ORGANIC CHEMISTRY I CHEMAC 221 section 01

LECTURE #01

Tues., Sept.6, 2005

Our textbook: P.Y. Bruice, Organic Chemistry, 4th Ed.

Also helpful: S. Eğe, Organic Chemistry, 5th Ed.
(on reserve in Vanier Library)

ASSIGNED READINGS:

TODAY'S CLASS: Bruice Ch1: 1.1-1.5

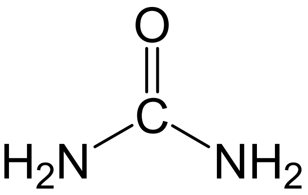
NEXT CLASS: sections 1.6-1.15

http://artsandscience.concordia.ca/facstaff/P-R/rogers

What is organic chemistry?

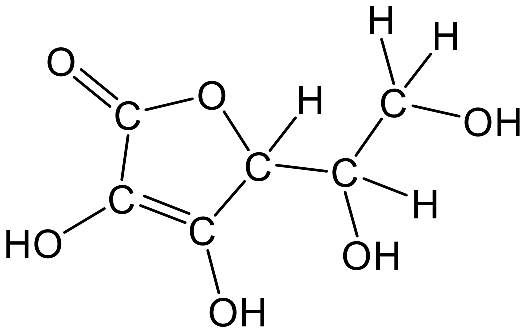
History:

- Jöns Jakob Berzelius (1807): "Organic compounds" come from living organisms; "inorganic compounds" = minerals
- Friedrich Wöhler (1828): made urea in the laboratory, starting from inorganic compounds



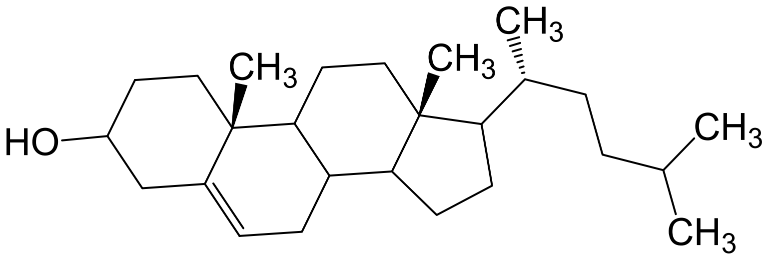
Urea

found in urine



Ascorbic acid

Vitamin C



Cholesterol

a component of membranes

Current definition:

Organic chemistry = chemistry of the compounds of carbon

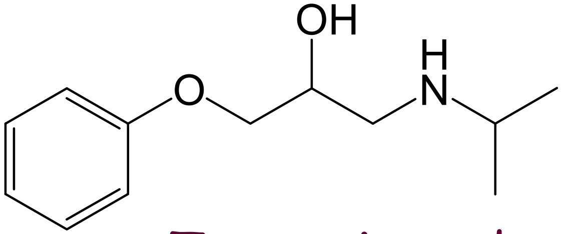
Key elements: C, H, N, O

Also important: F, Cl, Br, I, S, P (non-metals most common!)

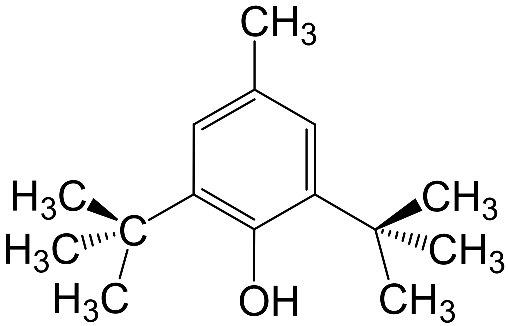
& some metals: Si, Li, Na, K, B, Al, Cr, Cu, Zn, Pd, Hg…

What do organic chemists do?

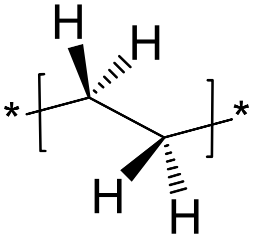
- Study relationship between structures of molecules & their properties and reactions
- Synthesize molecules with desired characteristics: pharmaceuticals, flavourings, pigments, plastics, fabrics…



Tenormin, a drug for treating heart disease



BHT, a preservative



Polyethylene, a plastic

Why do you need to study organic chemistry?

- To learn how organic matter reacts, and WHY
- To provide a basis for understanding biological processes
- To gain spatial and temporal organizational skills
- To practice thinking logically & solving complex problems
- To learn to recognize trends & extrapolate knowledge to unknowns…

How to study organic chemistry

- Like a language: *PRACTICE, & DON'T GET BEHIND.*

Verbal communication

TRAIN YOUR MIND:
Read the textbook
Learn proper vocabulary
Practice writing explanations
Practice solving problems

TRAIN YOUR MOUTH:
Discuss material with peers
Solve problems together
Practice explaining verbally

Pictorial communication

TRAIN YOUR EYE:
Interpret chemical drawings
See 3D shapes in flat drawings

TRAIN YOUR HAND:
Practice drawing in 3D
Practice writing structures
Write problems out every time

- Learning the general trends and rules will help you **minimize memorization & maximize comprehension.**

- Too much to try to memorize all!
- Most successful approach = practice.
- Study Guide: use as a tool, not as a crutch.

Chapter 1: Introduction to Organic Chemistry

Chapter Goals

- Review general chemistry principles: structure, bonding
- Expand knowledge & apply to organic compounds

- Review acid/base chemistry
- Expand to understand organic compounds as acids/bases

Chapter Outline: *This week*

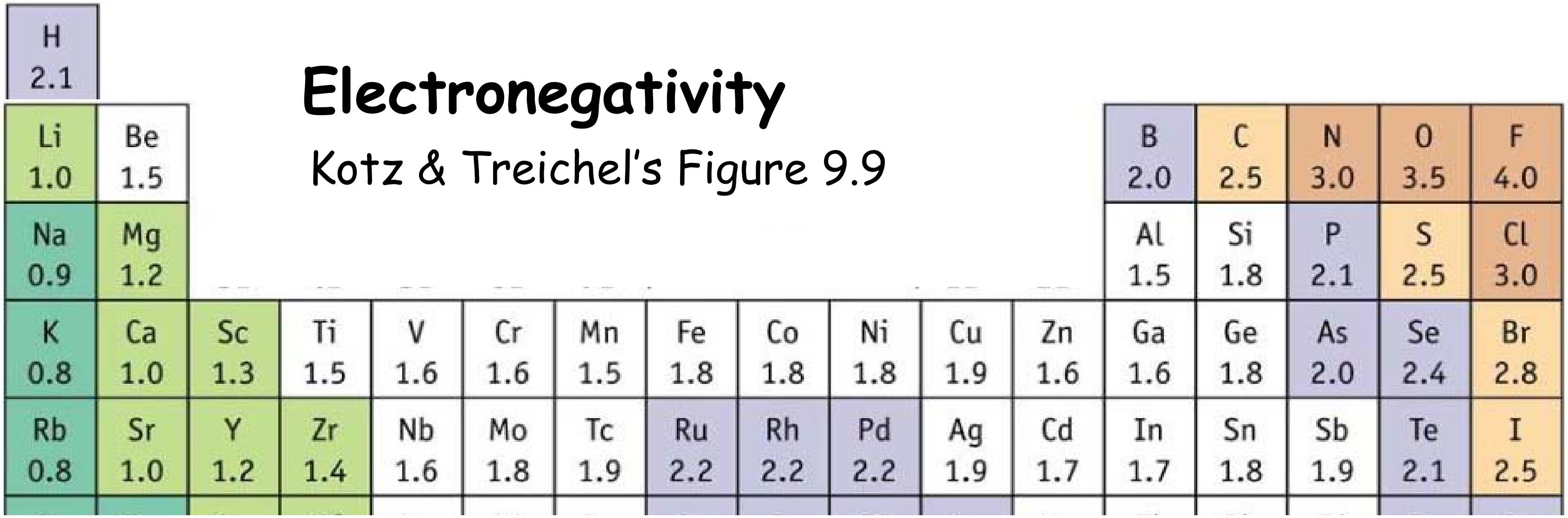
1.1-1.2	Atomic structure & electron distribution
1.3-1.4	Types of bonds & representing structures
1.5	Atomic orbitals
1.6	Introduction to molecular orbital theory
1.7-1.9	Bonding: single, double, triple bonds
1.10	Bonding in cations, anions, radicals
1.11-1.13	Bonding in simple compounds
1.14	Summary: Bond lengths, strengths & angles
1.15	Dipole moments of molecules

Chapter 1: Introduction to Organic Chemistry

Chapter Outline (cont'd): *Next week*

1.16	Review of acids & bases
1.17	Organic acids & bases: pK_a & pH
1.18	Effect of structure on pK_a
1.19	Introduction to delocalized electrons & resonance
7.2-7.5	Understanding & drawing resonance structures
7.10	Effect of electron delocalization on pK_a
1.20	Effect of pH on structure of organic compounds
1.21	Lewis acids & bases

Organic Chemistry: the chemistry of carbon



Electronegativity

Kotz & Treichel's Figure 9.9

H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	

Characteristics of Carbon:

1. Does not readily give up or accept e$^-$s *(e$^-$s = electrons)*
   WHY?
   - Intermediate electronegativity
     - effective nuclear charge too low to steal e$^-$s
     - effective nuclear charge too high to give away e$^-$s
2. Does readily share e$^-$s *(i.e., forms covalent bonds)*
   with other C atoms & other non-metal atoms

1.1 REVIEW: The Structure of an Atom

- An atom consists of:
  - protons: positively charged, "massive" particles
  - neutrons: neutral, massive particles
  - } nucleus
  - electrons: negative, very light, wave-like particles } "cloud"

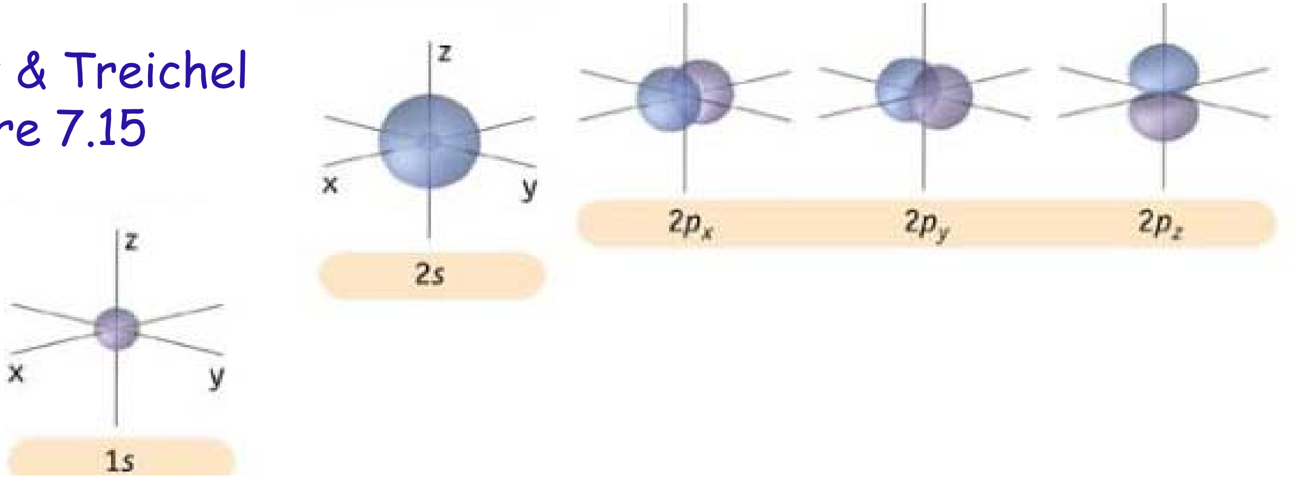
- Element's identity defined by # protons in atom's nucleus:
  - Atomic number = # of protons in atom's nucleus
  - Mass number = sum of # of protons & neutrons in atom
  - Isotopes: atoms with same atomic number but different mass numbers (difference is # of neutrons)
  - Atomic weight = average mass of an element's atoms based on natural abundances of isotopes

- Electrons not really particles floating in a cloud
  → such small particles are best described as waves…

1.2: REVIEW: The Distribution of Electrons in an Atom

Quantum mechanics: uses mathematical equations for wave motion to characterize motion of electrons around nucleus

- "Wave functions" (commonly called orbitals) tell us:
  1. the energy of an electron
  2. the volume of space around the nucleus where that electron is most likely to be found



Kotz & Treichel Figure 7.15

- If an orbital is closer to nucleus, it has lower energy
- Degenerate orbitals have the same energy

Where are the electrons are in a ground-state atom?

- Identify the element: # protons = # electrons

- Then assign the electron configuration,
  by following three rules:

1. The Aufbau principle: electrons occupy the orbitals with the lowest energy first

2. The Pauli exclusion principle:
   only two electrons can occupy one atomic orbital
   and the two electrons must have opposite spin

3. Hund's rule: electrons will occupy empty degenerate orbitals before pairing up in the same orbital

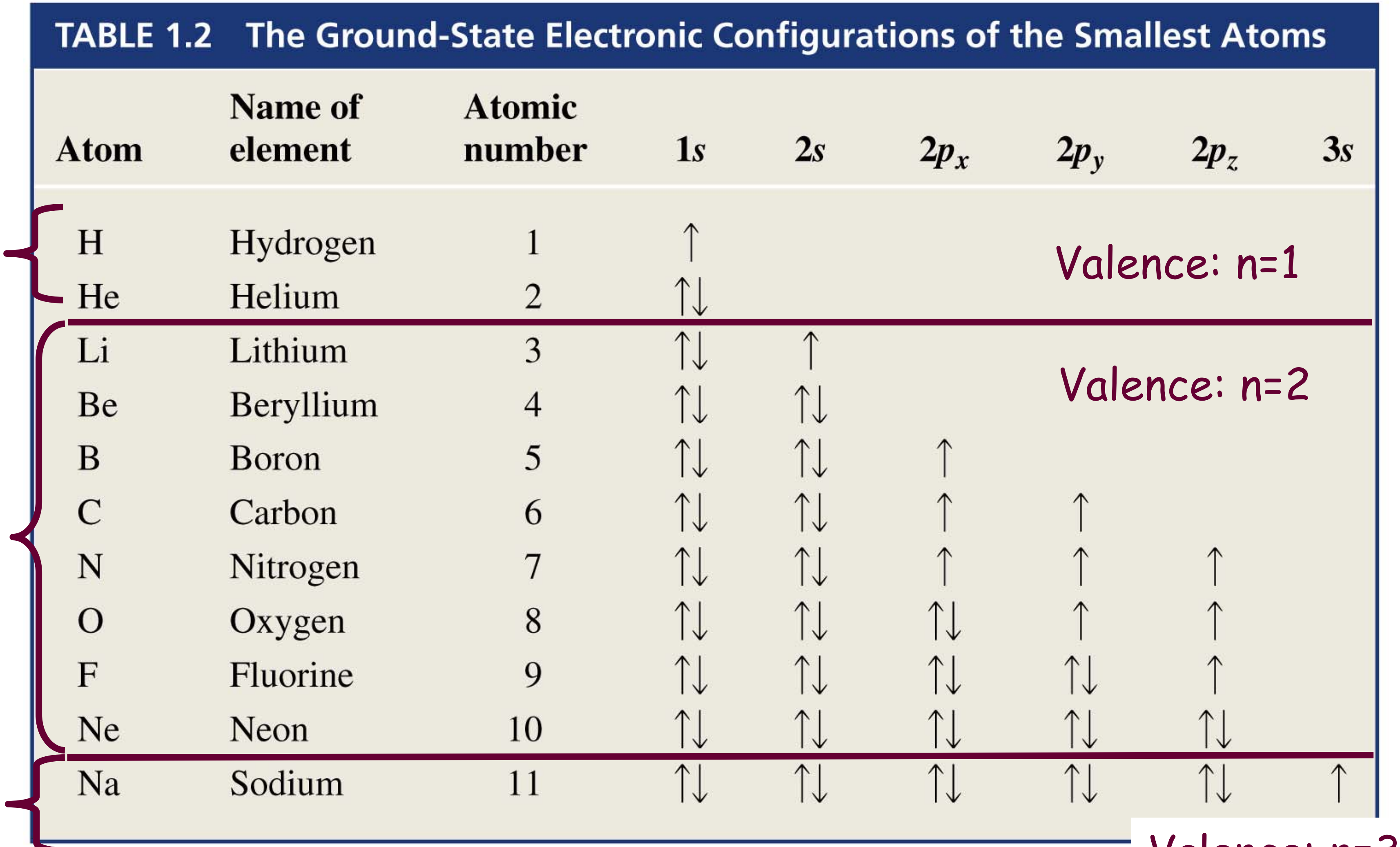


TABLE 1.2 The Ground-State Electronic Configurations of the Smallest Atoms

Atom	Name of element	Atomic number	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑

1st row (H, He): Valence: n=1

2nd row (Li–Ne): Valence: n=2

3rd row (Na): Valence: n=3

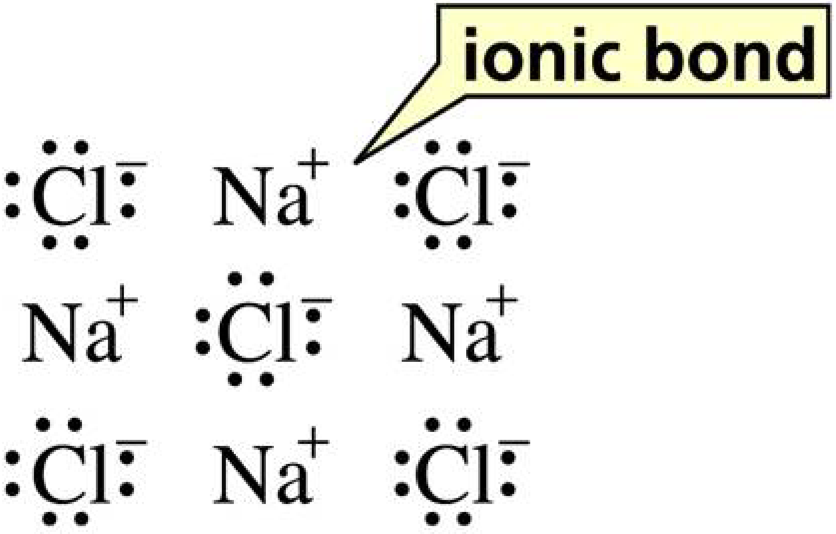
Remember: identifying the **valence shell** is important

- chemical bonds form such that each atom's valence shell becomes filled (by transferring electrons or by sharing)

1.3: REVIEW: Ionic, Covalent & Polar Bonds

Ionic compounds:

- form when an electropositive element (low electronegativity) transfers electron(s) to an electronegative element
- usually involve metals & nonmetals
- ionic bonds = electrostatic attractions between ions of opposite charge



sodium chloride

Covalent Compounds

Covalent bonding: valence e^-s attracted to 2 nuclei at once
e^-s occupy valence shells of both atoms

- Nonpolar covalent bonds: equal sharing of valence electrons by atoms of *equal electronegativity*
  e.g., H_2

- Polar covalent bonds: unequal sharing of valence e^-s between atoms with different electronegativities
  e.g., HF

Larger difference?
→ more polar

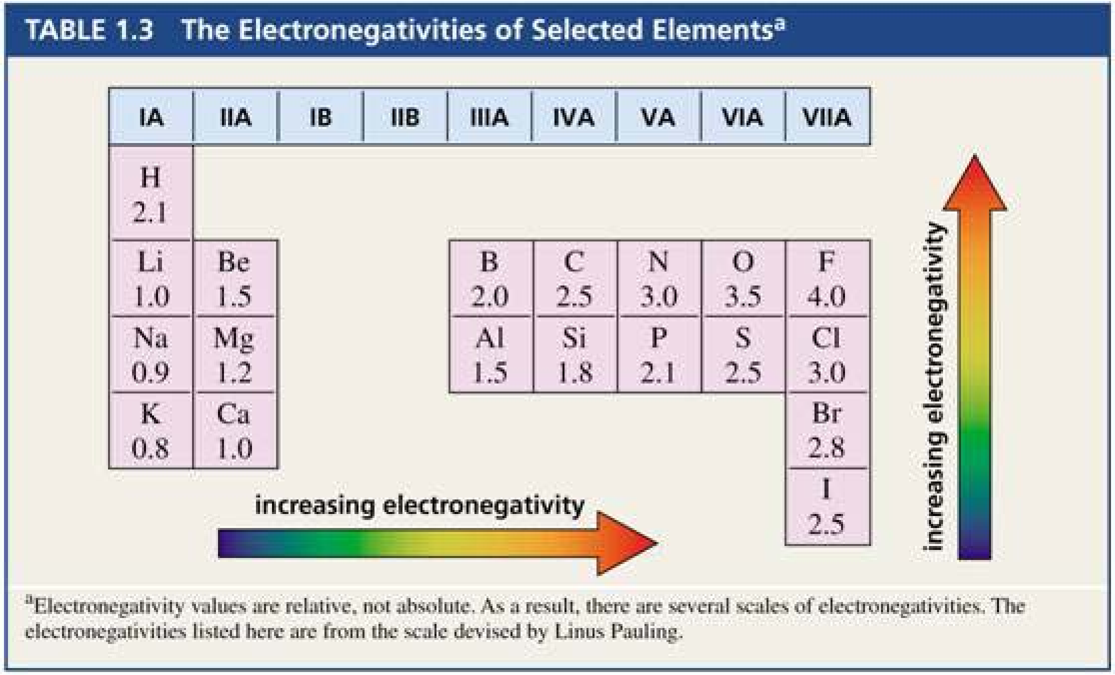


TABLE 1.3 The Electronegativities of Selected Elements[a]

IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

[a] Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

Important: know <u>relative</u> electronegativities of nonmetals

COMMON ONES: F > O > N, Cl > Br > I, S, C > H

Visualizing electron distribution in molecules: Electrostatic Potential Maps

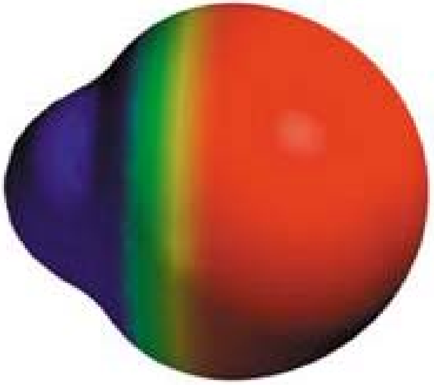
red < orange < yellow < green < blue

most negative electrostatic potential

most positive electrostatic potential

Pure covalent bond (nonpolar)
H—H

Polar covalent bond
H—F



Ion pair
Li^+ H^-

Why is it useful to picture polarity?

- Electron-rich atoms or molecules are attracted to electron-deficient atoms or molecules

⇨ **can predict physical & chemical properties!**

Polar bonds have a "Dipole moment"

- A polar bond has a negative end and a positive end
  → due to unequal distribution of electrons

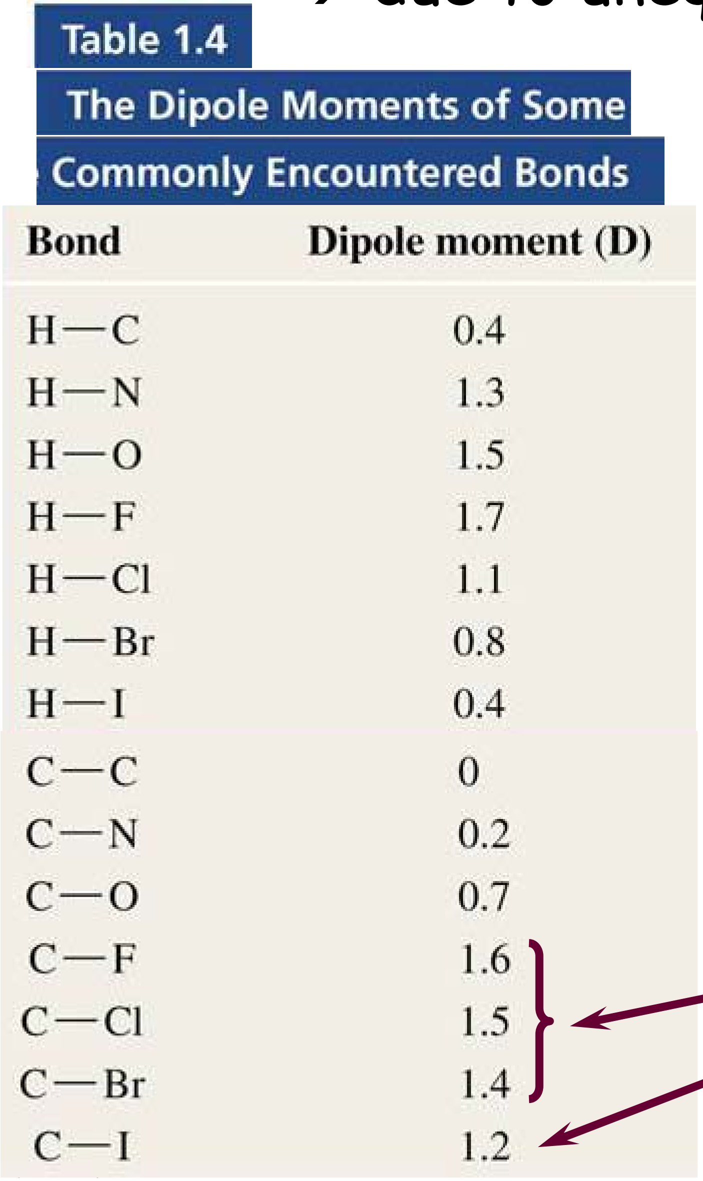


Table 1.4

The Dipole Moments of Some Commonly Encountered Bonds

Bond	Dipole moment (D)
H—C	0.4
H—N	1.3
H—O	1.5
H—F	1.7
H—Cl	1.1
H—Br	0.8
H—I	0.4
C—C	0
C—N	0.2
C—O	0.7
C—F	1.6
C—Cl	1.5
C—Br	1.4
C—I	1.2

dipole moment = $\mu = e \times d$

In units called Debyes, "D"

e : magnitude of the charge on the atom

d : distance between the two charges

Note:

- These dipole moments are averages of experimental measured dipoles
- Using electronegativity differences to predict polarity works fairly well, but is **not perfect**

- Suggestion: become familiar with the relative polarities shown here…

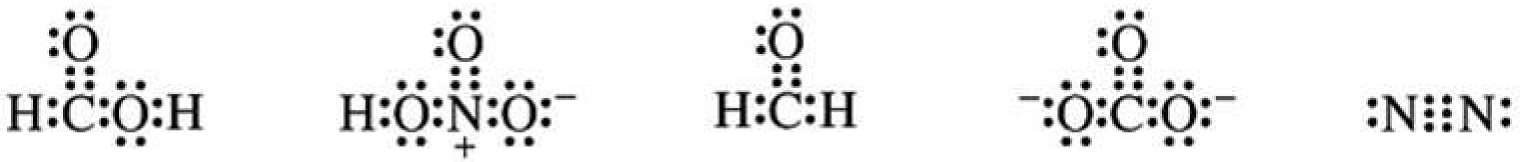
1.4 REVIEW & BEYOND: Representation of structure

- Lewis structures: include <u>all</u> valence electrons

  bonding e$^-$s: as pair of dots *OR* as a line
  nonbonding e$^-$s: as a pair of dots *(lone pairs)*

Lewis structures

Full dot structures



Simplified structures

<u>Important points to remember:</u>

- add up all valence e$^-$s & make bonds to satisfy valences
- left-over e-s left as lone pairs on atoms with higher electronegativity
- make multiple bonds to try to minimize formal charges on atoms

- 1st row elements: MUST obey duet rule
- 2nd row elements: MUST obey octet rule
- 3rd row & below: can exceed octet

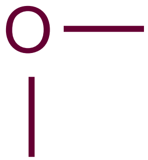
- Formal charge = # valence e$^-$s – [# lone pair e$^-$s + ½(# bonding e$^-$s)]

Common Bond Numbers: atoms with zero formal charge

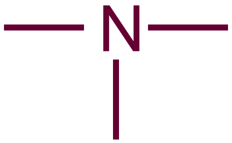
one bond

H— F— Cl— Br— I—

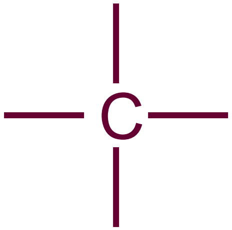
two bonds



three bonds



four bonds



How many lone pairs should each of these atoms have?

Typical ways to draw organic structures

- Kekulé structures: show all bonds but not lone pairs
- Condensed structures: formulas that show connectivity

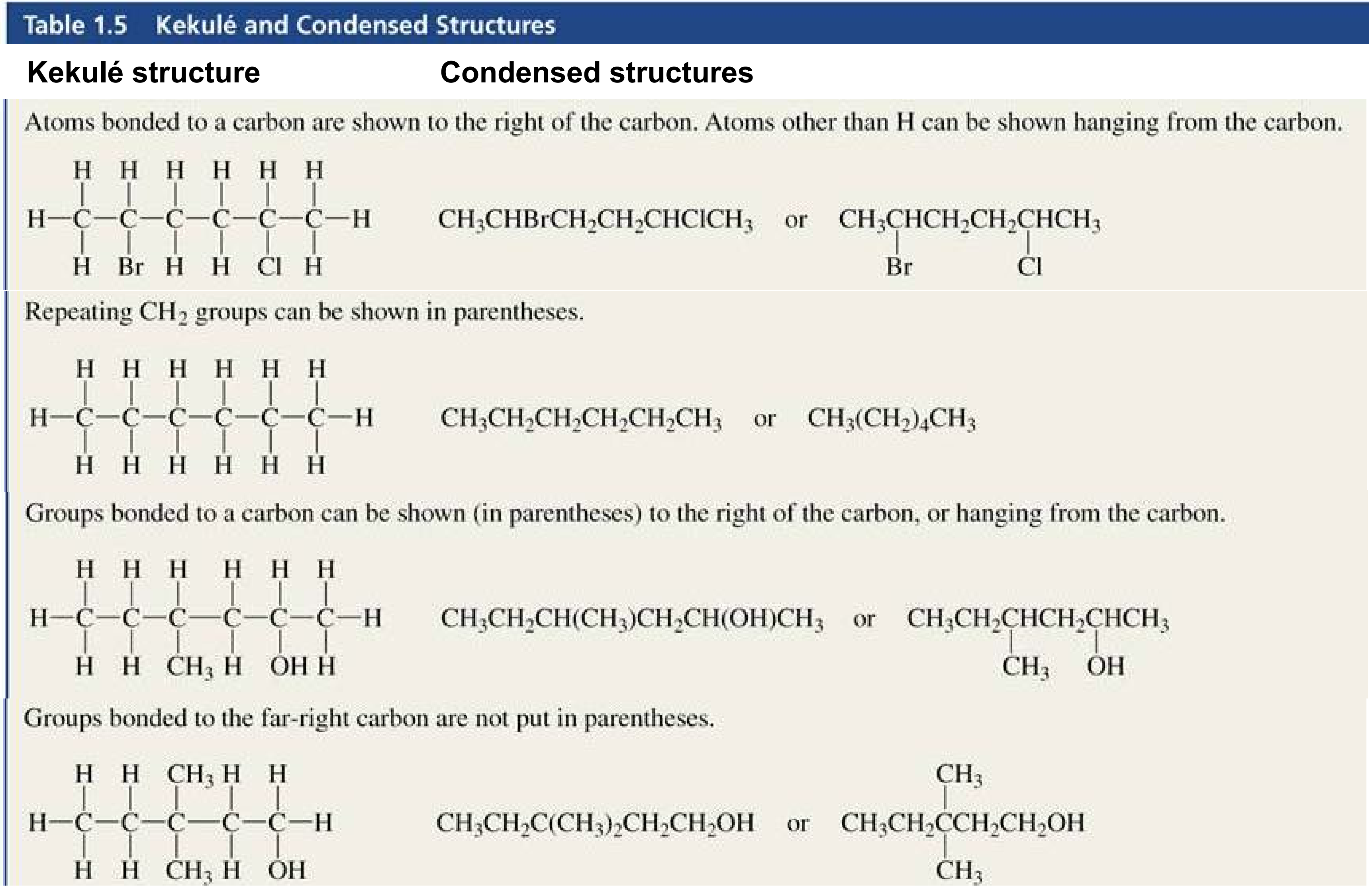
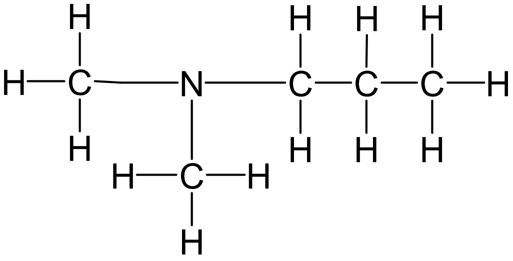
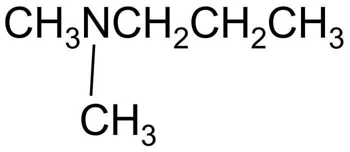
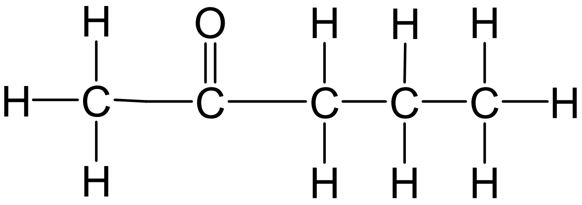
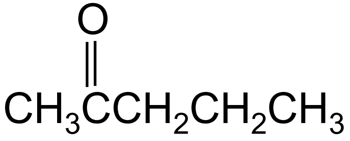
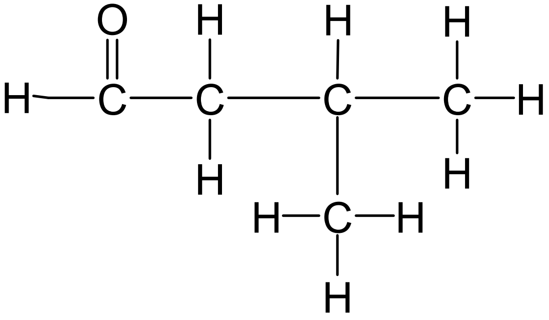
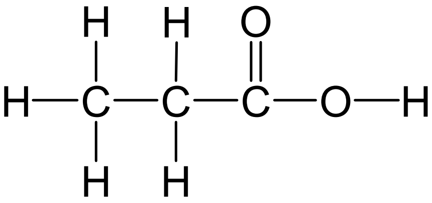


Table 1.5 Kekulé and Condensed Structures

Kekulé structure	Condensed structures
Atoms bonded to a carbon are shown to the right of the carbon. Atoms other than H can be shown hanging from the carbon.	
$\begin{array}{cccccccc} & H & H & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \vert & \vert & \\ & H & Br & H & H & Cl & H & \end{array}$	$CH_3CHBrCH_2CH_2CHClCH_3$ or $CH_3\underset{Br}{C}HCH_2CH_2\underset{Cl}{C}HCH_3$
Repeating CH_2 groups can be shown in parentheses.	
$\begin{array}{cccccccc} & H & H & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \vert & \vert & \\ & H & H & H & H & H & H & \end{array}$	$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$
Groups bonded to a carbon can be shown (in parentheses) to the right of the carbon, or hanging from the carbon.	
$\begin{array}{cccccccc} & H & H & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \vert & \vert & \\ & H & H & CH_3 & H & OH & H & \end{array}$	$CH_3CH_2CH(CH_3)CH_2CH(OH)CH_3$ or $CH_3CH_2\underset{CH_3}{C}HCH_2\underset{OH}{C}HCH_3$
Groups bonded to the far-right carbon are not put in parentheses.	
$\begin{array}{ccccccc} & H & H & CH_3 & H & H & \\ & \vert & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \vert & \\ & H & H & CH_3 & H & OH & \end{array}$	$CH_3CH_2C(CH_3)_2CH_2CH_2OH$ or $CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2OH$

Table 1.5 Kekulé and Condensed Structures

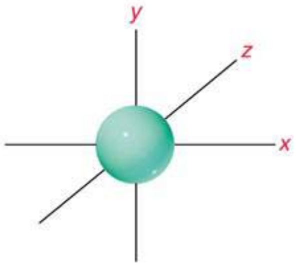
Kekulé structure	**Condensed structures**
Two or more identical groups considered bonded to the first atom on the left can be shown (in parentheses) to the left of that atom, or hanging from the atom.	
	$(CH_3)_2NCH_2CH_2CH_3$ or  $\underset{\displaystyle CH_3}{CH_3N}CH_2CH_2CH_3$
An oxygen doubly bonded to a carbon can be shown hanging off the carbon or to the right of the carbon.	
	 $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_3$ or $CH_3COCH_2CH_2CH_3$ or $CH_3C(=O)CH_2CH_2CH_3$
	
	

1.5 REVIEW: Atomic orbitals

The 1*s* & 2*s* Orbitals

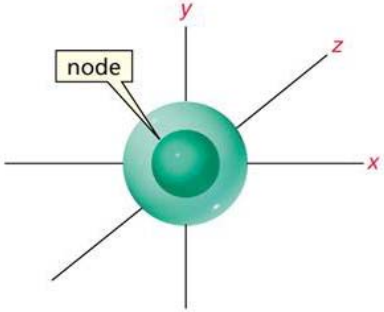
- Spherical

where
C's core
e^-s reside



1*s* atomic orbital

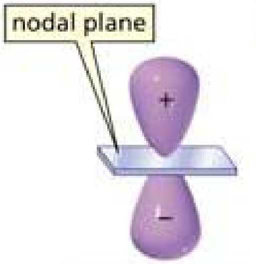
Part of
C's valence



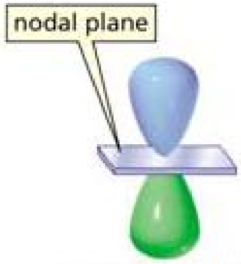
2*s* atomic orbital
node shown

The 2*p* Orbitals

- Dumbbell-shaped
- Opposite <u>mathematical</u> sign on either side of node (shown as +/- or colours)



2*p* atomic orbita

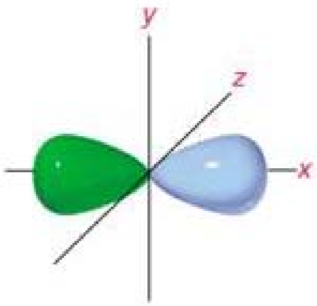


2*p* atomic orbital

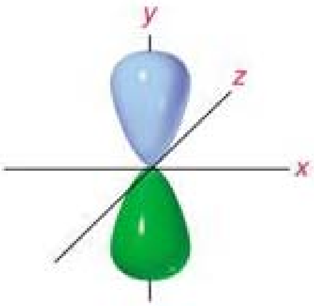
computer-generated
2*p* atomic orbital

←Lobes
actually
rather
diffuse

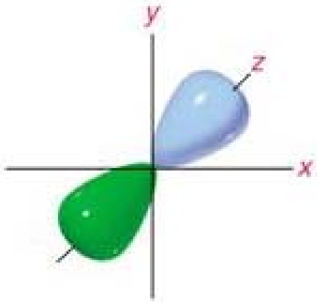
- 3 degenerate orbitals in 3 orientations:



$2p_x$ orbital



$2p_y$ orbital



$2p_z$ orbital

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: Bruice Ch.1: up to 1.15

Review: Chem205

- periodic trends
- drawing Lewis structure
- atomic & hybrid orbitals