bond
3. For each set of circumstances, determine what the distance of separation is between the + and – charges
    - Number of shells (periods)
    - Number of shells on + ion plus number of shells on – ion
4. Usually one variable, distance or (Q_+ and Q_-), can be considered constant while the other one varies. The one that varies is responsible for the difference in the measure
    - Neon has Q+=+8 while sodium has Q+=+1. Neon has 2 shells while sodium has 3 shells. Both differences lead to sodium's outermost electron being further away and less tightly bound.
    - Both attractions are a +2 ion with a -1 ion. Cl^- ion has same radius, but Mg^{2+} ion is smaller than Ca^{2+} ion, so separation distance between Q+ and Q- is smaller in $MgCl_2$, therefore harder to break the ionic bond.

Qualitative comparisons in strength of ionic bonding

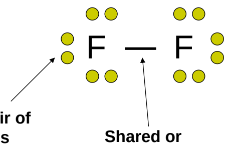
- Recall that Coulomb's law predicts that force of attraction between two oppositely charged objects depends on magnitudes of charges (direct) and on distance that separates them (indirect)
- Comparing the lattice energies of two ionic compounds depends on two factors:
    - Compare magnitudes of ionic charges over the same separation distance
    - Compare separation distance if the same ionic charges
    - (Both factors can work in the same direction)
    - (If factors work in opposing directions, you need to know more quantitative information to make a prediction)

Map of Chapter 8

- What holds ions together
    - Predicting qualitative trends
- What holds molecules together
    - Predicting enthalpy of reaction from bond energies
- Ionic vs. covalent character of bonds: polarity and electronegativity model
- Lewis structure model
    - Simple structures (octet rule), with single and multiple bonds
    - Resonance structures
    - More complicated structures (breaking the octet rule)
    - Formal charges
- Bond strength and length
    - Using Lewis structures to predict
    - Using Hess's law and bond enthalpies

Lewis Dot Structure Model

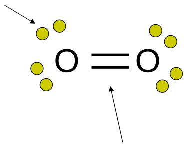
- Theory behind Lewis dot structures is that valence electrons are distributed as either
  - Pairs of electrons that are shared by two atoms (shared pairs)
  - Pairs of electrons that belong to a single atom (unshared, or lone pairs)



Lone pair of electrons

Shared or bonding pair of electrons

Lone pair of electrons (belongs exclusively to this oxygen)



Double bond (shared electrons get counted as belonging to both oxygen atoms)

Building Lewis Structures

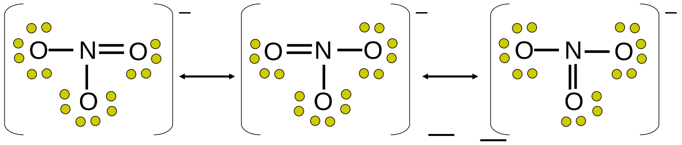
1. Determine central atom (atom with lowest electron affinity because electron density will spread as far as possible, given the opportunity)
2. Count total number of valence electrons in molecule
3. Arrange atoms around central atom
4. Start with single bonds
5. Place remaining valence electrons
6. Move electrons to form octets, making double or triple bonds where necessary

Check: Make sure you have conservation of electrons

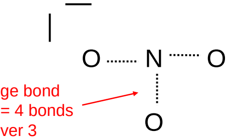
Predictions that can come from Lewis structures

- Resonance
- Bond order (useful for comparing strengths of bonds)
- Bond length comparisons (comparing one molecule to another)
- Formal charge (useful for predicting which resonance structures are most stable)

Resonance Structures



- What do these structures have in common?
- How are they different?
- Which of these is the actual structure of NO_3^-?

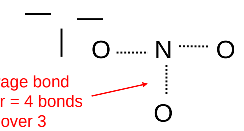


Average bond order = 4 bonds split over 3 locations = 4/3

Note: This is not a correct Lewis structure. It is drawn this way only to emphasize the bond order.

Bond Order and Bond Length/Strength

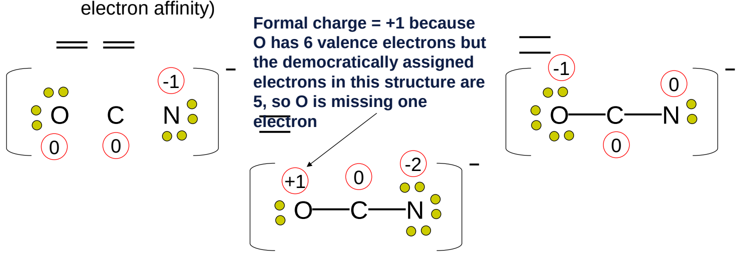
- Bond order
  - Single bond is bond order 1
  - Double bond is bond order 2
  - Triple bond is bond order 3
- Bond strength
  - The greater the bond order, the stronger the bond (the more energy required to break the bond)
- Bond length
  - The greater the bond order, the shorter the bond length



Average bond order = 4 bonds split over 3 locations = 4/3

Formal Charges and Alternative Structures

- *Formal charge* is a comparison between
  the valence electrons originally contributed by an atom
  and
  the electrons that it looks like the atom would have if all bonds were broken and electrons reassigned democratically.
- If more than one Lewis structure exists, *the most stable structure* is the one in which the formal charges make most sense
  - Negative formal charges on atoms with large electron affinity
  - Positive formal charges on atoms with small ionization energies (small electron affinity)



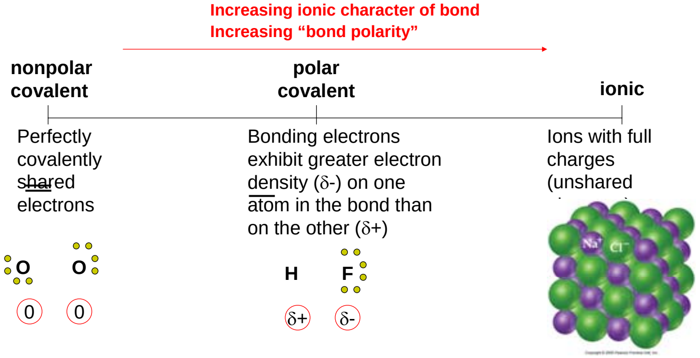
Formal charge = +1 because O has 6 valence electrons but the democratically assigned electrons in this structure are 5, so O is missing one electron

Ionic bonding in ionic compounds, and how Lewis structures begin to explain covalent bonding in molecular compounds

- Ionic vs. covalent bonding
  - Ionic bond is attraction between + and – ions, held together by Coulomb force of attraction acting across ion separation
  - Molecular bond is valence electrons shared between two atoms and attracted (but not necessarily equally) to both atoms in the bond
- Many aspects of molecular bonding can be modeled by Lewis structures
  - Bond order/strength and length
  - Resonance structures of molecules (or ions) and formal charges on individual atoms in the molecules (or ions)
  - *Bond polarity*
  - *Molecular geometry*

A Range of Bond Types

Bond “types” are not separable into a true dichotomy between covalent and ionic. Instead there is a range of covalent character vs. ionic character of bonds.



Increasing ionic character of bond
Increasing “bond polarity”

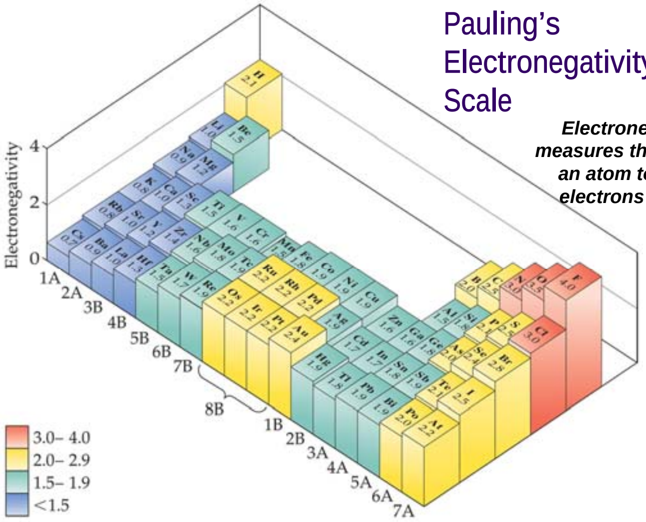
nonpolar covalent — Perfectly covalently shared electrons

polar covalent — Bonding electrons exhibit greater electron density (δ-) on one atom in the bond than on the other (δ+)

ionic — Ions with full charges (unshared

Pauling's Electronegativity Scale

Electronegativity measures the ability of an atom to attract electrons to itself



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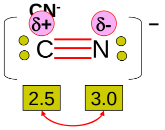
Electronegativities Allow You to Compare Bond Polarity

- Which bond is most polar? Which bond is least polar?
- Which end of the bond is the negative pole (greater electron density)? Which end is the positive pole (less electron density)?

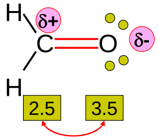
The bond between C and N in CN^-



Difference of 0.5

Is less polar than

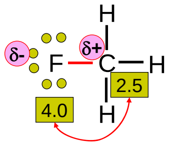
The bond between C and O in H_2CO



Difference of 1.0

Is less polar than

The bond between C and F in CH_3F

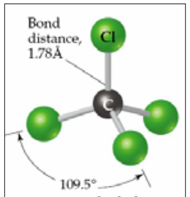


Difference of 1.5

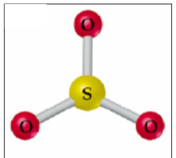
The electronegativity model, and amendments to the Lewis structure model

- The electronegativity model explains two things:
  - There is a gray area between covalent bonding and ionic bonding: ranging from not polar at all, to so completely polar that the electron transfers completely
  - You can compare the polarities of bonds within molecules, and ultimately you can predict the overall polarity of a molecule (by a vector sum of all the bond polarities in a molecule)
- There are exceptions to the octet rule in Lewis structures
  - Some atoms (notably Be, B and Al) can have less than an octet of electrons and be stable
  - Odd electron molecules are free radicals
  - Atoms that can have more than octet must have *d*-orbitals that can be used to create the beyond-octet options (so the atoms must be at atomic #13 and higher, i.e., having accessible *3d* orbitals and beyond)

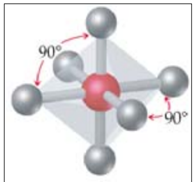
Molecular Geometries Observed



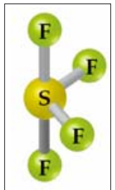
Tetrahedral



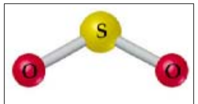
Trigonal planar



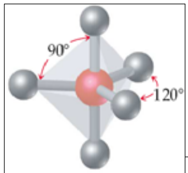
Octahedral



See-saw

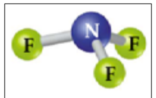


Bent

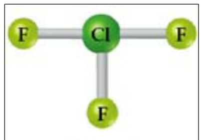


Trigonal bipyramidal

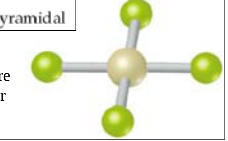
Linear



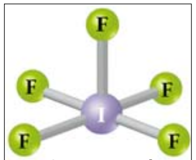
Trigonal pyramidal



T-shaped



Square planar



Square pyramid

Stretching Lewis Structure Theory

Procedure for drawing a Lewis structure (abbreviated)

1. Determine how many total valence electrons
2. Decide on central atom and arrange other atoms around it
3. Start with single bonds, make octets on all atoms (except H), making double or triple bonds where necessary

Amendment to procedure

4. If it's not possible to draw a simple structure, determine whether central atom can accommodate more than an octet

Which elements can accommodate more than an octet?

Any element that has access to un-used *d*-orbitals

All elements in period 3 have access to 3*d* orbitals

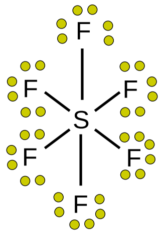
All elements in period 4 have access to either 3*d* or 4*d* orbitals, etc.

Summary: all elements at and beyond atomic #13

Examples of more than an octet on the central atom

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

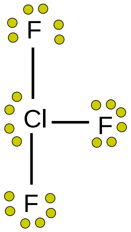
SF$_6$ ㊽



Electron domain geometry is: **octahedral**

Molecular shape is **octahedral**

ClF$_3$ ㉘

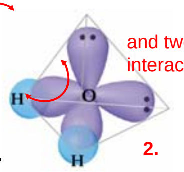


Electron domain geometry is: **trigonal bipyramid**

Molecular shape is **T-shaped**

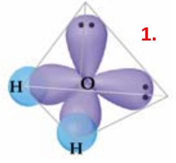
VSEPR

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



and two other interactions

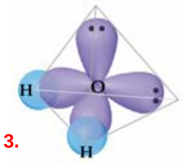
1. A lone pair of electrons repels another lone pairs of electrons



more than

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

more than

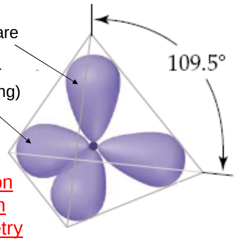


3. A pair of bonding electrons repels another pair of bonding electrons

VSEPR results

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

Locations where electrons are (whether bonding or non-bonding)

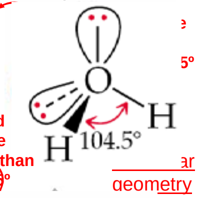


Electron domain geometry

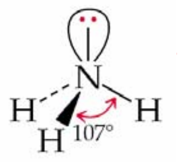
Lewis structure prediction:

All angles equal at 109.5º

VSEPR



Bond angle less than 109.5º



Bond angle less than 109.5º

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

and

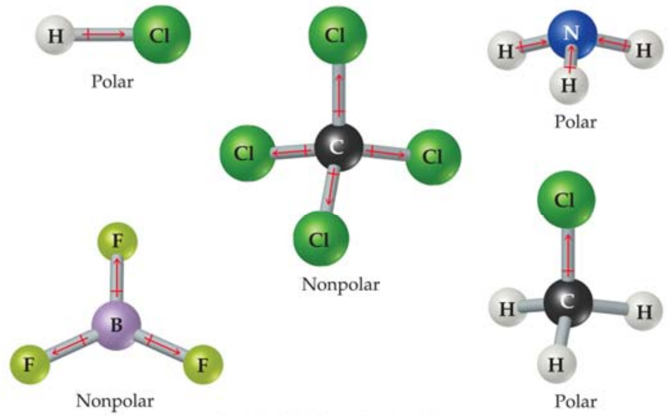
2. If the bond dipoles do not cancel each other out (cancellation happens when bond dipoles are symmetrically located)

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

Some molecules containing polar dipoles



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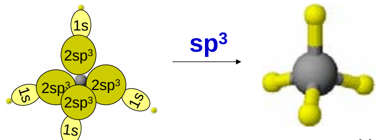
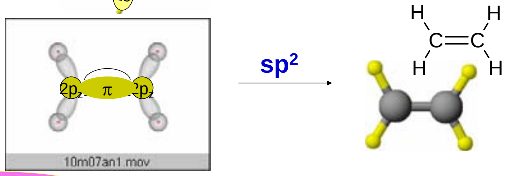
Valence Bond Theory

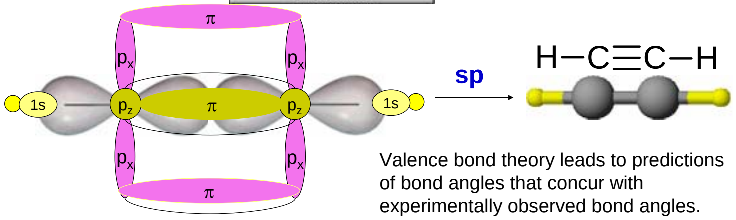
Central ideas:

1. Atomic orbitals initially form hybrids to get ready for bonding to form molecules/ions (costs a little bit of energy – less stable)
2. Bonds in molecules/ions are formed by the overlap of atomic orbitals (win back a lot of energy – much more stable)

Three Different Hybridizations of Carbon's Atomic Orbitals

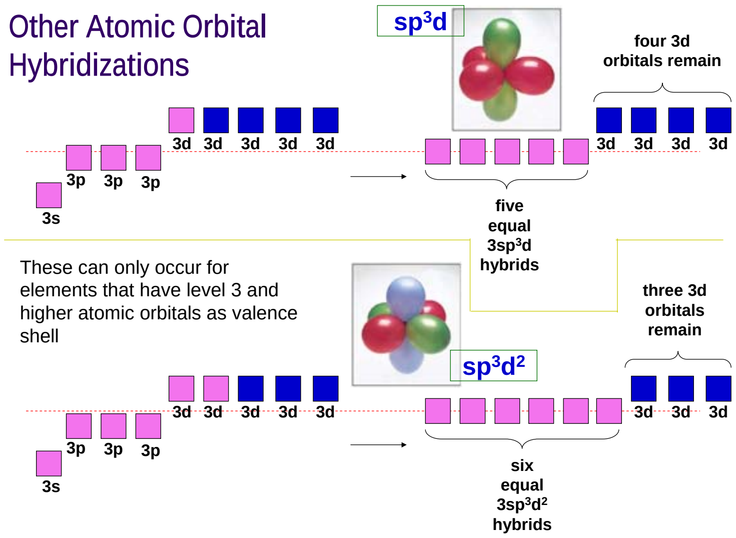






Valence bond theory leads to predictions of bond angles that concur with experimentally observed bond angles.

Other Atomic Orbital Hybridizations

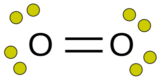


These can only occur for elements that have level 3 and higher atomic orbitals as valence shell

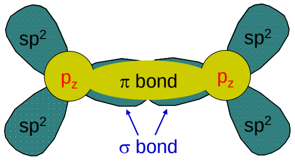
Lewis structure model + Valence bond theory

- Lewis structures model
  - Predict molecular geometry
  - Need to determine how many bonding and lone pair electrons surround a central atom
- Valence bond theory
  - Explains how bond angles arise
  - Different combinations of atomic orbitals are possible on different atoms
  - Making double and triple bonds requires reserving some p-orbitals
- Taken together, the two models explain most molecular geometries

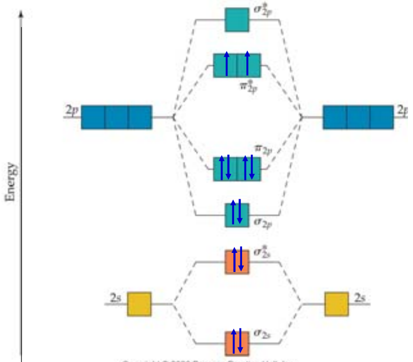
Valence Bond Theory vs. Molecular Orbital Theory for O_2



Lewis diagram predicts sp^2 hybridization on O atoms



1. Molecular shape predicted to be flat
2. Correct bond order 2 predicted
3. All orbitals are occupied by pairs of electrons – not paramagnetic



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1. No prediction about molecular shape
2. Correct bond order predicted (net pairs of electrons in bonding orbitals)
3. Some unpaired electrons – paramagnetic

Two competing theories that predict various properties of molecules

Valence bond theory	Molecular orbital theory
• Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)	• Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
• Lewis structure's electron pairs translated into quantum mechanics	• Wave functions (molecular orbitals) are formed from all bonding electrons in molecule
• Electrons in a particular bond are localized to specific valence bond orbitals	• Electrons in all bonds are spread out (delocalized) over all molecular bonding orbitals in molecule

Mathematically, the approaches are different.
Results (predictions) are often the same.