5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #12

Readings for today: Section 2.9 (2.10 in *3rd ed*) , Section 2.10 (2.11 in *3rd ed*), Section 2.11 (2.12 in *3rd ed*), Section 2.3 (2.1 in *3rd ed*), Section 2.12 (2.13 in *3rd ed*).
Read for Lecture #13: Section 3.1 (*3rd* or *4th ed*) – The Basic VSEPR Model, Section 3.2 (*3rd* or *4th ed*) – Molecules with Lone Pairs on the Central Atom.

Topics:
I. Breakdown of the octet rule
  Case 1. Odd number of valence electrons
  Case 2. Octet deficient molecules
  Case 3. Valence shell expansion
II. Ionic bonds
III. Polar covalent bonds and polar molecules

I. BREAKDOWN OF THE OCTET RULE

Case 1. Odd number of valence electrons

For molecules with an odd number of **valence** electrons, it is not possible for each atom in the molecule to have an octet, since the octet rule works by ____________ e^-s.

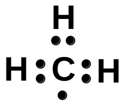
Example: CH_3

2) 3(1) + 4 = ______ valence electrons

3) 3(2) + 8 = ______ electrons needed for octet

4) 14 – 7 = ________ bonding electrons

H_3C



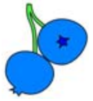
Radical species: molecule with an ________________ electron.

Radicals are usually very reactive. The reactivity of radical species leads to interesting (and sometimes harmful) biological activity.

Free radicals in biology: a paradox

Free radical species damage DNA.

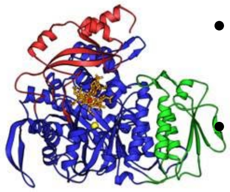
- Highly reactive oxygen radicals are a byproduct of metabolism and cause DNA damage.
- Cigarette smoke contains free radicals that can damage DNA in lung cells and lead to cancer.



antioxidant-rich blueberries

- Antioxidants (such as vitamin A, C, and E) reduce DNA damage in the body by "trapping" radicals.

Free radicals are essential for life.



- Free radicals are involved in cell signaling (see NO example on p. 2).
- Some enzymes use free radicals to carry out essential reactions in the body.

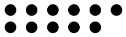
For example, a protein called ribonucleotide reductase (RNR) catalyzes an essential step in DNA synthesis and repair using a free radical species.

Some radicals are more stable. For example, NO

NO **N** **O**

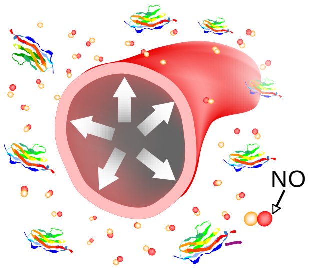
1) Draw skeletal structure

2) 5 + 6 = 11 valence electrons



3) 8 + 8 = 16 electrons needed for octet

4) 16 – 11 = ______ bonding electrons



vasodilation:
the widening of blood vessels

Figure by MIT OpenCourseWare.

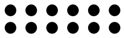
Nitric oxide, NO

- an important cell-signaling molecule in humans.
- diffuses freely across cell membranes and signals for the smooth muscle in blood vessels to relax, resulting in vasodilation and increased blood flow.
- a *radical species*, NO has a short lifetime in the body, which makes it an ideal messenger molecule between adjacent cells.
- You may be familiar with a drug that inhibits the breakdown of an NO binding partner (an enzyme), leading to increased blood flow: ________________.

Now let's think about molecular oxygen, O_2.

What we expect: O O

2) ________________ valence electrons



3) ________________ electrons needed for octet

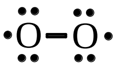
4) ________________ bonding electrons

5) Add two electrons per bond.

6) 2 bonding electrons remaining. Make double bond.

7) ________________ valence electrons – make lone pairs

Lewis method seems to work here, but in reality O_2 is a ________________!

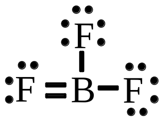


We need molecular orbital (MO) theory (Lecture #14).

Case 2. Octet deficient molecules

Some molecules are stable with an **incomplete** octet. Group 13 elements ____ and _____ have this property.

Consider BF_3



First, let's write the Lewis structure that achieves octets on every atom.

2) $3 + 3(7) =$ ______ valence electrons

3) $8 + 3(8) =$ ______ electrons needed for octet

4) $32 - 24 =$ ________ bonding e^{-}s

5) assign two electrons per bond.

6) $8 - 6 = 2$ extra bonding electrons

7) $24 - 8 = 16$ lone pair electrons

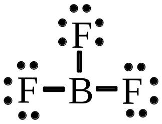
8) calculate formal charges:

$FC_B = 3 - 0 - (½)(8) = \mathbf{-1}$

$FC_{FDB} = 7 -$ ____ $- (½)($____$) =$ _______

$FC_F = 7 -$ ____ $- (½)($____$) =$ _______

But experiments suggest that all three B-F bonds have the same length, that of a ______________ bond.



$FC_B = 3 - 0 - (½)(6) = \mathbf{0}$

$FC_F = 7 - 6 - (½)(2) = \mathbf{0}$

The formal charges are more favorable for this structure.

Case 3. Valence shell expansion

Elements with n = or > 3 have empty ____ - orbitals, which means more than eight electrons can fit around the central atom.

Expanded valence shells are more common when the central atom is ______ and is bonded to small, highly electronegative atoms such as O, F, and Cl.

Consider PCl_5

Cl
Cl P Cl
Cl Cl

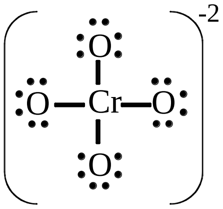
2) 5 + 5(7) = ______ valence electrons

3) 8 + 5(8) = ______ electrons needed for octet

4) 48 – 40 = ______ bonding e^-s

To make five P-Cl bonds, need ______ shared electrons. So 40 – 10 = 30 lone-pair electrons.

Consider CrO_4^{2-}



2) 6 + 4(6) + _____ = ______ valence electrons

3) 8 + 4(8) = ______ electrons needed for octet

4) 40 – 32 = ______ bonding e^-s

7) 32 – 8 = 24 lone-pair electrons.

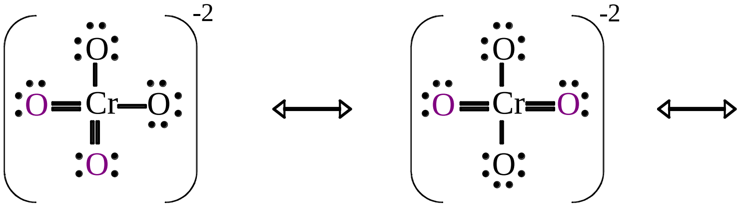
8) calculate formal charges:

$FC_{Cr} = 6 – 0 – (½)(8) = \mathbf{+2}$

$FC_O = 6 – 6 – (½)(2) = -1$

Total charge = 2 + 4(-1) = -2

But experimentally, Cr-O bond length and strength are between that of a single and double bond!



plus ________ other resonance structures.

$FC_{Cr} = 6 – 0 – (½)12 = \mathbf{0}$

$FC_{ODB} = 6 – 4 – (½)4 = \mathbf{0}$

$FC_O = 6 – 6 – (½)2 = \mathbf{-1}$

Valence shell expansion around Cr results in ________ formal charge separation. More stable Lewis structure.

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.

$$\mathrm{Na\ (g)} \longrightarrow \mathrm{Na^+\ (g) + e^-} \qquad \Delta E = \_\_\_\_\_\_ = \mathbf{494}\ \mathrm{kJ/mol}$$

$$\mathrm{Cl + e^-} \longrightarrow \mathrm{Cl^-\ (g)} \qquad \Delta E = -\ \mathrm{EA} = \_\_\_\_\_\ \mathrm{kJ/mol}$$

$$\mathrm{Na\ (g) + Cl\ (g)} \longrightarrow \mathrm{Na^+\ (g) + Cl^-\ (g)} \qquad \Delta E = +\ \_\_\_\_\_\_\_\_\ \mathrm{kJ/mol}$$

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

Problem: $\mathrm{Na\ (g) + Cl\ (g) \Rightarrow Na^+\ (g) + Cl^-\ (g)}$ has a positive ΔE. It ___________ energy.

Solution: Coulomb attraction.

$$\mathrm{Na^+\ (g) + Cl^-\ (g)} \longrightarrow \mathrm{NaCl\ (g)} \qquad \Delta E = -\ 589\ \mathrm{kJ/mol}$$

Net change in energy for the overall process:

$$\mathbf{Na\ (g) + Cl\ (g)} \longrightarrow \mathbf{NaCl\ (g)} \qquad \mathbf{\Delta E = \_\_\_\_\_\_\_\_\_\_\ kJ/mol}$$

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):

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

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.

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

Convert to kJ/mol

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

Simple ionic model predicts: $\Delta E = -\Delta E_d = -444$ kJ/mol

Experiments measure: $\Delta E = -\Delta E_d = -411$ kJ/mol

The discrepancy results from the following approximations:

- ignored repulsive interactions. Result:_________ ΔE_d than experimental value.
- treated Na^+ and Cl^- as ________________________.
- ignored quantum mechanics.

This simple model is applicable only to very ionic bonds.

III. POLAR COVALENT BONDS

Perfectly-ionic and perfectly-covalent bonds are the two extremes of bonding. In reality, most bonds fall somewhere in the middle.

A **polar covalent** bond is an ____________ sharing of electrons between two atoms with different electronegativities (χ).

Consider H-Cl versus H-H (Pauling electronegativity values are given):

H – Cl $\chi_H = 2.2$ $\chi_{Cl} = 3.2$

$H^{\delta+}\text{–}\ Cl^{\delta-}$

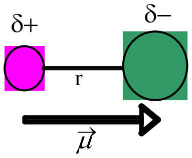
where δ is fraction of a full charge (e) that is asymmetrically distributed.

H – H H_2 is a “perfectly” covalent bond, $\delta = 0$.

Dipole moment

Asymmetric charge distribution results in an electric dipole, two unlike charges separated by a finite distance.

We can quantify charge separation by defining a dipole moment, $\vec{\mu}$.



$$\vec{\mu} = \overset{\text{C}}{\overset{\downarrow}{Q}} \bullet \overset{\text{m}}{\overset{\downarrow}{\vec{r}}}$$

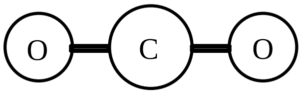
Magnitude of charge
Separation where Q = |δe|

Dipole moment is measured in C•m or in debye

1 debye = 1 D = 3.336 x 10^{-30} C•m

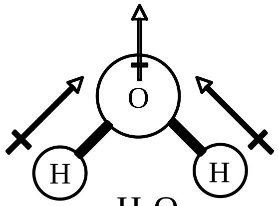
In chemistry, the arrow points toward the negative charge in a polar bond.

Polar molecules have a non-zero net dipole moment.



CO_2

_______________ molecule



H_2O

_______________ molecule

χ_H = 2.2

χ_C = 2.6

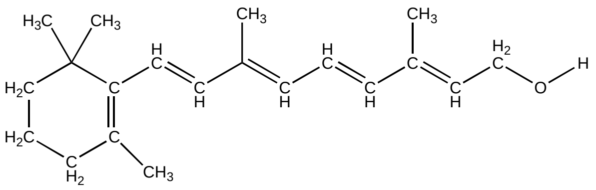
χ_N = 3.0

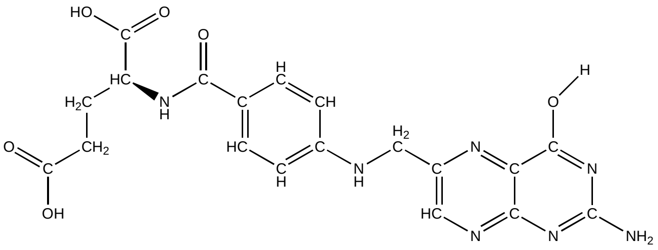
χ_O = 3.4

In large organic molecules and in biomolecules, such as proteins, we often consider the number of polar groups within the molecule.

For example, let's compare vitamin A to vitamin B9

Which vitamin contains a higher number of polar bonds? vitamin ________





Vitamin A

Vitamin B9 (____________________)

__________________ soluble

__________________ soluble