5.111 Lecture Summary #9 Friday, September 26, 2014

Readings for today: Sections 2.1-2.3 – Ionic Bonds, Sections 2.14-2.16 - The Strengths and Lengths of Covalent Bonds
Read for Lecture #10: Section 2.5 – 2.8 Lewis Structures (Same sections in 5th and 4th ed.)

Topics:
I. Trends in Periodic Table Continued
- A. IE (completed in lecture #8)
- B. Electron affinity (completed in lecture #8)
- C. Electronegativity
- D. Atomic and ionic radii and Isoelectronic atoms

II. Ionic bonds
III. Covalent bonds
IV. Polar Covalent bonds

C. ELECTRONEGATIVITY (χ)

Electronegativity is the net ability of an atom to attract an electron from another atom. Linus Pauling first proposed this idea in 1932.

Mulliken's electronegativity scale developed two years later is conceptually easier.

electronegativity (χ) $\propto$ ______ (______+ ______)

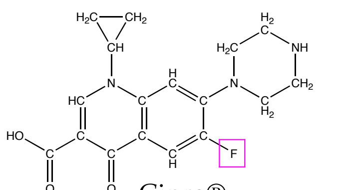
An atom with high electronegativity is an electron ________________ .
An atom with low electronegativity is an electron _________________.

In their own words:

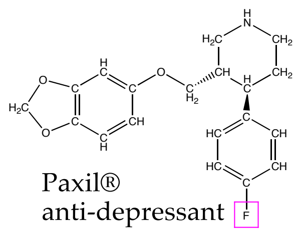
Bacteria have developed resistance to many antibiotics, and there is need for current and future scientists to develop new types of antibiotics. Kateryna discusses her research on enzymes that catalyze a carbon-chlorine bond-formation, and how taking advantage of chlorine's electronegativity may lead to new medications to fight bacteria and other "bugs" that make us sick.

Electronegativity in Drug Design: Fluorine Atoms in Drugs

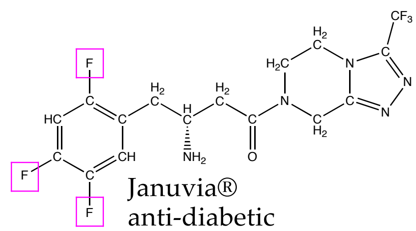
Although carbon-fluorine (C-F) bonds are not known to be present in the human body, C-F bonds are incorporated into a number of drugs.



Cipro®
broad-spectrum antibiotic

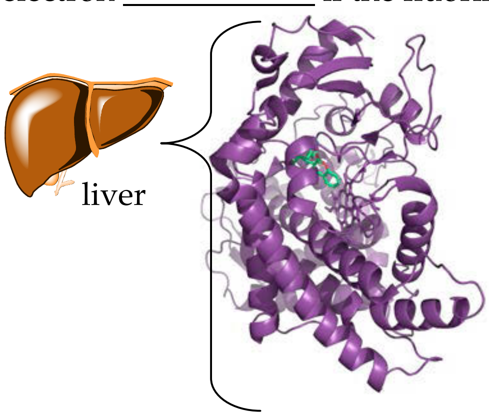


Paxil®
anti-depressant



Januvia®
anti-diabetic

Why??? One reason is that F, due to its high electronegativity, can make a molecule electron ___________ if the fluorine is appropriately positioned on an aromatic ring.



Cyp enzyme bound to a drug

Since oxidation involves losing an electron, a drug that is electron-poor will be _______________ to oxidize.

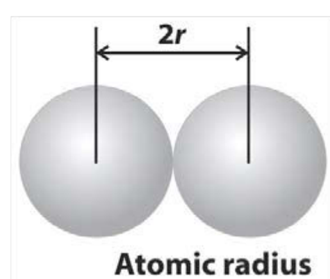
Drugs are metabolized by a class of proteins in the liver called cytochrome P450 (or Cyp) enzymes.

Fluorination can increase a drug's metabolic stability by making it less susceptible to oxidation by Cyp enzymes.

For a brief article on a strategy developed in the Buchwald lab at MIT for installing fluorine into medically relevant molecules, see http://web.mit.edu/newsoffice/2009/drug-synthesis-0813.html.

D. ATOMIC and IONIC RADII

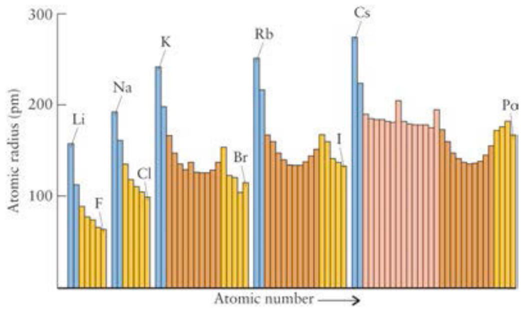
The atomic size is defined as the value of r below which 90% of electron density is contained.

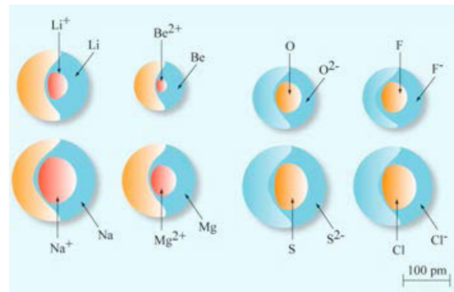


Z_{eff} is an important determinant of atomic radius across the table and n is an important determinant going down.
Z_{eff}_________________across the periodic table, and the atomic radius __________________.

n **increases** down the periodic table, and the atomic radius **increases**.

The radii of ions differ from the radii of their parent atom.





Cations (+ charged ions) have radii that are ___________than their parent atoms.

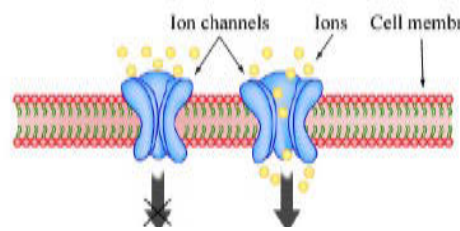
Anions (- charged ions) have radii that are **larger** than their parent atoms.

Like atomic radii, ionic radii increase within a group going down the periodic table.

The Role of Atomic and Ionic Radii in Ion Channel Selectivity

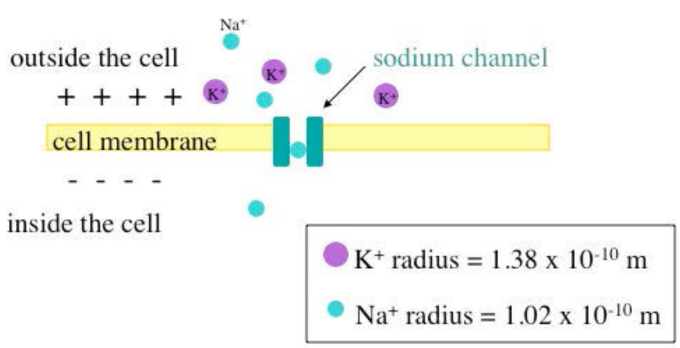
Ion channels

* prevalent in _________________ and muscle cells
* regulate the influx of ions into cells.
* enable rapid electrical signaling in neurons.
* **are selective for specific ion.**



Order the following from *smallest* to *largest*: Na^+, K^+, K. _____ < _____ < _____

Figure by MIT OpenCourseWare.



Sodium ion channels are selective for Na^+ in the presence of other ions, including K^+.

Sodium channels include a tiny pore (~0.4 nm wide) that is *just* wide enough to accommodate a sodium ion with an associated water molecule.

Too small for potassium ions!

ISOELECTRONIC ATOMS / IONS have the same electron configuration.

For example, all $\mathbf{1s^2\ 2s^2\ 2p^6}$ ions are isoelectronic with Ne.

_____, _____, _____, Ne, _____, _____, _____, _____

_______________ radius than neutral parent   _______________ radius than neutral parent

II. IONIC BONDS

Ionic bonds involve the complete ____________ of (one or more) electrons from one atom to another with a bond resulting from the electrostatic attraction between the cation and anion.

Consider the formation of NaCl from the neutral atoms, Na and Cl.

Na (g)	⟶	Na^+ (g) + e^-	ΔE = ______ = **494** kJ/mol
Cl + e^-	⟶	Cl^- (g)	ΔE = **– EA** = ______kJ/mol
Na (g) + Cl (g)	⟶	Na^+ (g) + Cl^- (g)	ΔE = **+** ________ kJ/mol

$\Delta E = IE_{Na} + (-EA_{Cl}) = 145$ kJ/mol

Problem: Na (g) + Cl (g) ⇒ Na^+ (g) + Cl^- (g) has a positive ΔE. It __________ energy.

Solution: Coulomb attraction.
Na^+ (g) + Cl^- (g) ⟶ NaCl (g) ΔE = – 589 kJ/mol

Net change in energy for the overall process:

Na (g) + Cl (g) ⟶ NaCl (g) ΔE = __________ kJ/mol

The mutual attraction between the oppositely-charged ions releases energy. The net energy change for the formation of NaCl is a **decrease** in energy.

We can calculate the Coulomb attraction based on the distance between the two ions (assume here that the ions are point charges):

$$U(r) = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}$$

for 2 unlike charges,
z = charge numbers of the ions and
e = absolute value of the charge of an e^- (1.602×10^{-19} C)

Calculate U(r) for Na^+ and Cl^-. NaCl has a bond length (r) = 2.36Å.

$$U(r) = \frac{(\quad)(\quad)(1.602 \times 10^{-19}\ C)^2}{4\pi(8.854 \times 10^{-12}\ C^2J^{-1}m^{-1})(2.36 \times 10^{-10}\ m)} =$$

Convert to kJ/mol

$U(r) = -9.7\underline{7}4 \times 10^{-19}$ J x __________ x _________________ =

Simple ionic model predicts: ΔE for forming NaCl (g) from Na(g) + Cl(g)= - 444 kJ/mol

Experiments measure: ΔE for forming NaCl (g) from Na(g) + Cl(g) = - 411 kJ/mol

The discrepancy results from the following approximations:

- ignored repulsive interactions. Result:__________ $\Delta E_{predict}$ than experimental value.
- treated Na^+ and Cl^- as ___________________________.
- ignored quantum mechanics.

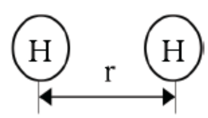
This simple model is applicable only to very ionic bonds.

III. COVALENT BONDS

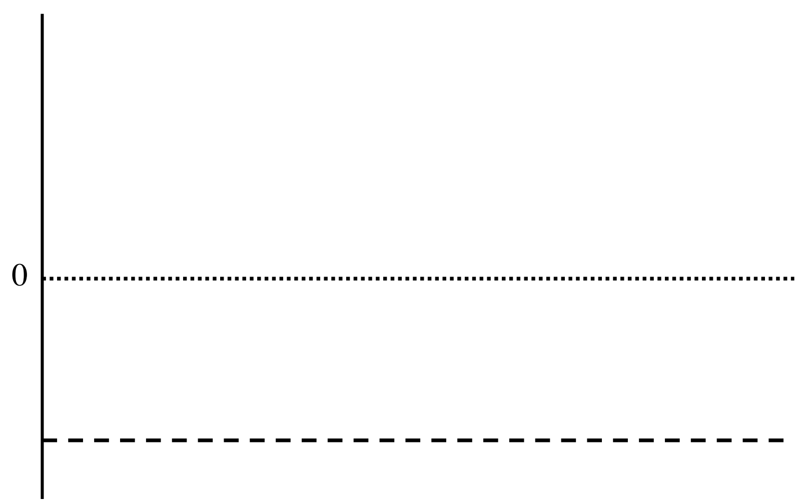
Chemical bonds form between atoms when the arrangement of the nuclei and electrons of the bonded atoms results in a ______________ (more negative) energy than that for the separate atoms.

A **covalent bond** is a pair of electrons _______________ (sometimes equally, sometimes not) between two atoms. Covalent bonds form between nonmetals.

In bonding, r = distance between nuclei.



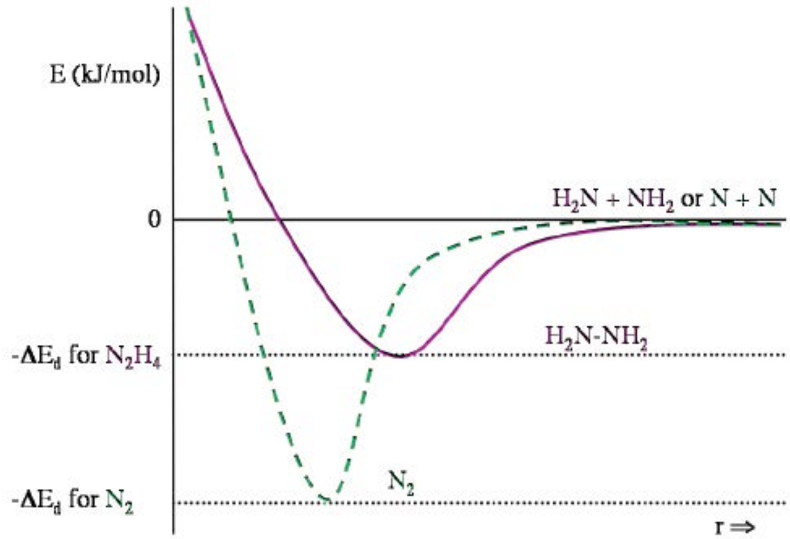
We can plot the energy of the two H-atoms as a function of internuclear distance, r.



Energy of interaction = nuclear-nuclear repulsion + electron-nuclear attraction + electron-electron repulsion

ΔE_d = **dissociation energy**, the energy required to separate bonded atoms (a measure of **bond strength**).
ΔE_d for H_2 = 424 kJ/mol

We can compare the bond strengths.



Compare the N-N bond in H_2N-NH_2 and N≡N:

Which bond is stronger?

__________________(deeper energy well)

Which bond is shorter?

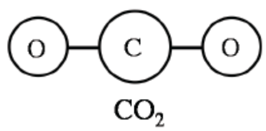
____

Carbon monoxide has one of the strongest bonds (dissociation energy = 1062 kJ/mol) and I_2 has one of the weakest (dissociation energy = 139 kJ/mol).

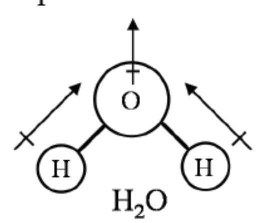
IV. POLAR COVALENT BONDS/POLAR MOLECULES

A polar covalent bond is an **unequal sharing** of e^-s between two atoms with different electronegativities (χ). In general, a bond between two atoms with an χ difference of > _____ and < _____ (on the Pauling scale) is considered polar covalent.

Polar molecules have a non-zero net dipole moment.



_____________ molecule



_____________ molecule

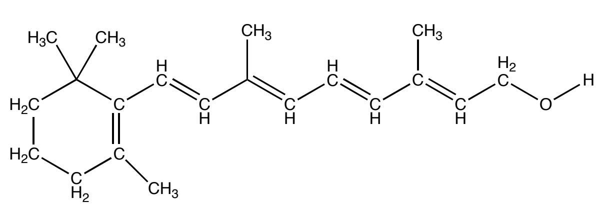
$\chi_H = 2.2$

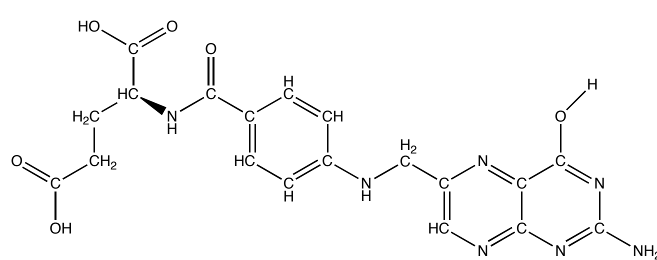
$\chi_C = 2.6$

$\chi_N = 3.0$

$\chi_O = 3.4$

In large organic molecules and in biomolecules, we often consider the number of polar groups within the molecule. For example: which vitamin contains a higher number of polar bonds? vitamin ________





Vitamin A

__________________soluble

Vitamin B9 (_______________________)

__________________ soluble

5.111 Principles of Chemical Science
Fall 2014