Reading, etc.

- We will start Chapter 3 today - some material comes from Chapter 1.
- Material related to Chapter 4 begins next week – Read all of this is material on symmetry..
- Later half of Chapter 3 - coming late next week. This is a lot of new stuff for most of you - try to read ahead.
- e-mail to trh@mail.chem.tamu.edu

Class 1.3 Electron Configurations, Periodic Properties, & the Periodic Table

Friday, Sept. 3

CHEM 462

T. Hughbanks

Electronegativity

- Pauling: "the power of an atom in a molecule to attract the electrons to itself."
- Mulliken Electronegativity: directly related to IE and EA:

$$\chi = (^1/_2)[IE + EA]$$

- Based on your knowledge of IE and EA variations, how would you expect electronegativity to vary in the periodic table?

Pauling Electronegativity

- Assume we know the homonuclear bond dissociation energies, D_{AA} and D_{BB}. Pauling reasoned that if there was no electronegativity difference between A and B, then the "ideal" bond energy, D_{AB}, would be the mean: $D_{AB}(\text{calc.}) = (^1/_2)(D_{AA} + D_{BB})$
- Note: in 1937, Pauling switched to using the geometric mean: $D_{AB}(\text{calc.}) = [D_{AA} \cdot D_{BB}]^{1/2}$
- Most experimental heteronuclear bond strengths, $D_{AB}(\text{exp.})$, are larger than $D_{AB}(\text{calc.})$, which Pauling thought was due to a stabilizing ionic component to the bond.

Pauling Electronegativity

- The electronegativity difference between A and B was defined using the difference in the experimental and calculated heteronuclear bond energies:

$$\chi_A - \chi_B = [D_{AB}(\text{exp.}) - D_{AB}(\text{calc.})]^{1/2}$$

or $\Delta\chi_{AB} = [\Delta D_{AB}]^{1/2}$ (units of ΔD_{AB} = eV)

or $\Delta\chi_{AB} = .102[\Delta D_{AB}]^{1/2}$ (units = kJ/mol)

- Arbitrarily, Pauling chose the electronegativity of Fluorine to be 4.0, from which all other values are obtained by differences.

Examples

Bond	kJ/mol	
		$\Delta D_{AB} = D_{AB}(\text{exp.}) - D_{AB}(\text{calc.})$
H–H	434	$D_{AB}(\text{calc.}) = [D_{AA} \cdot D_{BB}]^{1/2}$
F–F	158	$\Delta D_{HF} = 535 - 262 = 273$
H–F	535	$\boldsymbol{\Delta\chi_{HF}} = .102[273]^{1/2} = \mathbf{1.69}$
H–Cl	404	$\Delta D_{HCl} = 404 - 324 = 80$
Cl–Cl	242	$\boldsymbol{\Delta\chi_{HCl}} = .102[80]^{1/2} = \mathbf{0.91}$
H–Br	339	$\Delta D_{HBr} = 339 - 289 = 50$
Br–Br	193	$\boldsymbol{\Delta\chi_{HBr}} = .102[50]^{1/2} = \mathbf{0.72}$
H–I	272	$\Delta D_{HI} = 272 - 256 = 16$
I–I	151	$\boldsymbol{\Delta\chi_{HI}} = .102[16]^{1/2} = \mathbf{0.41}$

Electronegativity

- Values are approximate, scale arbitrary
- Highest electronegativity: F, $\chi = 4.0$
- Lowest electronegativity: Cs, $\chi = 0.7$
- Generally, electronegativity increases as you move up or to the right in the periodic table.

Electronegativity Difference

- In a purely covalent bond, the 2 atoms are identical: H_2, N_2, etc.
  - same electronegativity $\rightarrow$ even sharing
- In an ionic bond, one atom has high electronegativity, one low: NaCl

  $\chi(\text{Na}) = 0.9$, $\chi(\text{Cl}) = 3.0 \rightarrow \Delta\chi = 2.1$

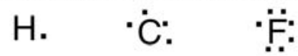
  Chlorine pulls an electron away from sodium, forming ions.

Polar Bonds

- For most bonds, $\Delta\chi$ is moderate, not zero
- This gives an intermediate case: electrons are shared, but not equally.
- CO: $\chi(\text{C}) = 2.5$, $\chi(\text{O}) = 3.5 \Rightarrow \Delta\chi = 1.0$
- Bond is “polar covalent.”

Lewis Structures

- Easy, useful way of representing valence electrons in a molecule (compared to the real physics).
- One electron = one dot; examples:



- One pair of shared electrons = one line
- Two pairs = two lines, etc.

Writing Lewis Structures

- There are systematic methods for doing this, which I will use follow loosely.
- Various texts put different emphasis on the "octet rule" for identifying 'stable" Lewis structures. The octet rule is used to a greater extent when considering molecules involving first-row atoms.
- For a simple scheme, Lewis structures (including Pauling's "resonance" ideas) are powerful - but they are still just a

Lewis Structures

Systematic method

1. Treat ions separately.
2. Count the valence e^-'s.
3. Set up the bonding framework, using two e^-'s per bond
4. 3 pairs of nonbonding e^-'s on each outer atom, except H (assuming enough e^-'s)
5. Remaining e^-'s to inner atoms

Lewis Structures, cont.

Systematic method

6. Find formal charge on each atom.
7. Minimize formal charges by shifting e^-'s to make double and triple bonds.
   (a) 2nd row atom → 4 occupied valence orbitals ($8e^-$'s → *"octet rule"*)
   (b) other atoms → formal charge to zero.

Formal Charges

- A useful "accounting device," not the real charge on the atoms (because e^-s in bonds not equally shared).

  FC = (# valence e^-'s in free atom) - (# valence e^-'s assigned in structure)

- Sum of FC's = zero for a neutral molecule, or total charge on an ion.
- Minimize FC's to get "best" structure.

Examples - no octet rule violations

CH_4 (methane)
C_2H_6 (ethane)
CCl_4 (carbon tetrachloride)
Br_2, O_2, N_2 (bromine, oxygen, nitrogen)
H_2O, NH_3 (water, ammonia)
C_2H_4, C_3H_6 (ethene, propene)
HCOOH (formic acid)
$(NH_2)_2CO$ (urea)

Lewis Structures & Resonance

- In many cases, no single Lewis structure adequately represents the distribution of electrons in a molecule. In such cases, we represent the electron distribution as a combination of Lewis structures.
- Real molecule does NOT "bounce" between the different resonance structures!

Resonance — Examples

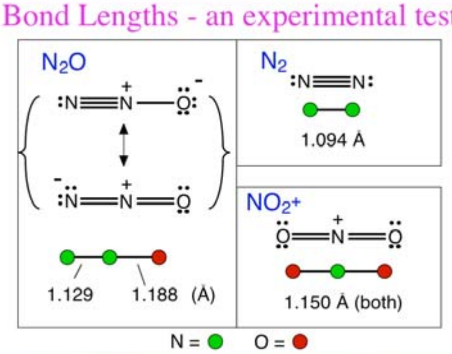
- equivalent resonance structures:

  O_3(ozone), NO_2^-, NH_4NO_3, $CaCO_3$, C_6H_6(benzene)

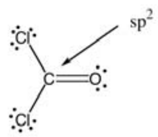
- resonance structures are inequivalent, but at least two are important:

  N_2O (nitrous oxide), NCO^- (cyanate), $CH_3CONHCH_3$(N-methylacetamide)— an example of an amide bond.

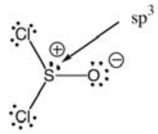
Bond Lengths - an experimental test



Adding hybridization; $COCl_2$ vs $SOCl_2$

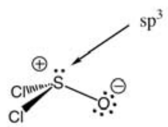


Existence of double bond implies a "unhybridized" p orbital engaged in π bonding, therefore... C atom geometry must be trigonal-planar

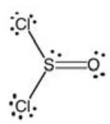


In the structure obeying octet rule, there's no S=O (double) bond, implying sp^3 hybridization at S and pyramidal geometry (tetrahedral including the lone-pair) around S

More on $SOCl_2$



Lone-pairs on Cl are understood - and omitted here.



A common depiction, with an S=O bond. This makes some inorganic chemists happy because it reduces the formal charges but it confuses students who don't understand that the double bond involves use of 3d orbitals on S (which is questionable anyway).

Octet 'Violations'

- Electron "deficient" molecules (e.g., BF_3)
- Even more serious: B_2H_6 - complete failure of classical structure theory

  "There are no electron deficient molecules, only theory deficient chemists." – K. Wade
- "Hypervalence" - e.g., PCl_5, SF_4
- Though not necessary, non-octet structures are often drawn - e.g., SO_3, SO_4^{2-}

Some Properties of Bonds; Bond Dissociation Enthalpies

A–B (g) → A(g) + B(g)   ΔH > 0

ΔH is the <u>bond dissociation enthalpy</u>

CH_4 (g) → C(g) + 4H(g)

ΔH = 4 ´(avg. C-H bond enthalpy)

Tabulated values are averages over a large database of values from individual molecules.

Trends in Bond Dissociation Enthalpies

Where lone-pairs of electrons don't cause complications,bond strengths usually decrease down a main group series, eg.,

C–C	345 kJ/mol
Si–C	301
Ge–C	242

Lone-pair repulsions can upset the trend:

O–O	145 kJ/mol - weak bonds!
S–S	250
Se–Se	170

Some Properties of Bonds; Saturation vs Unsaturation

p bonding stronger for row 2 elements

Examples:

Carbon: graphite and diamond almost equally stable (ΔG ~ 2 kJ/mol)

Silicon: only diamond-like form known

N_2 vs P_4; O_2 vs S_8 (and other catenated forms); SiO_2 vs CO_2