5.111 Lecture Summary #11 Wednesday, October 1, 2014

Readings for today: Section 2.9-2.12 (Same sections in 5^{th} and 4^{th} ed.)
Read for Lecture #12: Section 3.1 – The Basic VSEPR Model, Section 3.2 – Molecules with Lone Pairs on the Central Atom. (Same sections in 5^{th} and 4^{th} ed.)

Topics:

Breakdown of the octet rule
- **Case 1.** Odd number of valence electrons
- **Case 2.** Octet deficient molecules
- **Case 3.** Valence shell expansion

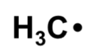
I. BREAKDOWN OF THE OCTET RULE

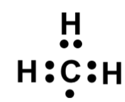
Case 1. Odd number of valence electrons

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 pairing e^-s.

Example: CH_3

2) 3(1) + 4 = ______ valence electrons
3) 3(2) + 8 = ______ electrons needed for octet
4) 14 – 7 = ________ bonding electrons





Radical species: molecule with an ________________ electron.

Most free radicals are very reactive. The reactivity of radical species leads to interesting (and sometimes harmful) biological activity.

Free Radicals in Biology: a Paradox

Free radical species**________________ *DNA*.**

Highly reactive oxygen radicals are a byproduct of metabolism and cause DNA damage.

Cigarette smoke also contains free radicals.

Figure by MIT OpenCourseWare.

Free radicals are essential for life.

Free radicals are involved in critical signaling pathways in or between cells, and in critical enzymatic reactions.

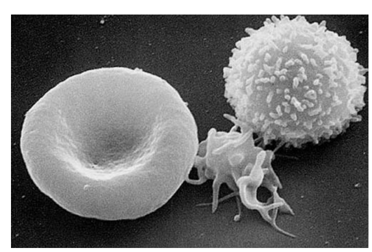


Image from public domain.

O_2^{-1} radicals are produced by our ___________ blood cells to kill invading microorganisms.

Nitric oxide is another important radical involved in cell signaling.

Nitric oxide, ______

- 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*, nitric oxide has a short lifetime in the body, which makes it an ideal messenger molecule between adjacent cells.

Nitric Oxide

1) Draw skeletal structure

2) 5 + 6 = 11 valence electrons

3) 8 + 8 = 16 electrons needed for octet

4) 16 ï 11 = ______ bonding electrons

7) remaining valence electrons ______

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 ï make lone pairs

Lewis method seems to work here, but doesn't give the correct structure.
In reality O2 is a _______________!

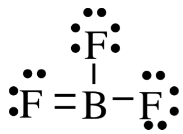
A birradical has two unpaired electrons on either the same or different atoms.

We need molecular orbital (MO) theory to rationalize why the biradical structure is correct (Lecture #13).

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

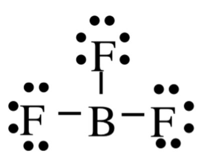
8) calculate formal charges:

$FC_B = 3 - 0 - (½)(8) = \mathbf{-1}$

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

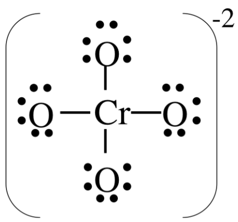
2) 5 + 5(7) = ______ valence electrons

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

4) 48 – 40 = ______ bonding e -s

To make five P-Cl bonds, need ______ shared electrons. 40 – 10 = 30 lone-pair electrons, and each Cl has an octet. We must expand the octet of P to have a structure that makes sense.

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.

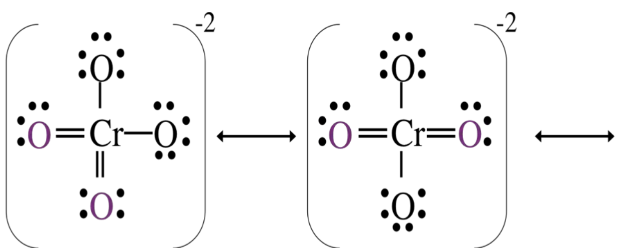
8) calculate formal charges:

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

$FC_{O} = 6 - 6 - (½)(2) = -1$

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.