Chemistry 1B-AL

Fall 2016

sessions ~~Lectures~~ 10-11-12

“Classical” theories of bonding and molecular geometry (ch 13)

- Lewis electron-dot structures
- Bond lengths, energies and ΔH
  (back to pp. 615-622, much of this in Chem 1C)
- **V**alence **S**tate **E**lectron-**P**air **R**epulsion (VSPER)
- Polarity of polyatomic molecules (p 600-606)

why octets?

filling of ns^2np^6 uses atomic orbitals of similar energy to form covalent bond

(note H requires only 2 electrons)

Zumdahl ‘steps’ (p. 623)

- Sum the valence electrons from all atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.

- Use a pair of electrons to form a bond between each pair of bound atoms.

- Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second (and higher) row atoms.

how to get octet Lewis structures

Gene’s pathetic method:

- use atomic Lewis valence electron diagrams (LVEDs)
- mess around to get octet structures

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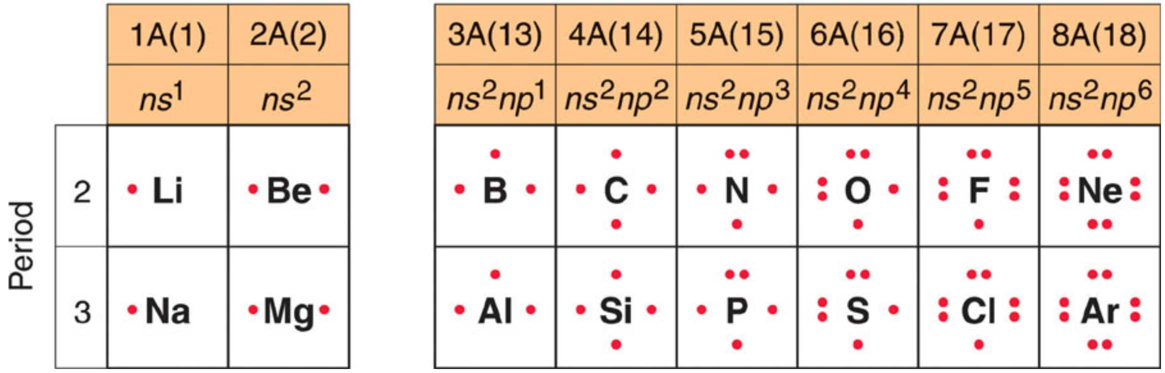
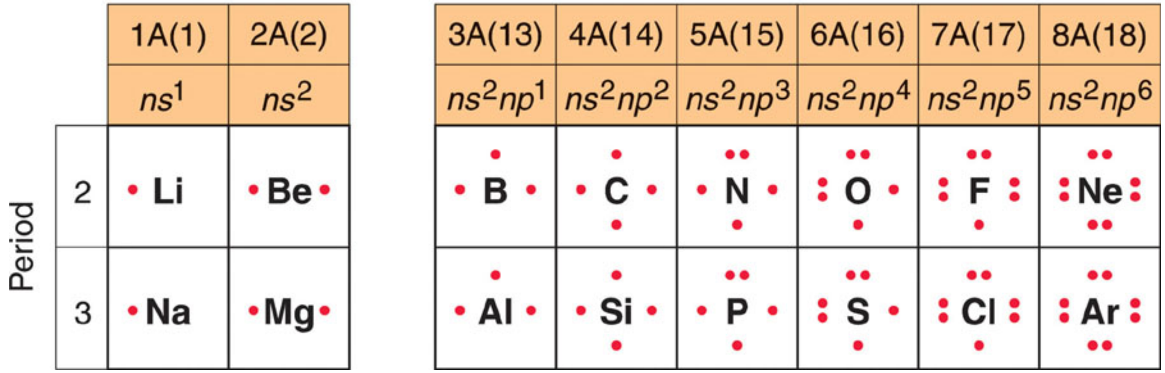

1A(1)
2A(2)
3A(13)
4A(14)
5A(15)
6A(16)
7A(17)
8A(18)
ns1
ns2
ns2np1
ns2np2
ns2np3
ns2np4
ns2np5
ns2np6
Period
2
3
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar

Note from LVEDs (usual bonding configurations to give complete shells)


1A(1)
2A(2)
3A(13)
4A(14)
5A(15)
6A(16)
7A(17)
8A(18)
ns1
ns2
ns2np1
ns2np2
ns2np3
ns2np4
ns2np5
ns2np6
Period
2
3
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar

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- H atom shares 1 pair of e’s (peripheral or ‘terminal’ atom)
- C atom shares 4 pairs of e’s
- N atom shares 3 pairs of e’s and has 1 non-bonding pair of e’s
- O atom shares 2 pairs of e’s and has 2 non-bonding pairs of e’s
  sometimes O^{-} sharing 1 pair of e’s and 3 non-bonding pairs
- F atom shares 1 pair of e’s and has 3 non-bonding pairs of e’s (peripheral or ‘terminal’ atom)
- similar for period 3 atoms

examples for molecules with single bonds

- Example 13.6e (p. 625) CF_4
- NH_2^{-}
- CH_3OH
- C_2H_6O (structural isomers)

  (CH_3OCH_3)

  (CH_3CH_2OH)

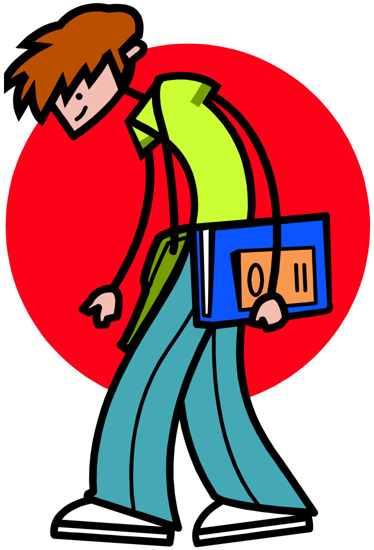
Multiple bonds

If, after step sharing single pairs of electrons a central atom still does not have an octet, make a multiple bond by changing a lone pair from one of the surrounding atoms into a bonding pair to the central atom.

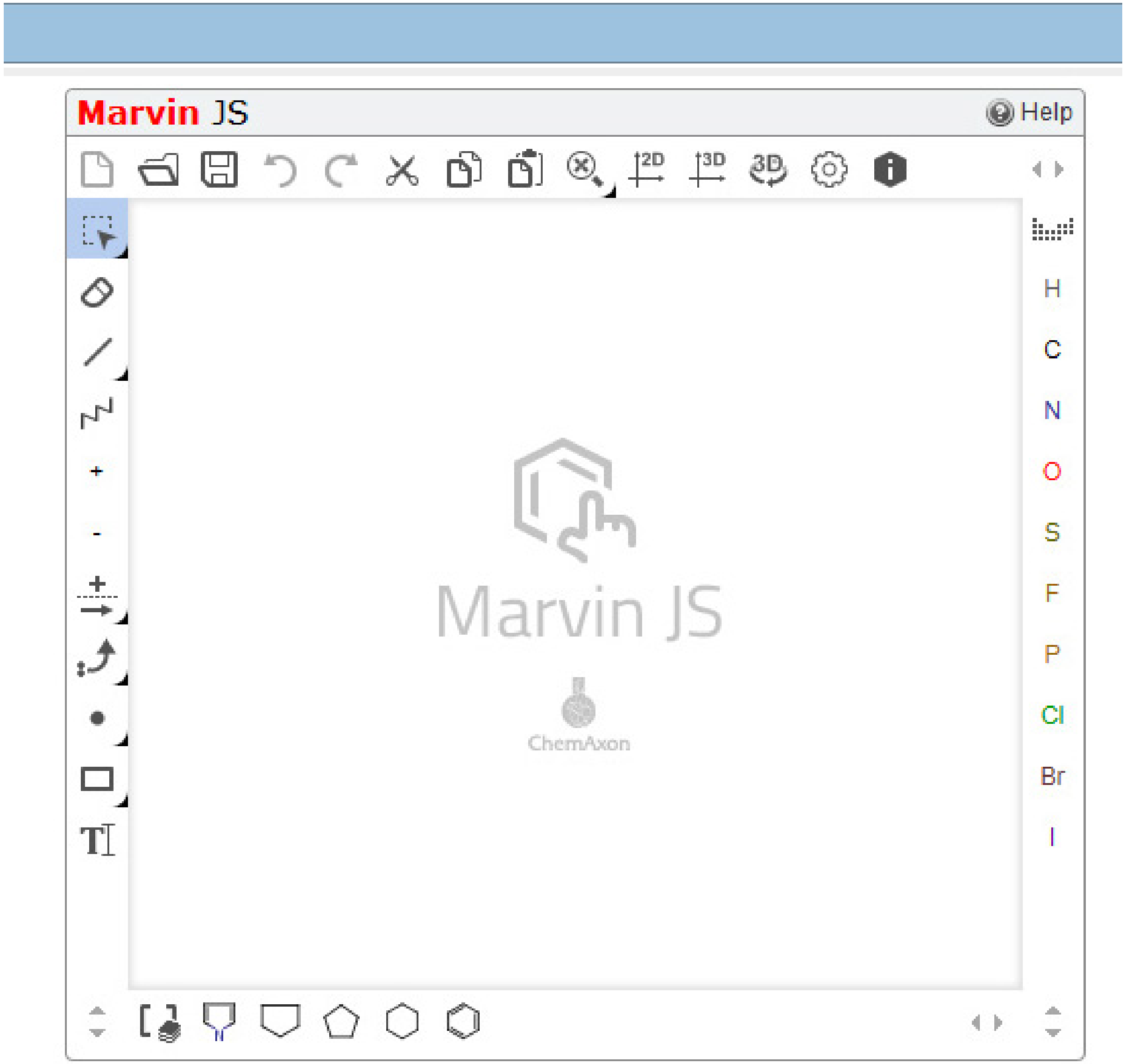
examples

- C_2H_4
- C_2H_2
- COF_2

MASTERING LEWIS STRUCTURES = PRACTICE PRACTICE PRACTICE



WebAssign and Marvin JS (HW4 #35)

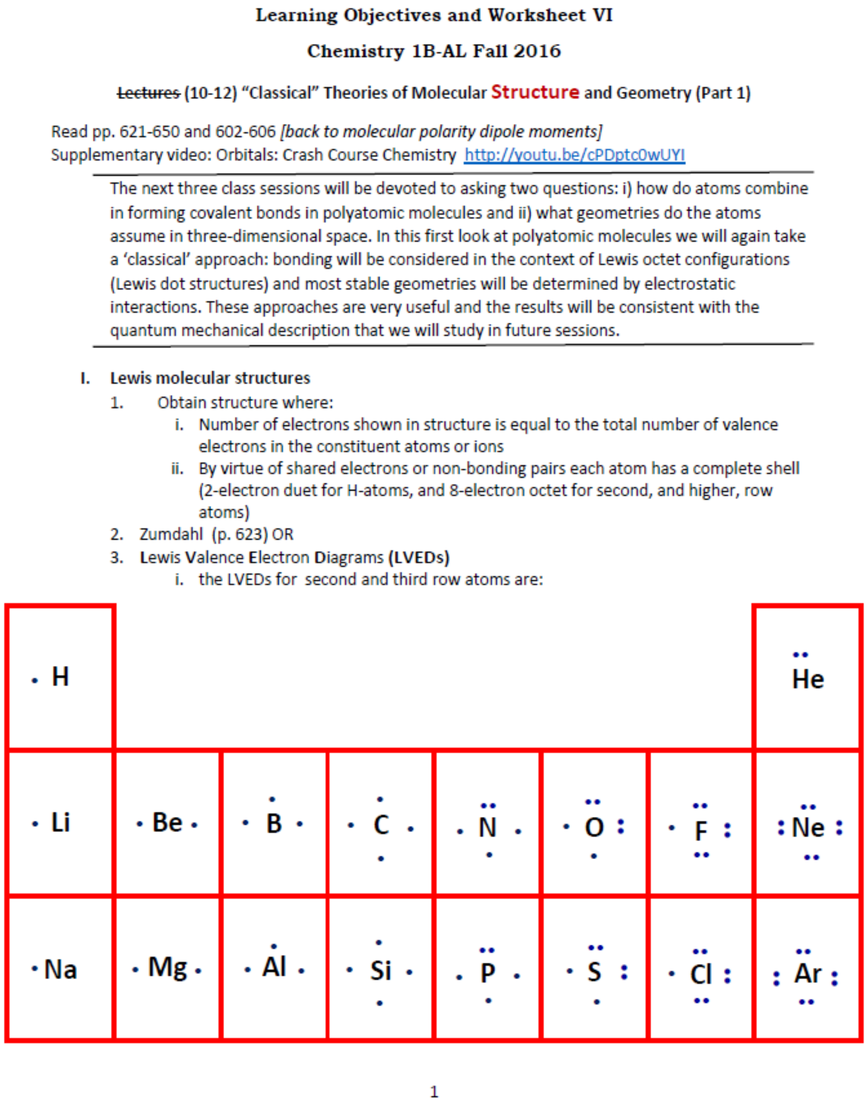

Marvin JS
Help
H
C
N
O
S
F
P
Cl
Br
I
Marvin JS
ChemAxon

HW#4-hints

Resonance Structures
and
Formal Charge

(Pp 626-627, 631-634)

covered worksheet VI I.1-I.5



Learning Objectives and Worksheet VI

Chemistry 1B-AL Fall 2016

~~Lectures~~ (10-12) "Classical" Theories of Molecular **Structure** and Geometry (Part 1)

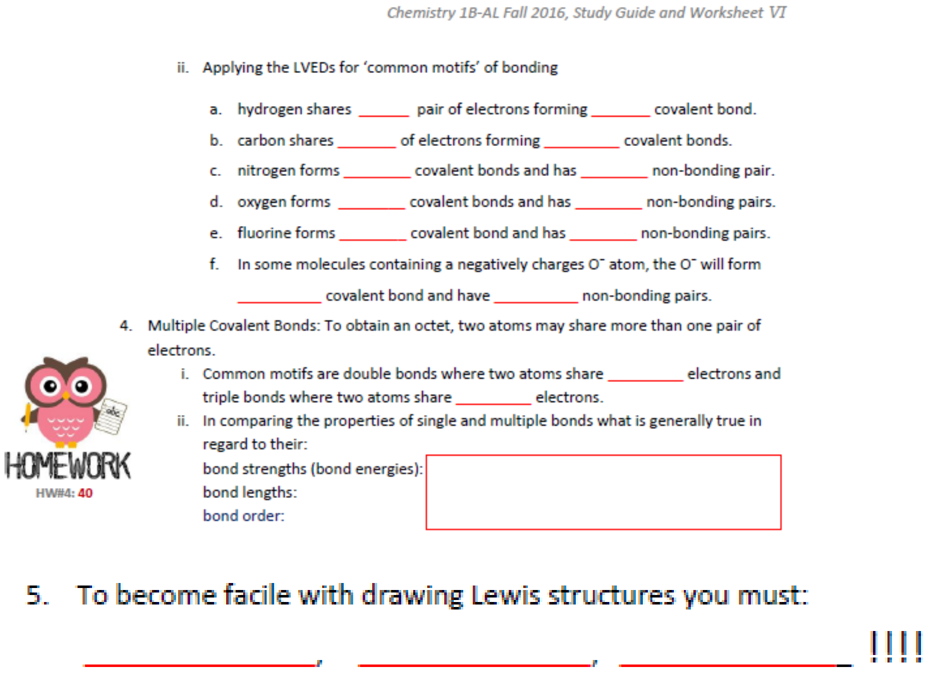
Read pp. 621-650 and 602-606 *[back to molecular polarity dipole moments]*
Supplementary video: Orbitals: Crash Course Chemistry http://youtu.be/cPDptc0wUYI

The next three class sessions will be devoted to asking two questions: i) how do atoms combine in forming covalent bonds in polyatomic molecules and ii) what geometries do the atoms assume in three-dimensional space. In this first look at polyatomic molecules we will again take a 'classical' approach: bonding will be considered in the context of Lewis octet configurations (Lewis dot structures) and most stable geometries will be determined by electrostatic interactions. These approaches are very useful and the results will be consistent with the quantum mechanical description that we will study in future sessions.

I. **Lewis molecular structures**
1. Obtain structure where:
   - i. Number of electrons shown in structure is equal to the total number of valence electrons in the constituent atoms or ions
   - ii. By virtue of shared electrons or non-bonding pairs each atom has a complete shell (2-electron duet for H-atoms, and 8-electron octet for second, and higher, row atoms)
2. Zumdahl (p. 623) OR
3. Lewis **V**alence **E**lectron **D**iagrams (**LVEDs**)
   - i. the LVEDs for second and third row atoms are:

· H							:He
· Li	· Be ·	· Ḃ ·	· Ċ ·	· N̈ ·	· Ö :	· F̈ :	: N̈e :
· Na	· Mg ·	· Ȧl ·	· Ṡi ·	· P̈ ·	· S̈ :	· C̈l :	: Är :

1



Chemistry 1B-AL Fall 2016, Study Guide and Worksheet VI

ii. Applying the LVEDs for 'common motifs' of bonding

a. hydrogen shares ______ pair of electrons forming _______ covalent bond.
b. carbon shares _______ of electrons forming _________ covalent bonds.
c. nitrogen forms ________ covalent bonds and has ________ non-bonding pair.
d. oxygen forms ________ covalent bonds and has ________ non-bonding pairs.
e. fluorine forms ________ covalent bond and has ________ non-bonding pairs.
f. In some molecules containing a negatively charges O⁻ atom, the O⁻ will form __________ covalent bond and have __________ non-bonding pairs.

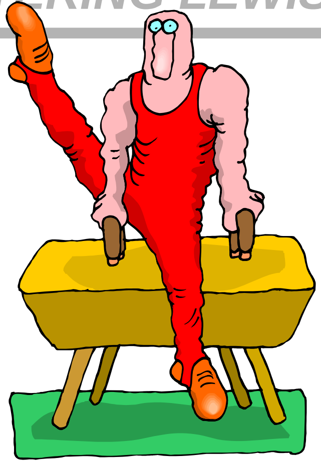
4. Multiple Covalent Bonds: To obtain an octet, two atoms may share more than one pair of electrons.
   - i. Common motifs are double bonds where two atoms share _________ electrons and triple bonds where two atoms share _________ electrons.
   - ii. In comparing the properties of single and multiple bonds what is generally true in regard to their:
     bond strengths (bond energies):
     bond lengths:
     bond order:

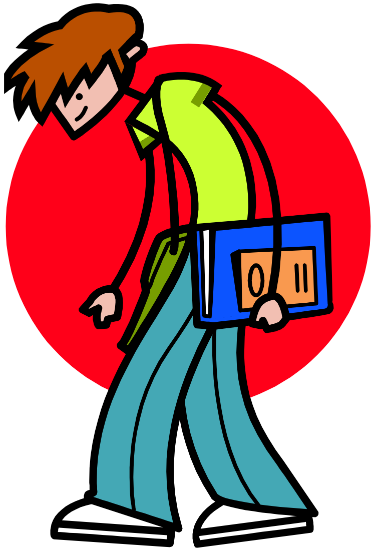
HOMEWORK
HW#4: 40

5. To become facile with drawing Lewis structures you must:

_________________, _________________, _________________ !!!!

MASTERING LEWIS STRUCTURES *= PRACTICE PRACTICE PRACTICE*





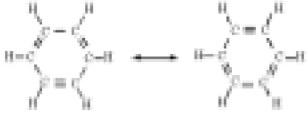
this video (clickers Q's next class) cover: ***worksheet VI II.1-2*** *and*

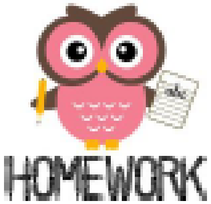
RESONANCE STRUCTURES

II. Resonance Structures

1. All resonance structures of a molecule have identical stoichiometric formulas; all isomeric structures of a molecule have identical stoichiometric formulas. What is the distinction between the meaning of different resonance structures and different isomeric structures ?

2. What experimentally measured property would distinguish between C_6H_6 existing as a mixture of the two structures below and as a resonance hybrid of the structures?



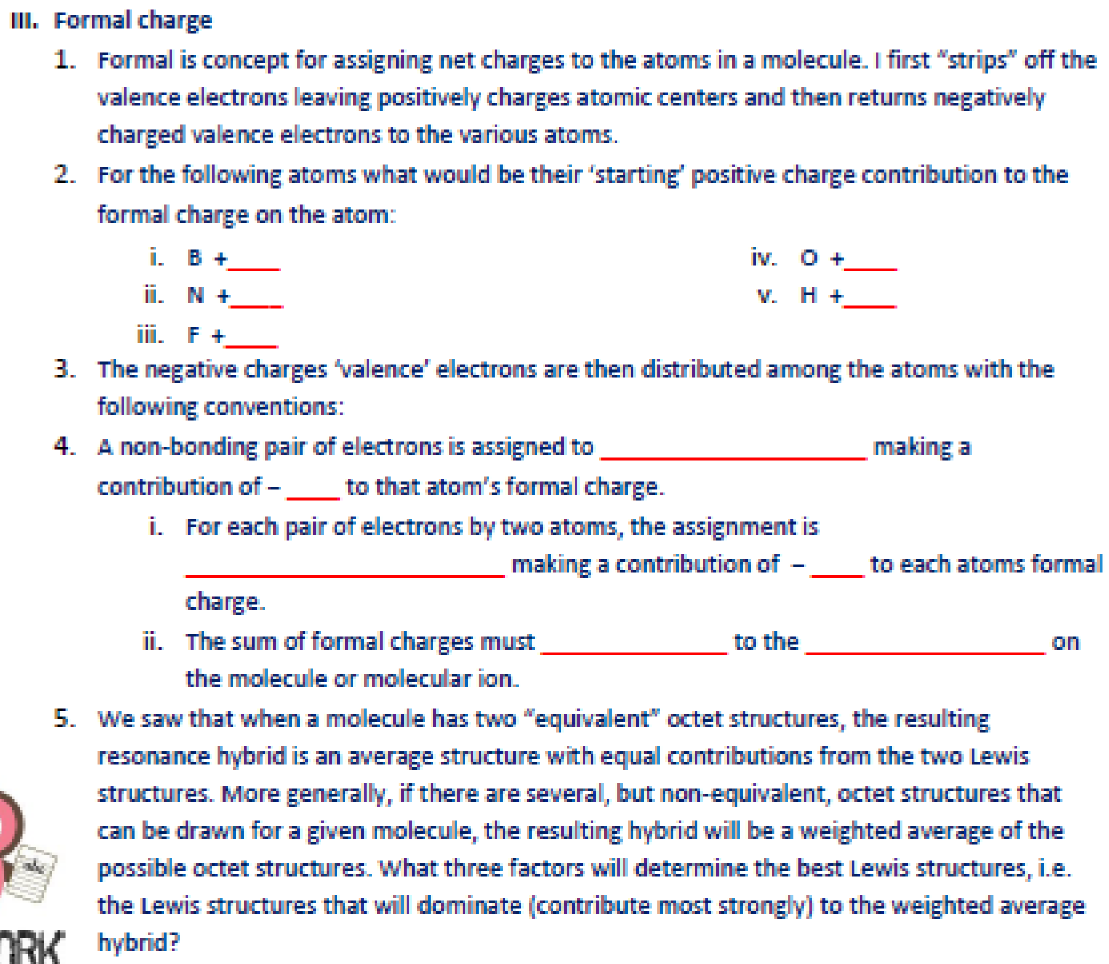


HW#4: 41, 42, 59

2

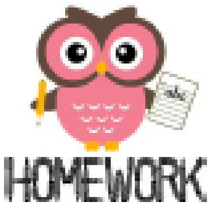
this video (clickers Q's next class) cover: and worksheet VI III.1-5

FORMAL CHARGE



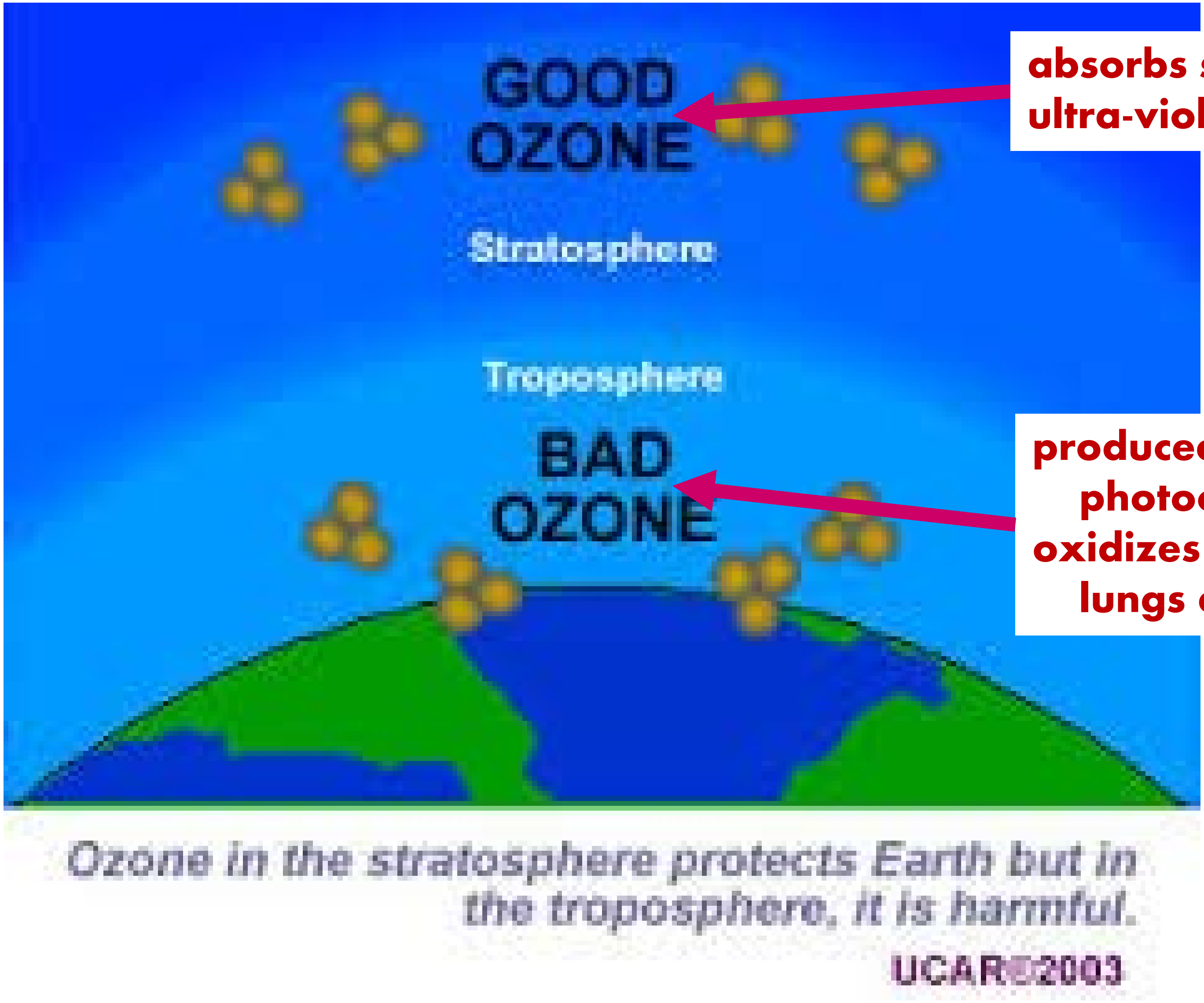
III. Formal charge

1. Formal is concept for assigning net charges to the atoms in a molecule. I first "strips" off the valence electrons leaving positively charges atomic centers and then returns negatively charged valence electrons to the various atoms.
2. For the following atoms what would be their 'starting' positive charge contribution to the formal charge on the atom:
   - i. B +____
   - ii. N +____
   - iii. F +____
   - iv. O +____
   - v. H +____
3. The negative charges 'valence' electrons are then distributed among the atoms with the following conventions:
4. A non-bonding pair of electrons is assigned to ____________________ making a contribution of – ____ to that atom's formal charge.
   - i. For each pair of electrons by two atoms, the assignment is ________________________ making a contribution of – ____ to each atoms formal charge.
   - ii. The sum of formal charges must ______________ to the __________________ on the molecule or molecular ion.
5. We saw that when a molecule has two "equivalent" octet structures, the resulting resonance hybrid is an average structure with equal contributions from the two Lewis structures. More generally, if there are several, but non-equivalent, octet structures that can be drawn for a given molecule, the resulting hybrid will be a weighted average of the possible octet structures. What three factors will determine the best Lewis structures, i.e. the Lewis structures that will dominate (contribute most strongly) to the weighted average hybrid?



HW#4: 43, 44, 510

but first: the good and the bad


GOOD
OZONE
Stratosphere
Troposphere
BAD
OZONE

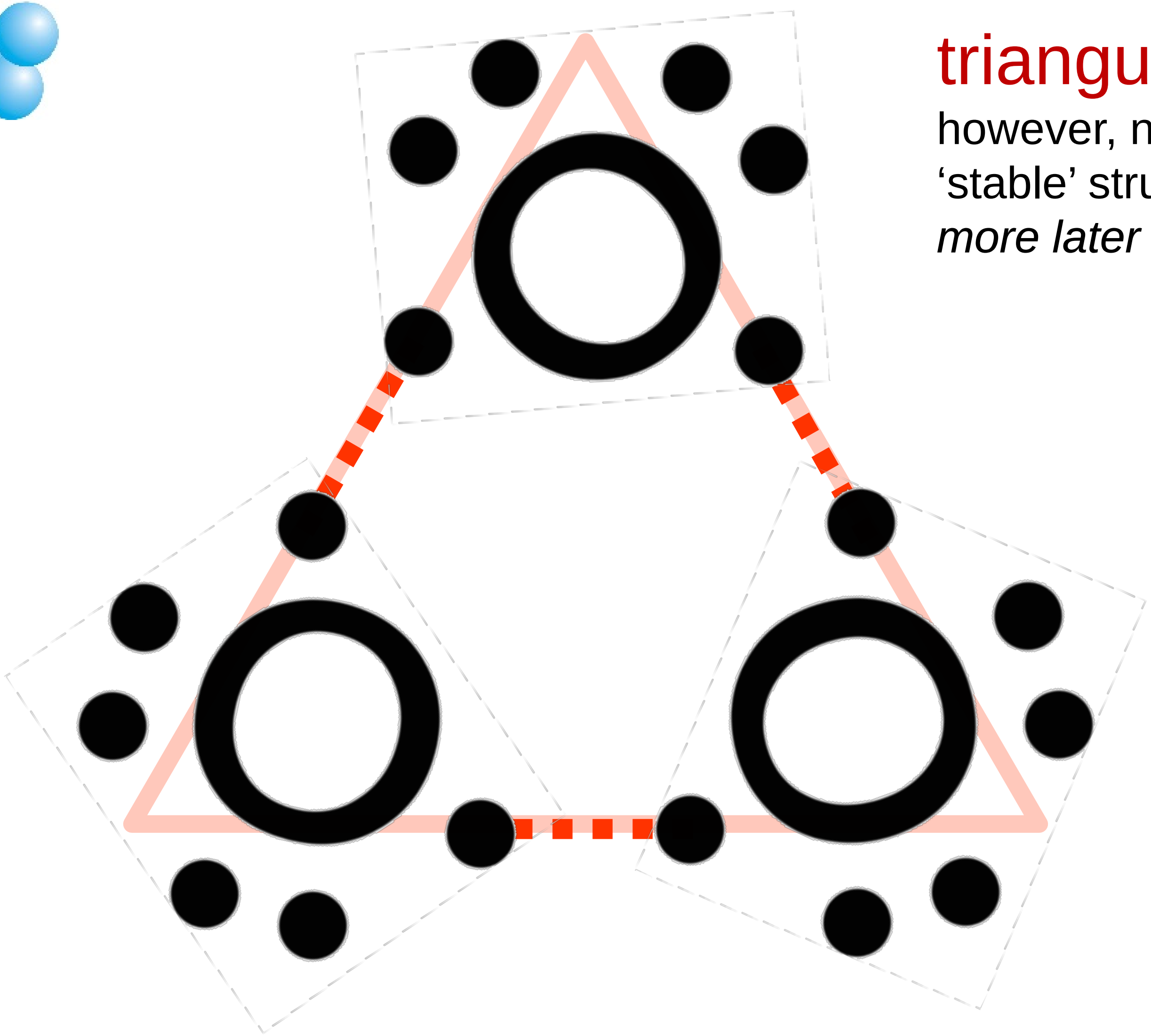
Ozone in the stratosphere protects Earth but in the troposphere, it is harmful.

UCAR©2003

absorbs sun's harmful ultra-violet radiation

produced by photochemical smog; oxidizes materials like lungs and tires

ozone (octet structure)

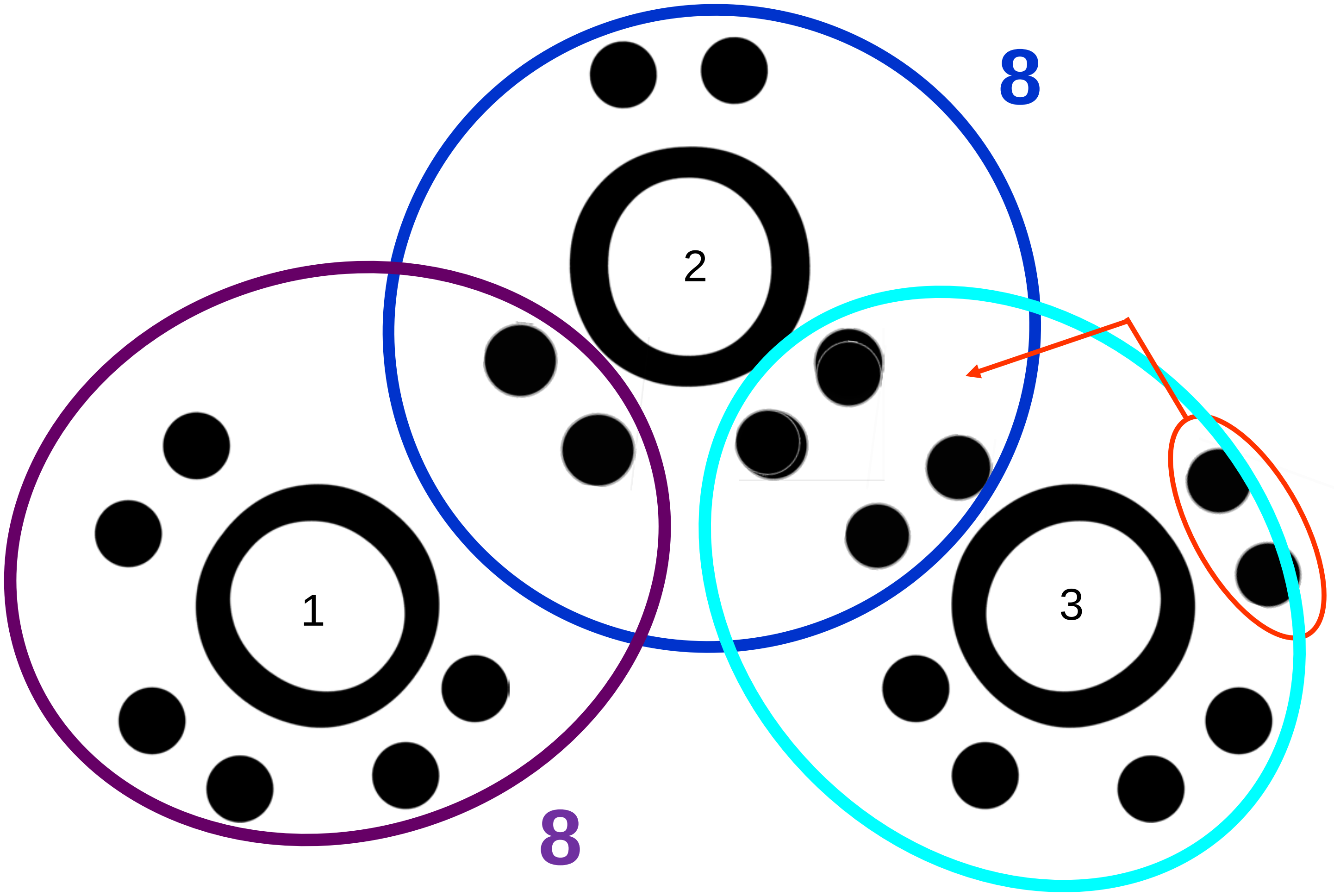


triangular ??,

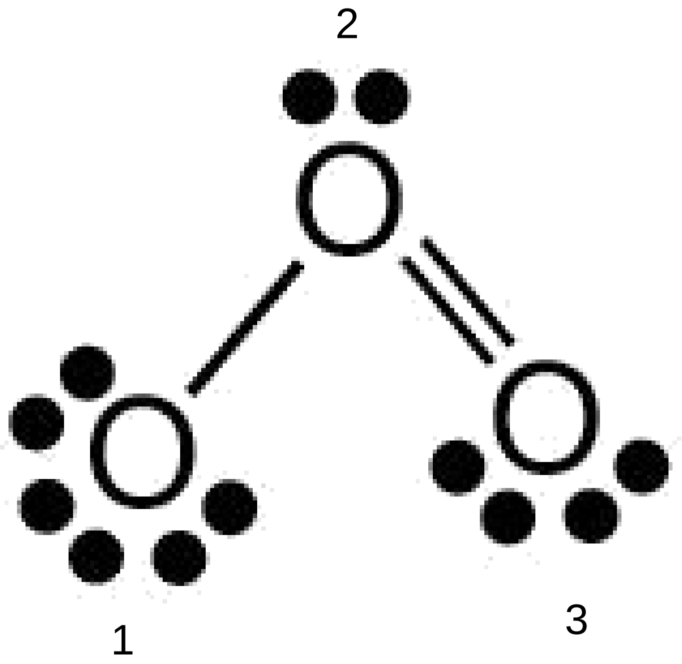
however, not the most ‘stable’ structure of O_3

more later

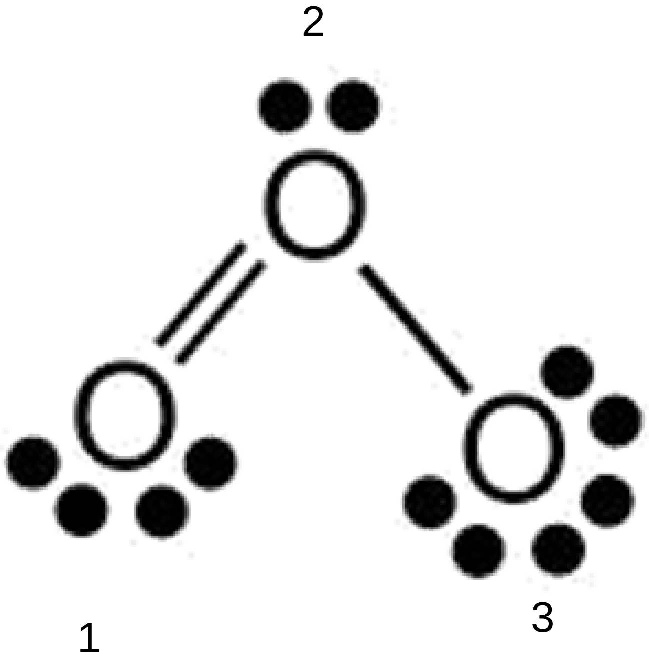
an octet structure



O_3 the more the merrier



if this structure ?

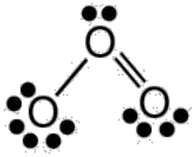


why not this structure too ?

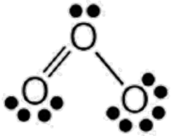
equivalent Lewis structures

(not isomers)

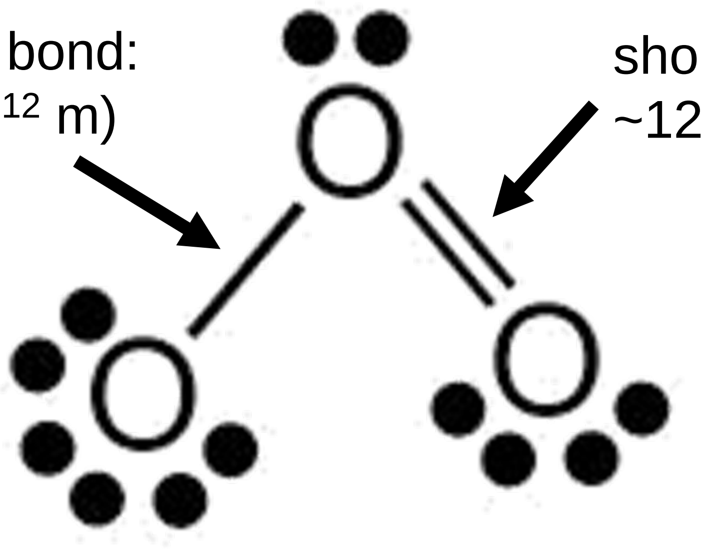
non-equivalent bonds



what do these structures imply?



two different O-O bond lengths



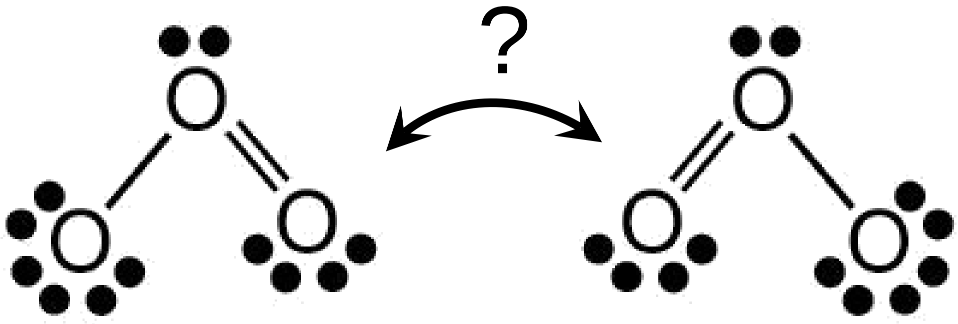
longer single bond:
~143 pm (10^{-12} m)

shorter double bond:
~123 pm (10^{-12} m)

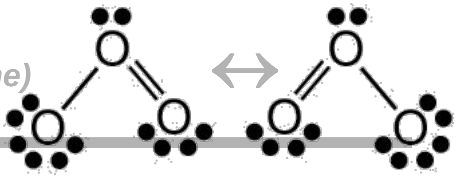
resonance structures and delocalization (13.11 pp 626-627)

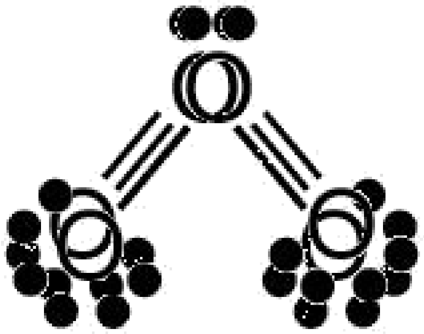
- resonance structures (forms) more than one possible electronic structure (not isomers)
  e.g. O_3 (ozone)

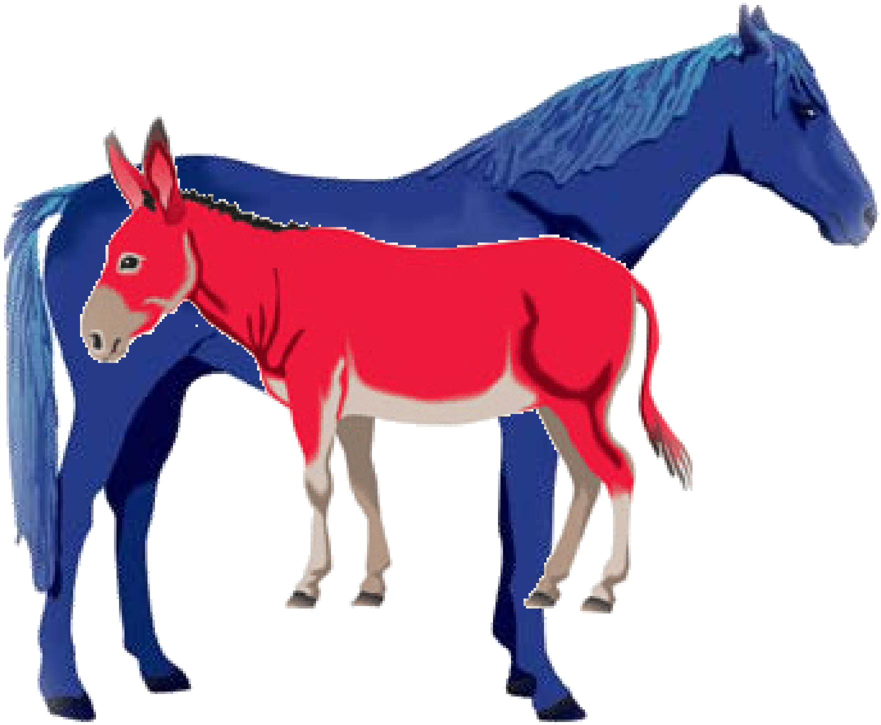
- how does the actual structure of O_3 reflect the two resonance structures or resonance hybrids ??

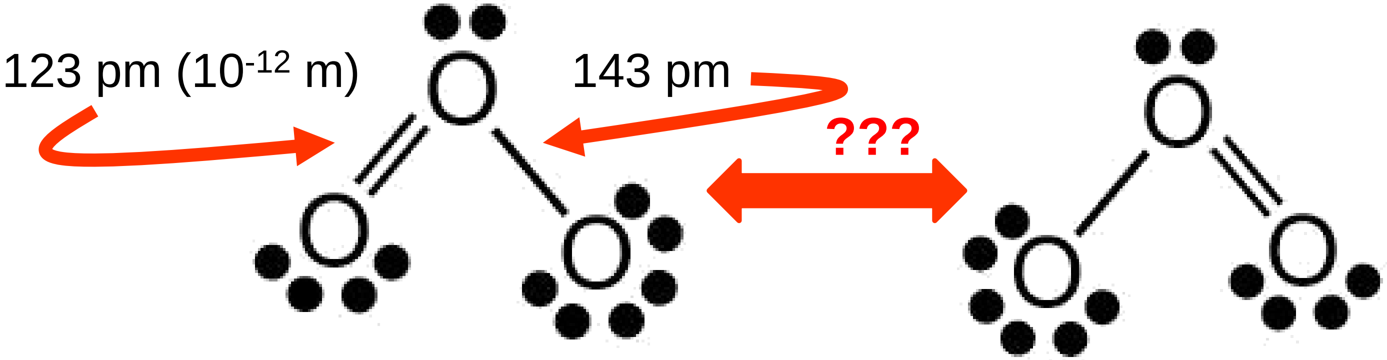


not this (red donkey ↔ blue horse) (Sienko and Plane)







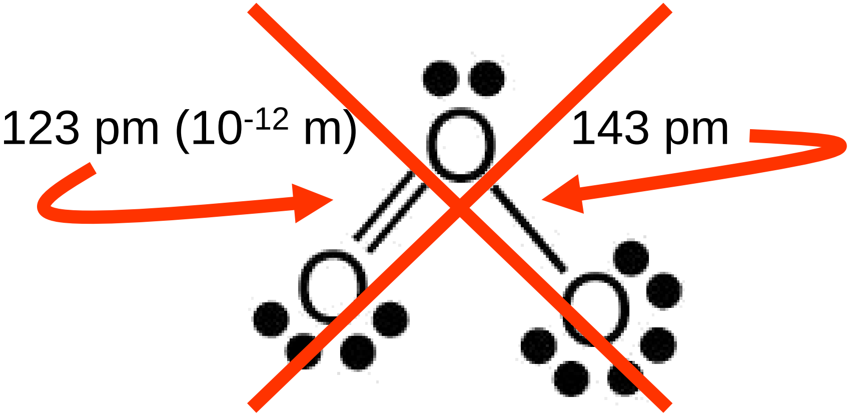

123 pm (10^{-12} m)

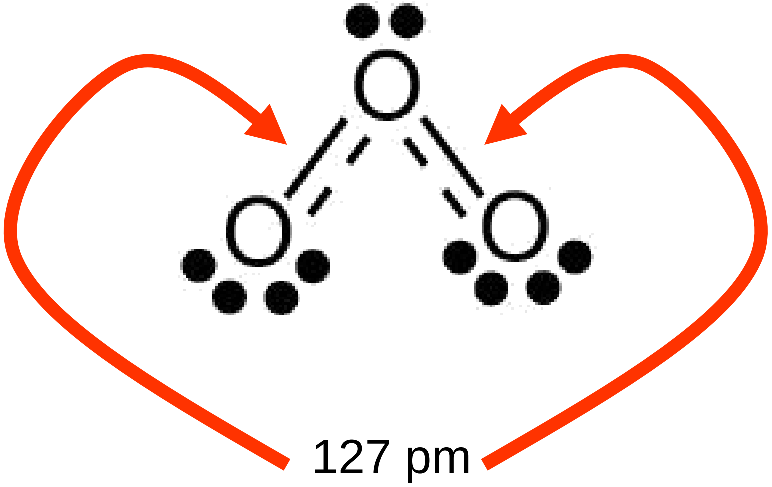
143 pm

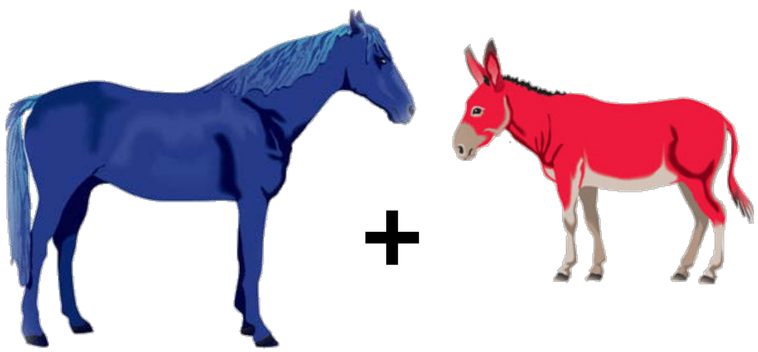
???

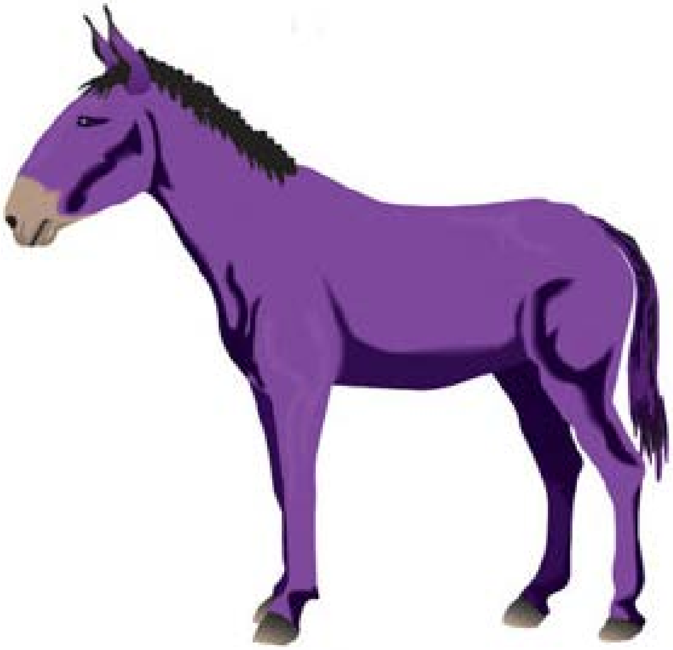
original articulation:
Sienko, M. J. and Plane, R. A.
Chemistry Toronto: McGraw-Hill,
1964 p.94

*but an average of resonance forms (**purple mule**) (delocalized ozone)*


123 pm (10^{-12} m)
143 pm







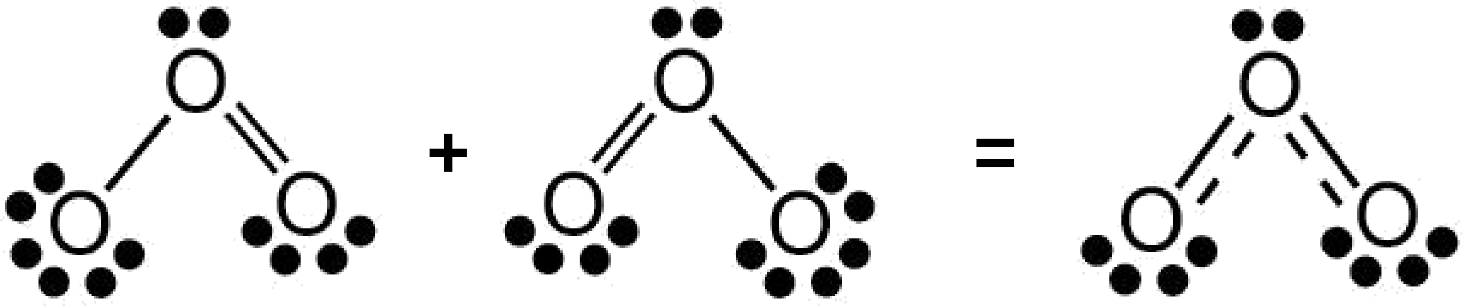
Purple mule

resonance structures and delocalization (13.11 pp 626-627)

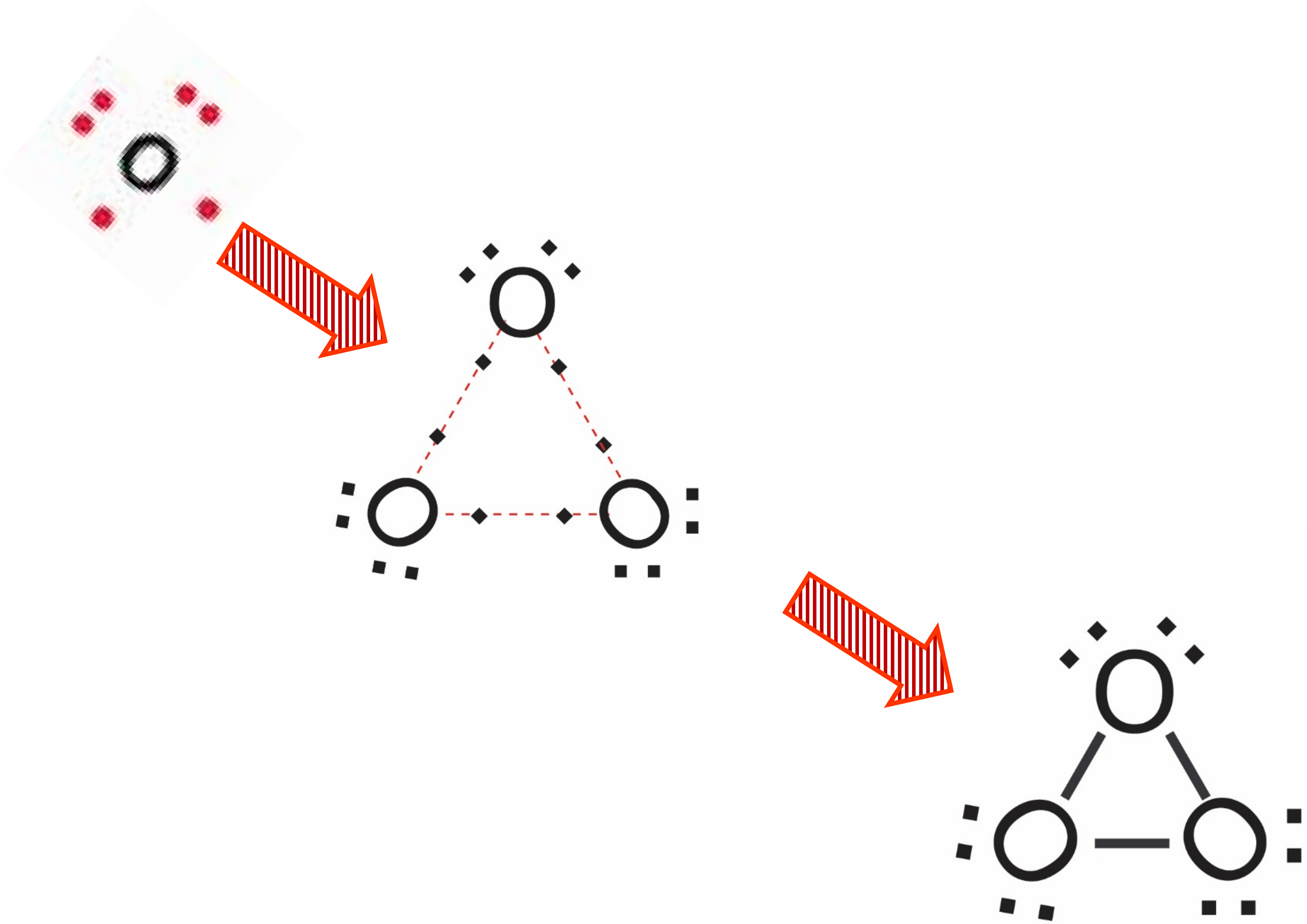
- resonance structures (forms) are more than one possible electronic structure (not isomers)

  e.g. O_3 (ozone)

- actual structure is average (hybrid) of possible resonance structures

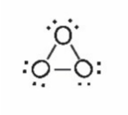


(now is later !!) O_3 ring structure



???

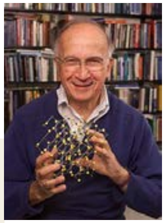
octet, 18 valence e’s



triangular cyclic O_3

The Story of O
Roald Hoffmann
The Ring

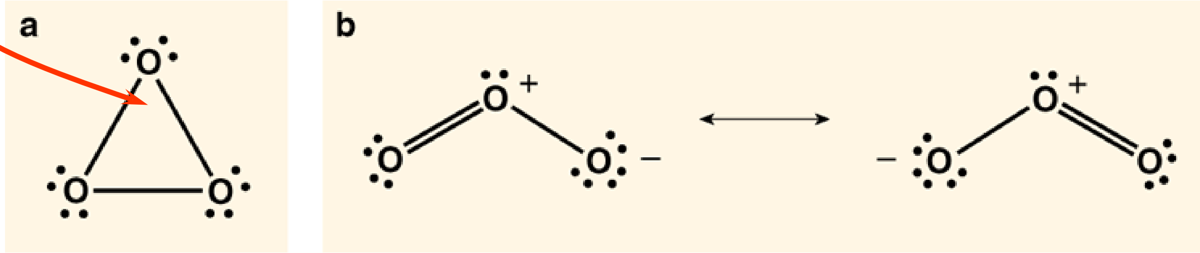
AMERICAN
Scientist
Covering science
for a century



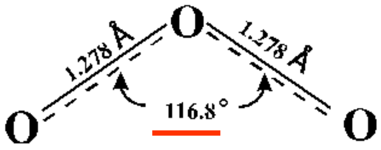
So now we have oxygen chemistry in the atmosphere, in the cell,
in a decontamination process. But have we exhausted all of oxygen's secrets?
http://www.americanscientist.org/issues/pub/the-story-of-o/5 This Article from Issue January-February 2004

60° bond angles are "strained" (unstable);

[discuss later in term (quantum mechanics)]


a
O
O
O
b
O
O
O
+
−
O
O
O
+
−

□


O
O
O
1.278 Å
1.278 Å
116.8°

Indeed, the best calculations today confirm the metastability of this ring. Cyclic ozone lies about **130 kilojoules per mole above normal O_3** but has a barrier of no less than 95 kilojoules per mole preventing conversion to the open form.

examples of resonance structures

- $[CO_3]^{2-}$ ➡
- C_6H_6 (in class)

formal charge on an atom in a molecule:

Formal charge is a way of associating electrons in a molecule with the various atoms thus allowing one to calculate the (approximate) net charge on the atom.

formal charge on an atom in a molecule:

Conceptual steps:

1. remove each atom’s valence electrons leaving a residual positive ‘core’ charge on the atom;
   e.g. H^+ , N^{+5} O^{+6} , etc

2. the total negative charge assigned to each atom arises from:
   a. electrons in a each covalent bond are divided equally between the atoms forming the bond
   b. electrons in non-bonding pairs are assigned to the atom on which they reside

3. the sum of formal charges must equal the total charge on the atom or ion

formal charge

$$\text{formal charge} = \overbrace{+\ \#\text{ of valence electrons }_{\text{(in neutral atom)}}}^{\textit{positive core charge}}$$

$$\begin{array}{l}\textit{negative charge}\\ \textit{from electrons}\\ \textit{assigned to atom}\end{array}\left\{\begin{array}{l} -\ \#\text{ of nonbonding electrons}\\ \\ -\ \tfrac{1}{2}\ \#\text{ of bonding electrons}\end{array}\right.$$

formal charge vs oxidation number (p 633, ~~p 126~~)

- formal charge = # of valence electrons (in neutral atom)
  – # of nonbonding electrons
  – ½ # of bonding electrons

Chem 1A
nr

- oxidation number = valence electrons
  – nonbonding electrons
  – ‘assigned’ bonding electrons†

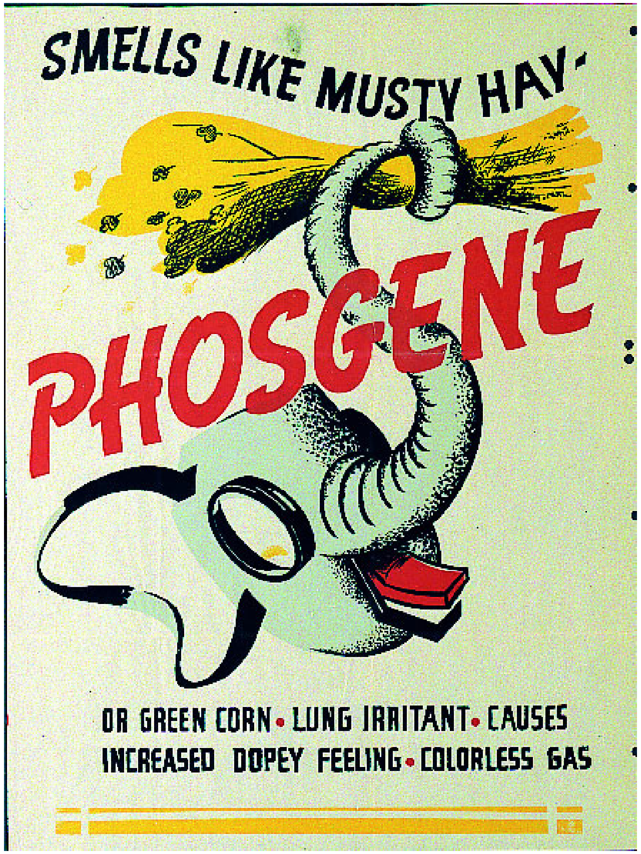
† *bonding electrons ‘assigned’ to more electronegative atom in bond*

formal charge and stability of resonance forms

- for non-equivalent resonance forms, the resonance form is preferable *(makes a greater contribution to the average resonance hybrid)* if it has:
    - *small formal charges*
    - *like charges NOT on adjacent atoms*
    - *negative formal charges reside on more electronegative atoms*

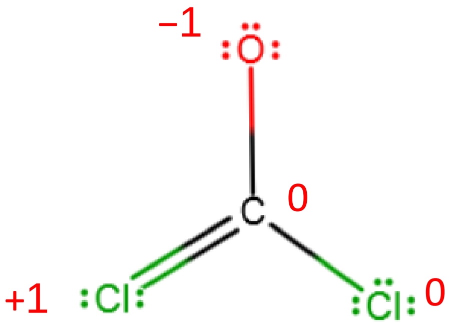
- example：phosgene $COCl_2$

$COCl_2$:phosgene

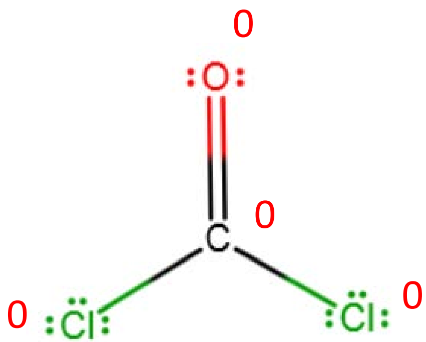

SMELLS LIKE MUSTY HAY-
PHOSGENE
OR GREEN CORN • LUNG IRRITANT • CAUSES
INCREASED DOPEY FEELING • COLORLESS GAS

$COCl_2$: non-equivalent resonance forms

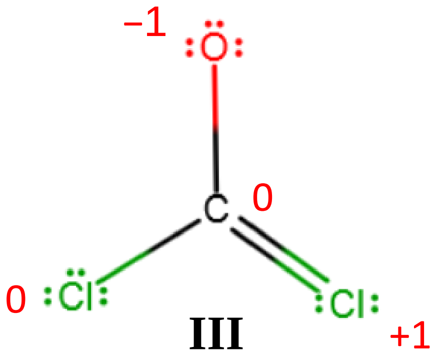
octet structures:


−1
O
C
0
+1
Cl
Cl
0

I


0
O
C
0
0
Cl
Cl
0

II


−1
O
C
0
0
Cl
Cl
+1

III

Formal Charge:

O= +6-6-½ (2)=−1

C= +4-0-½ (8)= 0

Cl= +7-4-½ (4)=**+1**

Cl= +7-6-½ (2)= 0

+1 on Cl unfavorable

O= +6-4-½ (4)= 0

C= +4-0-½ (8)= 0

Cl= +7-6-½ (2)= 0

Cl= +7-6-½ (2)= 0

O= −1

C= 0

Cl= 0

Cl= **+1**

+1 on Cl unfavorable

II structure with greatest contribution
I and III minor contributions

KEEP
CALM
IT'S
ALL
DONE

Zumdahl Table 2.5 and 13.5, Silberberg figure 9.3

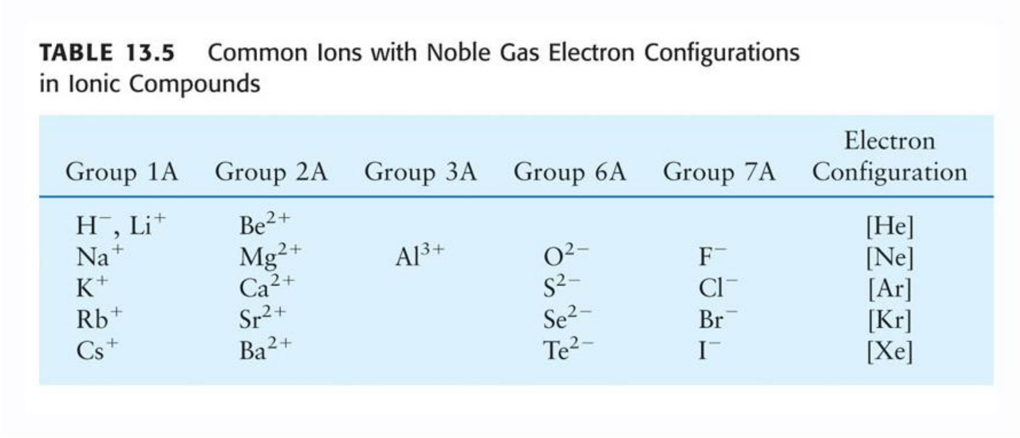
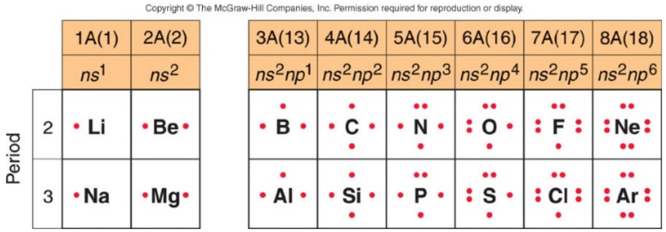


TABLE 13.5 Common Ions with Noble Gas Electron Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]

erved.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1A(1)
2A(2)
3A(13)
4A(14)
5A(15)
6A(16)
7A(17)
8A(18)
ns1
ns2
ns2np1
ns2np2
ns2np3
ns2np4
ns2np5
ns2np6
Period
2
3
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar

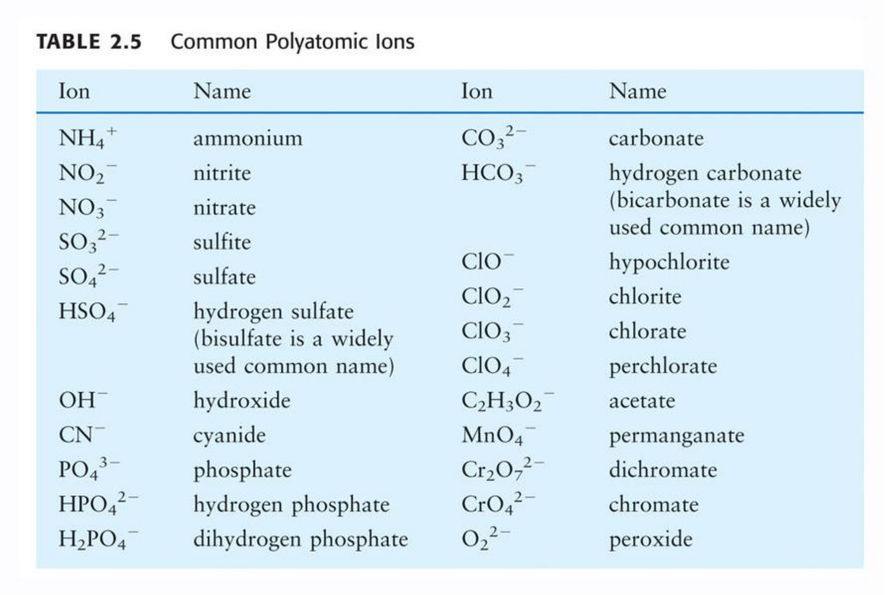

TABLE 2.5 Common Polyatomic Ions

Ion	Name	Ion	Name
NH_4^+	ammonium	CO_3^{2-}	carbonate
NO_2^-	nitrite	HCO_3^-	hydrogen carbonate (bicarbonate is a widely used common name)
NO_3^-	nitrate		
SO_3^{2-}	sulfite		
SO_4^{2-}	sulfate	ClO^-	hypochlorite
HSO_4^-	hydrogen sulfate (bisulfate is a widely used common name)	ClO_2^-	chlorite
		ClO_3^-	chlorate
		ClO_4^-	perchlorate
OH^-	hydroxide	$C_2H_3O_2^-$	acetate
CN^-	cyanide	MnO_4^-	permanganate
PO_4^{3-}	phosphate	$Cr_2O_7^{2-}$	dichromate
HPO_4^{2-}	hydrogen phosphate	CrO_4^{2-}	chromate
$H_2PO_4^-$	dihydrogen phosphate	O_2^{2-}	peroxide

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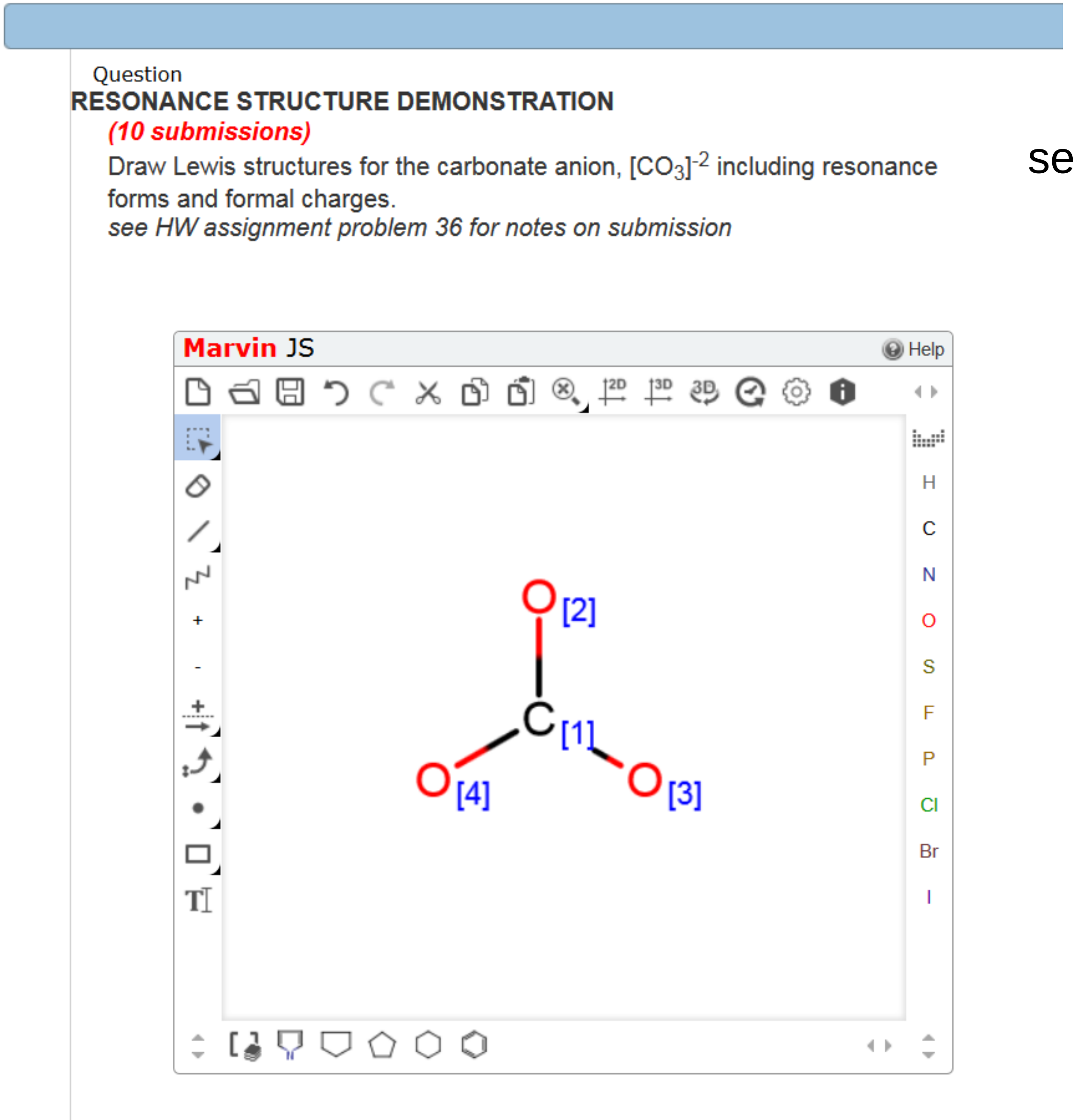
KNOW:

NH_4^+, NO_3^-, SO_4^{2-}, HSO_4^-,
CN^- , OH^-, PO_4^{3-}, CO_3^{2-},
HCO_3^-, $C_2H_3O_2^-$, MnO_4^-

Marvin JS Resonance Structure (HW#5 37, 44)



Question

RESONANCE STRUCTURE DEMONSTRATION

(10 submissions)

Draw Lewis structures for the carbonate anion, $[CO_3]^{-2}$ including resonance forms and formal charges.

see HW assignment problem 36 for notes on submission

Marvin JS
Help
H
C
N
O
S
F
P
Cl
Br
I
O [2]
C [1]
O [4]
O [3]

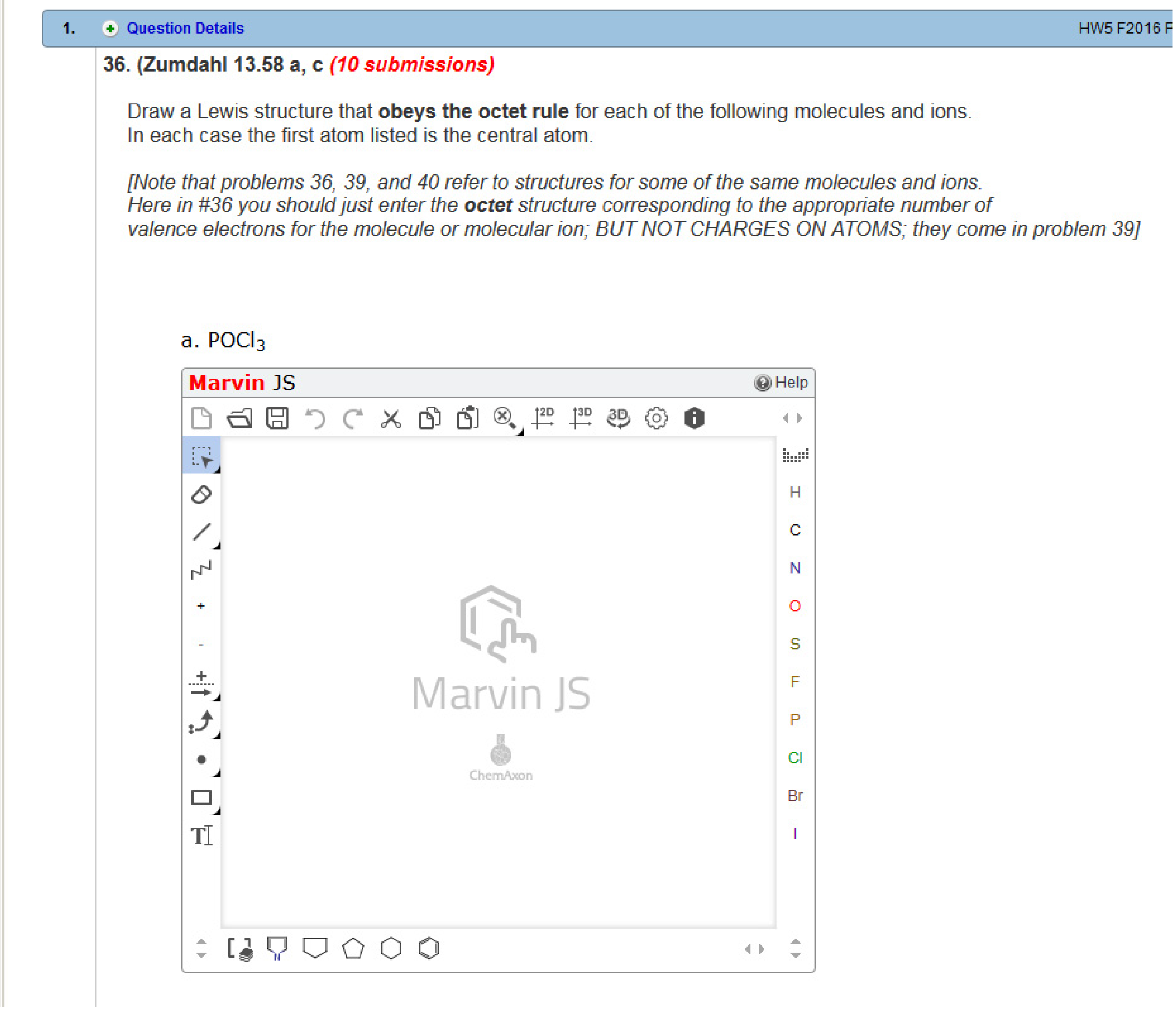
see additional video06a

Exceptions (13.12 pp 627-636)

EXPLAINED BY QUANTUM MECHANICS

- electron deficient atoms: Be, B
    - examples BeH_2 and BF_3
    - quantum mechanics explains
- Free radicals
    - odd number of electrons
    - example CH_3
    - quantum mechanics explains
- 10, 12, 14, 16 electron shells for larger atoms with low-lying d-orbitals
    - structures with ‘expanded’ shells often have preferable formal charges
    - examples PCl_5, H_2SO_4, $[SO_4]^{2-}$, XeO_4

HW5 (some of same molecules/ions in each)
*36 **OCTET** (no charges), 39 **OCTET CHARGES**, 40 non-OCTET charges*



1. Question Details HW5 F2016 F

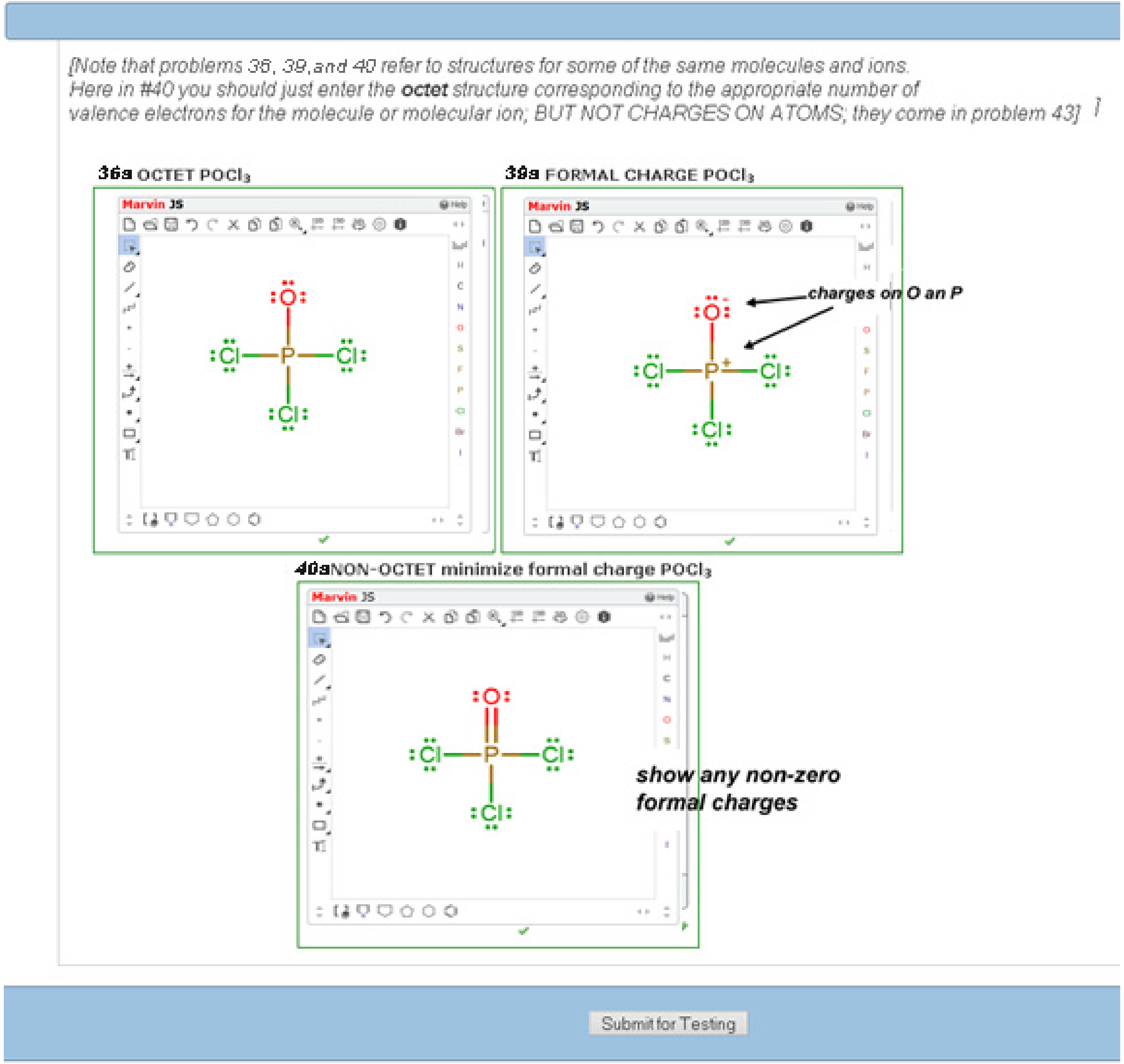
36. (Zumdahl 13.58 a, c *(10 submissions)*

Draw a Lewis structure that **obeys the octet rule** for each of the following molecules and ions.
In each case the first atom listed is the central atom.

*[Note that problems 36, 39, and 40 refer to structures for some of the same molecules and ions.
Here in #36 you should just enter the **octet** structure corresponding to the appropriate number of
valence electrons for the molecule or molecular ion; BUT NOT CHARGES ON ATOMS; they come in problem 39]*

a. $POCl_3$

HW#5 probs 36, 39, 40



[Note that problems 36, 39, and 40 refer to structures for some of the same molecules and ions.
Here in #40 you should just enter the **octet** structure corresponding to the appropriate number of
valence electrons for the molecule or molecular ion; BUT NOT CHARGES ON ATOMS; they come in problem 43]

36a OCTET $POCl_3$

39a FORMAL CHARGE $POCl_3$

charges on O an P

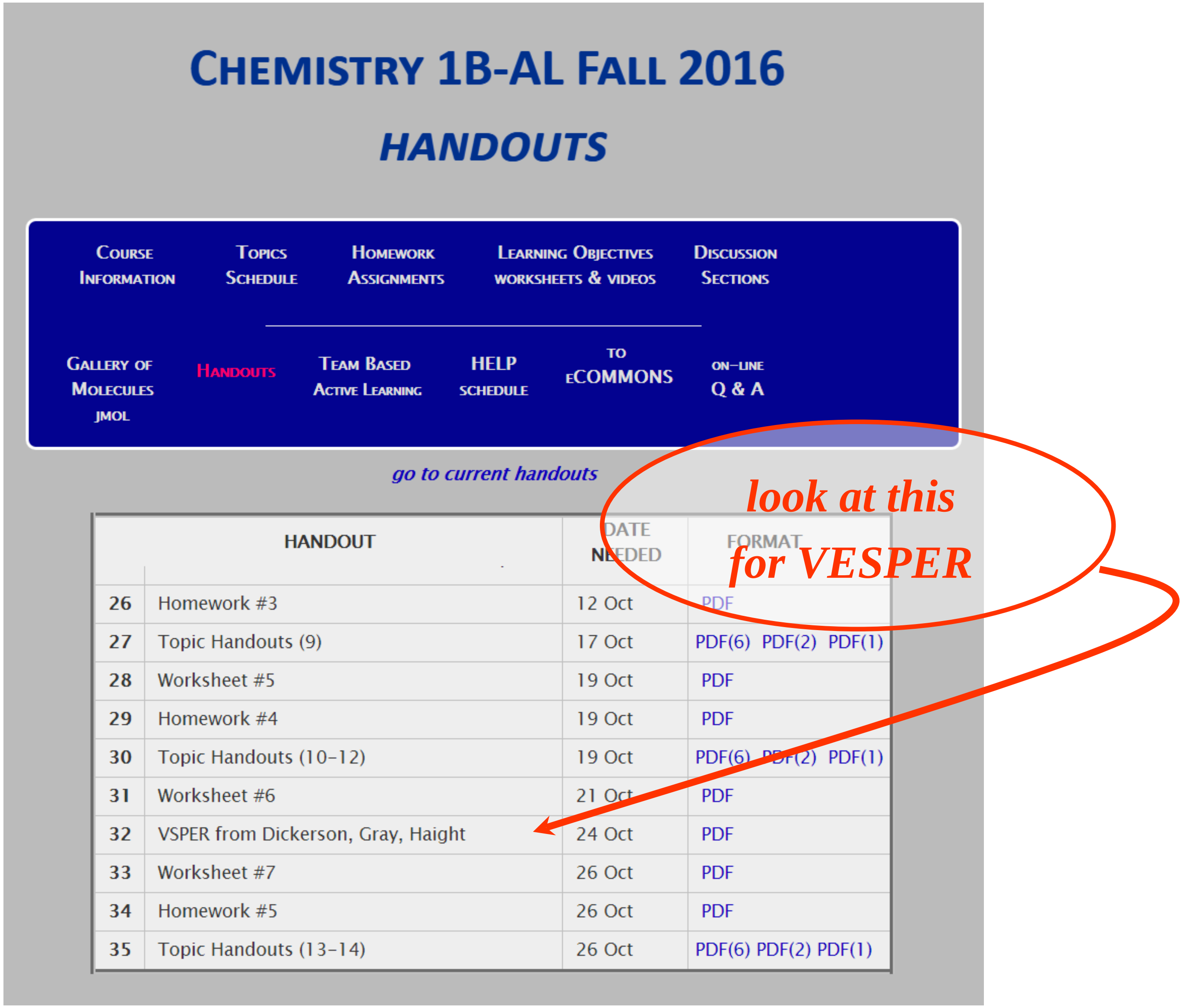
40a NON-OCTET minimize formal charge $POCl_3$

show any non-zero formal charges

Marvin JS
O
P
Cl
Cl
Cl
Marvin JS
O
P+
Cl
Cl
Cl
Marvin JS
O
P
Cl
Cl
Cl
Submit for Testing

Heads up!

heads up: very useful handout



CHEMISTRY 1B-AL FALL 2016

HANDOUTS

COURSE INFORMATION
TOPICS SCHEDULE
HOMEWORK ASSIGNMENTS
LEARNING OBJECTIVES WORKSHEETS & VIDEOS
DISCUSSION SECTIONS
GALLERY OF MOLECULES JMOL
HANDOUTS
TEAM BASED ACTIVE LEARNING
HELP SCHEDULE
TO ECOMMONS
ON-LINE Q & A
go to current handouts

	HANDOUT	DATE NEEDED	FORMAT
26	Homework #3	12 Oct	PDF
27	Topic Handouts (9)	17 Oct	PDF(6) PDF(2) PDF(1)
28	Worksheet #5	19 Oct	PDF
29	Homework #4	19 Oct	PDF
30	Topic Handouts (10–12)	19 Oct	PDF(6) PDF(2) PDF(1)
31	Worksheet #6	21 Oct	PDF
32	VSPER from Dickerson, Gray, Haight	24 Oct	PDF
33	Worksheet #7	26 Oct	PDF
34	Homework #5	26 Oct	PDF
35	Topic Handouts (13–14)	26 Oct	PDF(6) PDF(2) PDF(1)

look at this for VESPER

back to section 13.8 “bond energies” (616-619)

- the properties (e.g. bond length and bond energy) of localized bonds of a given type are ‘somewhat’ transferable from molecule to molecule

- one can approximately calculate the relative ‘energy’ (enthalpy) of a substance by adding the bond energies of its constituent bonds

- since bond energies vary somewhat from compound to compound, we tabulate average bond energies

ARE responsible for: *bond lengths and bond energies (qualitative)*

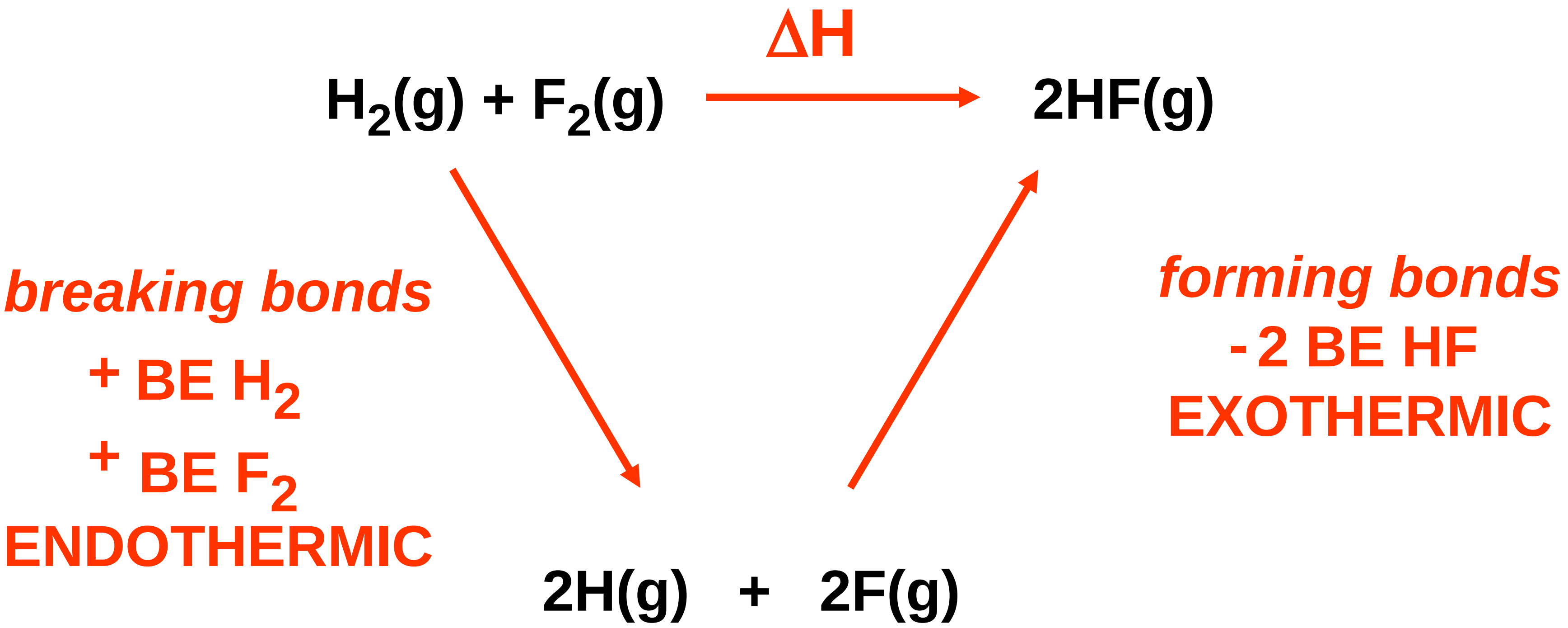
- For a given type of covalent bonding (single, double, triple) atomic covalent radius determines bondlength (figure Silberberg 9.13)

- For a given type of atoms the bondlength will be
  (single) > (double) > (triple) (Table 13.7)

- Bond energies (strengths) will follow the trend (triple) > (double) > (single) (Table 13.7)

- Bond order single b.o.=1, double b.o.=2, triple b.o. =3 (more in chapter 14)

NOT responsible for: *calculating $\Delta H_{REACTION}$ from bond energies (sec 13.8 chem 1C)*



ΔH

$H_2(g) + F_2(g) \longrightarrow 2HF(g)$

breaking bonds

$+$ BE H_2

$+$ BE F_2

ENDOTHERMIC

forming bonds

- 2 BE HF

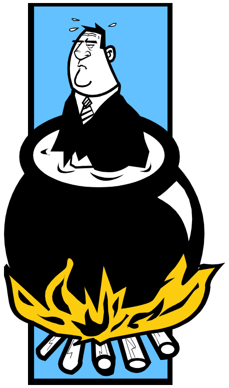
EXOTHERMIC

$2H(g) + 2F(g)$

$$\Delta H_{reaction} = BE\ (H_2) + BE(F_2) - 2BE(HF)$$

$$\Delta H_{reaction} = +\Sigma\ BE\ (\text{bonds broken}) - \Sigma\ BE\ (\text{bonds formed})$$

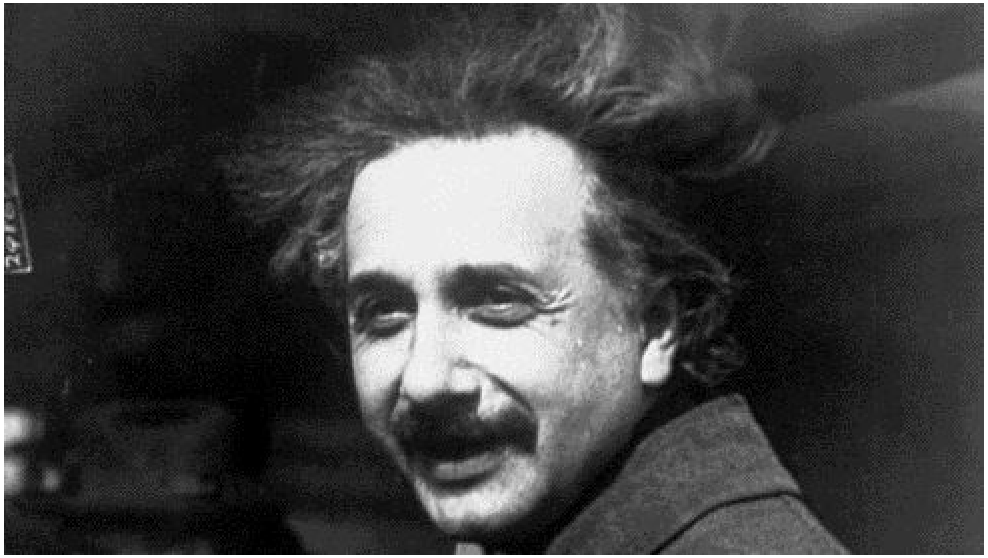
TIME TO GET GOING: MIDTERM#2, Nov 9th



or

else

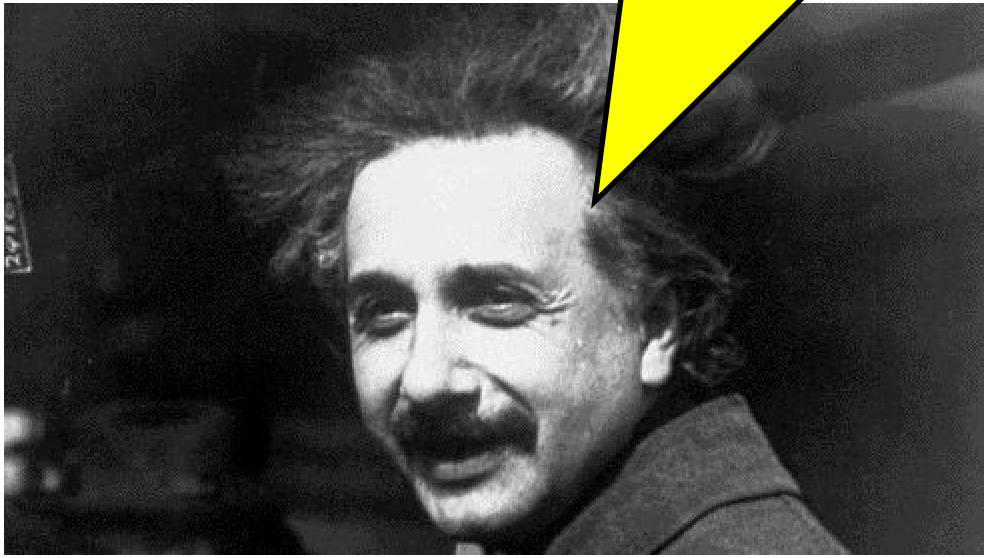
Study HINT



albert,
tell me,
how is it that you do so
well on your CHEM 1B-02
homework?

Marie Curie

my dear marie,
my secret is that I go to
Ana’s sections
and Joselyn’s LSS tutorials
and use staff OFFICE HOURS.



Albert Einstein

Valence **S**tate **E**lectron-**P**air **R**epulsion (VSPER)

“classical” (electrostatic) theory of molecular geometry

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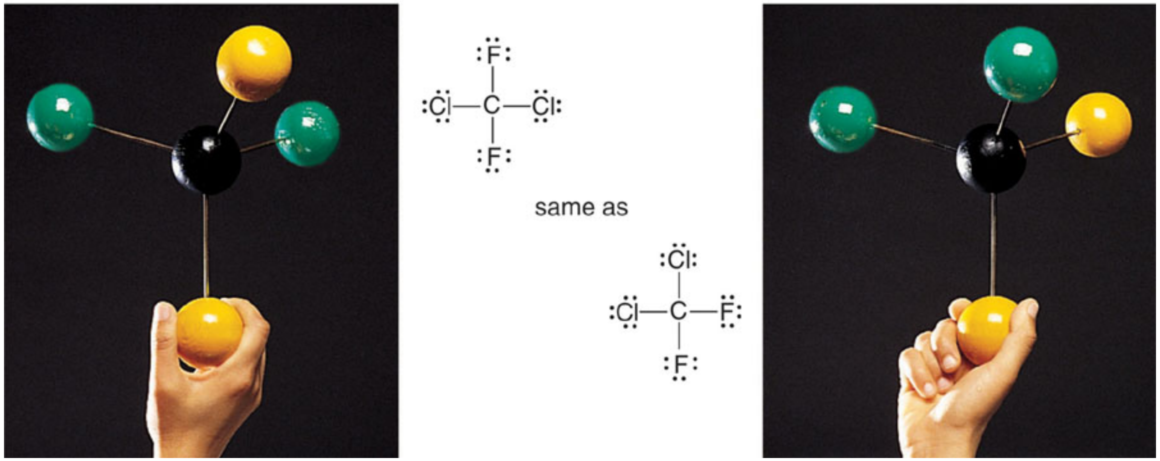
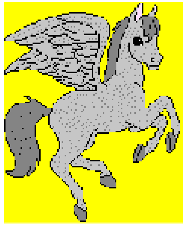
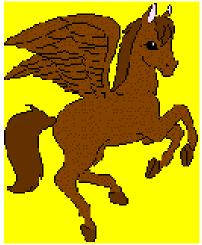


translation of book review of J.H. van't Hoff's 1874 *Sur les formules de structure dans l'espace*

by Kolbe in 1877



"Not long ago I expressed the view that the lack of general education and of thorough training in chemistry of quite a few professors of chemistry was one of the causes of the deterioration of chemical research in Germany. . . Will anyone to whom my worries may seem exaggerated please read, if he can, a recent memoir by Herr van't Hoff on *The Arrangement of Atoms in Space,* a document crammed to the hilt with outpourings of childish fantasy. This Dr. J.H. van't Hoff, employed by the Veterinary College at Utrecht, has, so it seems, not taste for accurate chemical research. He finds it more convenient to mount his Pegasus (evidently taken from the stables of the Veterinary College) and to announce how, on his daring flight to Mount Parnassus, he saw atoms arranged in space."



a knowledge of molecular geometry is essential in biological chemistry

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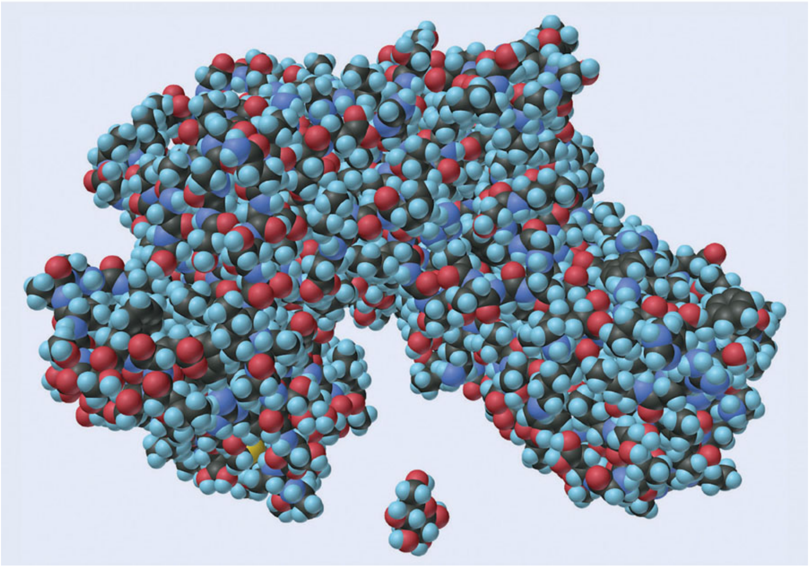
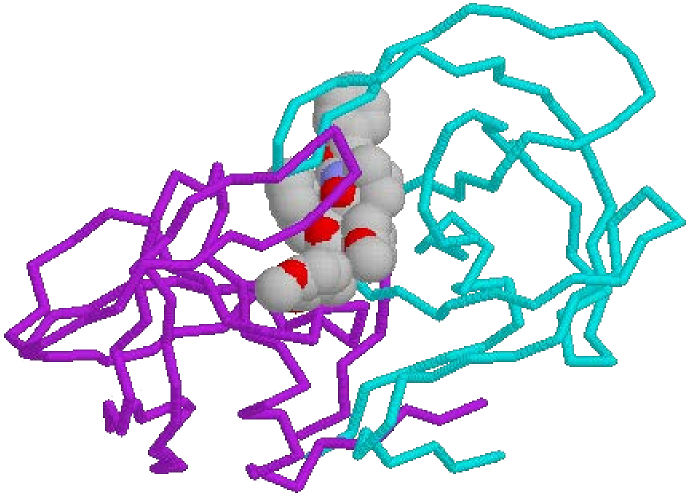
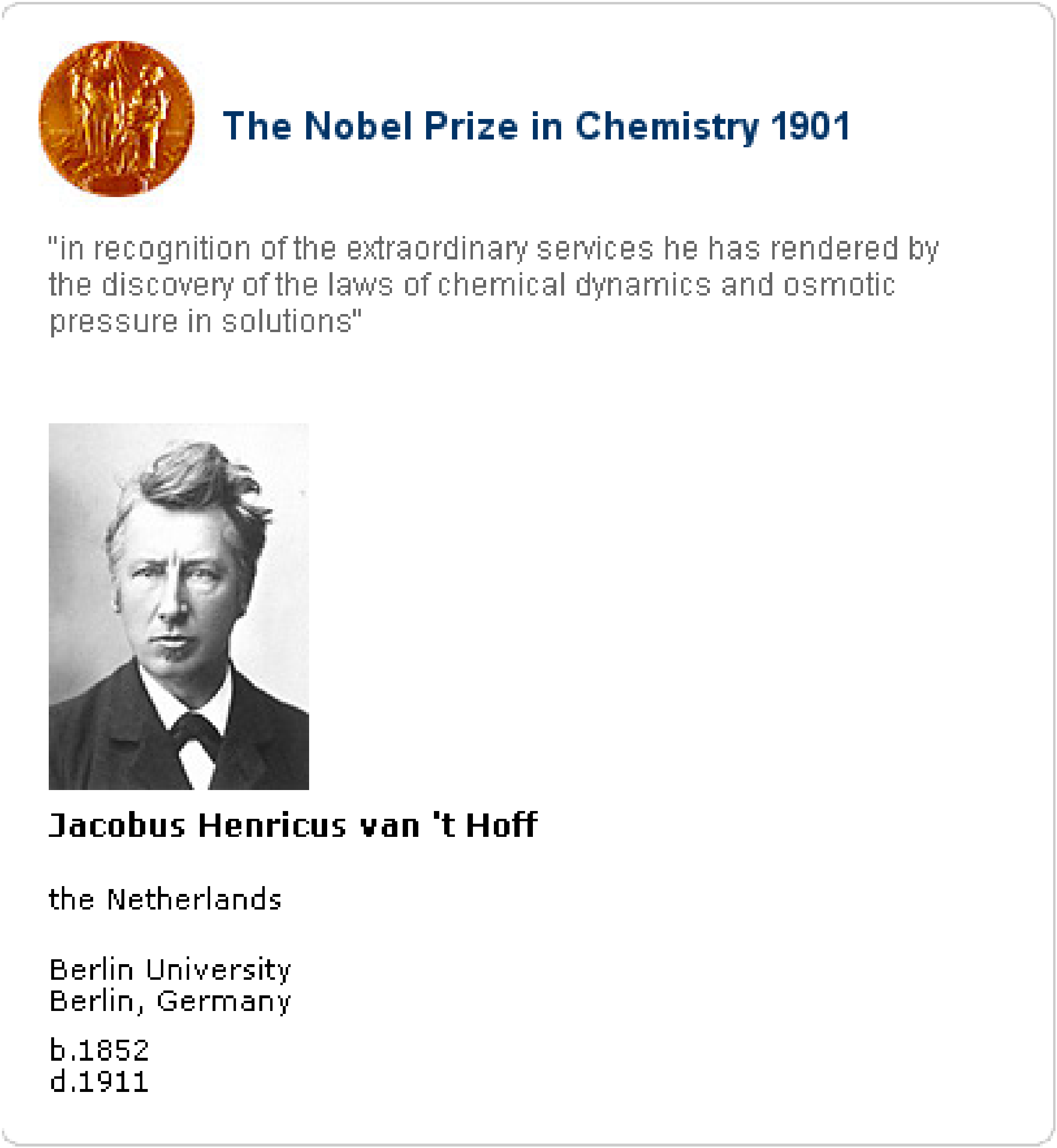




enzyme + sugar

HIV-protease complex

van’ Hoff had the last laugh



The Nobel Prize in Chemistry 1901

"in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions"

Jacobus Henricus van 't Hoff

the Netherlands

Berlin University
Berlin, Germany

b.1852
d.1911

Basic premises of VSEPR

- ELECTRON GROUPS (non-bonding electron-pairs and covalent electron-pairs) are electron dense regions in a molecule
- these ELECTRON GROUPS will arrange themselves in space around a central atom to minimize their mutual electrostatic repulsion
- this minimum repulsion configuration determines the ELECTRONIC GEOMETRY
- the arrangement of the covalent pair regions determines MOLECULAR GEOMETRY

electron groups

- An electron group (electron dense region) can be:
  - lone pair
  - single bond
  - multiple bond (counts as only as 1 electron group)

- The number of electron groups around the central atom is the steric number (SN)

examples of steric number (SN)

- CH_4 SN=4
- NH_3 SN=4
- BeH_2 SN=2
- C_2H_4 SN=3
- C_2H_2 SN=2

the minimum repulsion "electronic" geometries are (table 13.8)

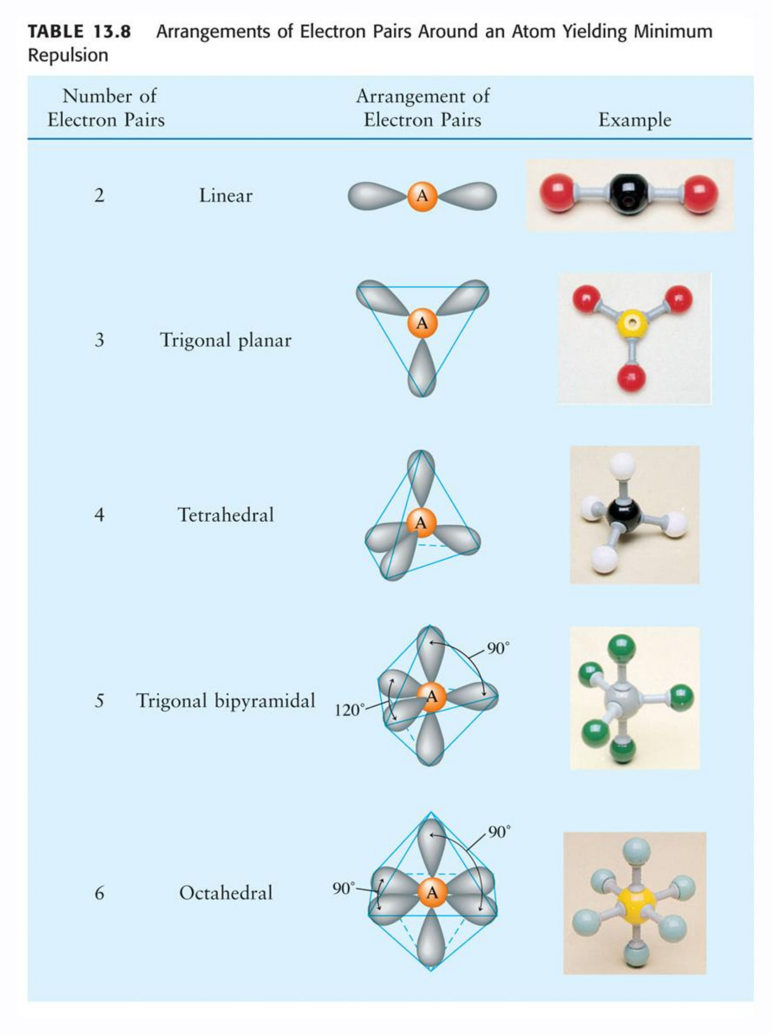


TABLE 13.8 Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

Number of Electron Pairs		Arrangement of Electron Pairs	Example
2	Linear		
3	Trigonal planar		
4	Tetrahedral		
5	Trigonal bipyramidal		
6	Octahedral		

A
90°
120°
90°
90°

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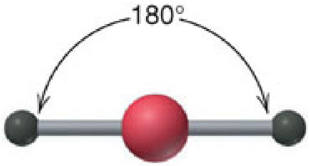
WWW Links Ch. 13
VSEPR

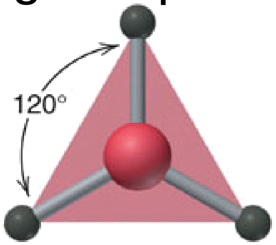
the minimum repulsion “electronic” geometries are (fig. 10.2, Silb)

SN=2
linear



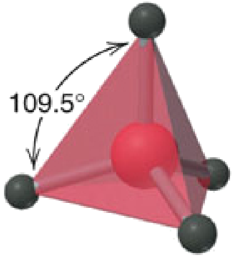
Linear

SN=3
trigonal planar



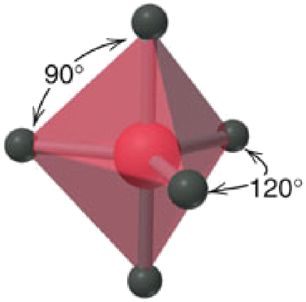
Trigonal planar

SN=4
tetrahedral



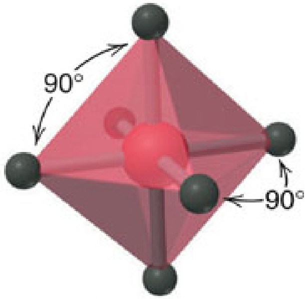
Tetrahedral

SN=5
trigonal bipyramidal



Trigonal bipyramidal

SN=6
octahedral

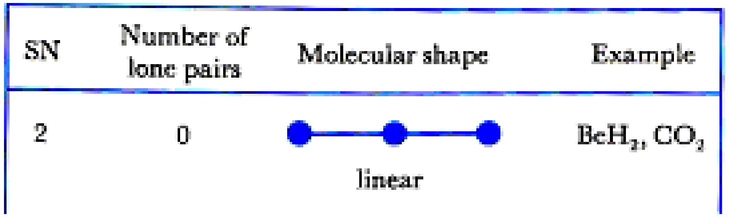


Octahedral

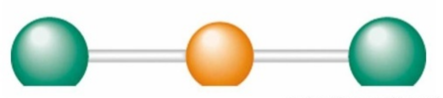
SN≡ number of electron groups

SN=2: linear electronic geometry, linear molecular geometry

[from Handout #17]



SN	Number of lone pairs	Molecular shape	Example
2	0	linear	BeH_2, CO_2



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Cl-------Be-------Cl

$BeCl_2$ (p. 628)

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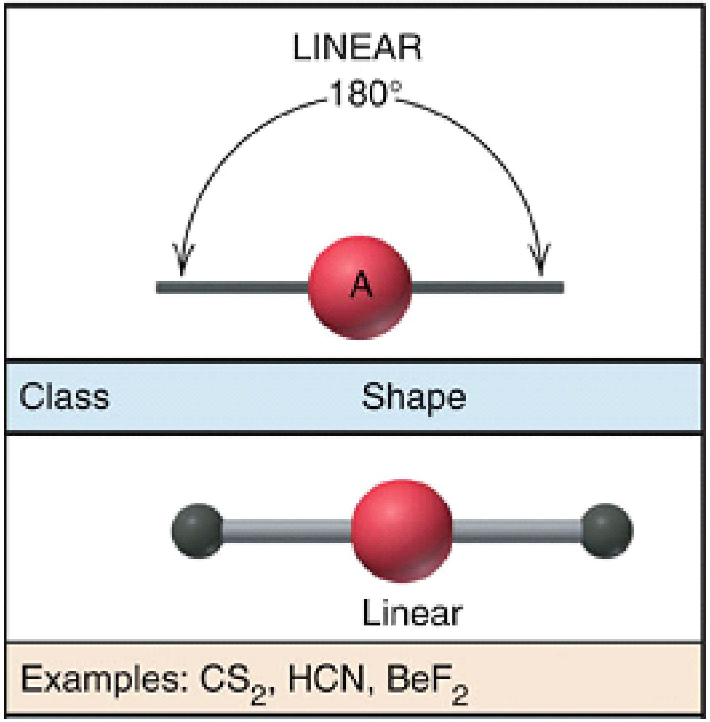

LINEAR
180°
A
Class
Shape
Linear
Examples: CS_2, HCN, BeF_2

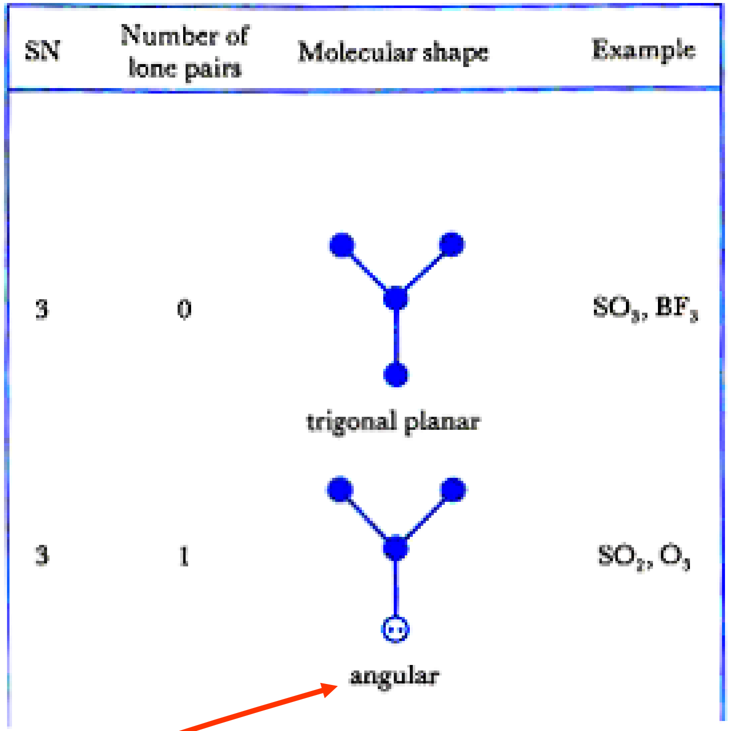
fig Silb 10.3

$BeCl_2$ ⇨

SN=3, electronic geometry is trigonal planar

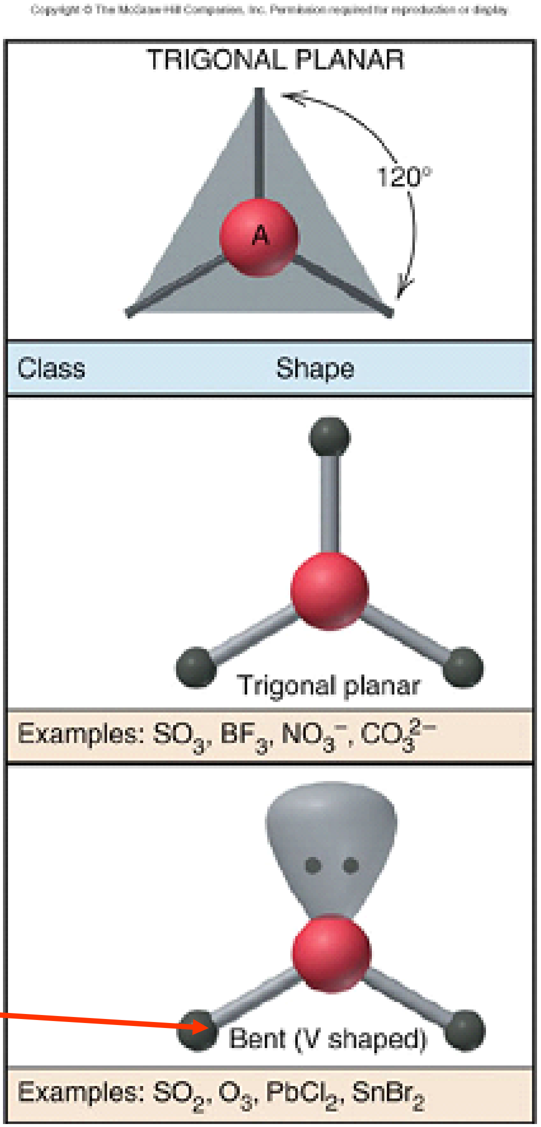
examples: BF_3 SO_2

[from Handout #17]



SN	Number of lone pairs	Molecular shape	Example
3	0	trigonal planar	SO_3, BF_3
3	1	angular	SO_2, O_3

angular=bent=V-shape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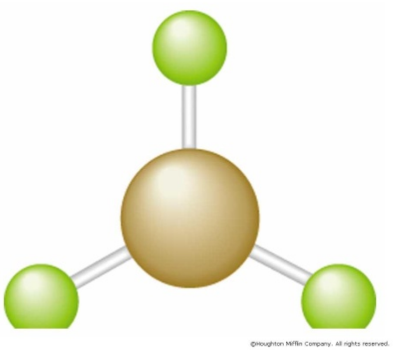
TRIGONAL PLANAR
A
120°
Class
Shape
Trigonal planar
Examples: SO_3, BF_3, NO_3^-, CO_3^{2-}
Bent (V shaped)
Examples: SO_2, O_3, $PbCl_2$, $SnBr_2$

BF_3 ⇒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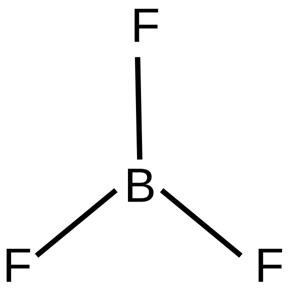
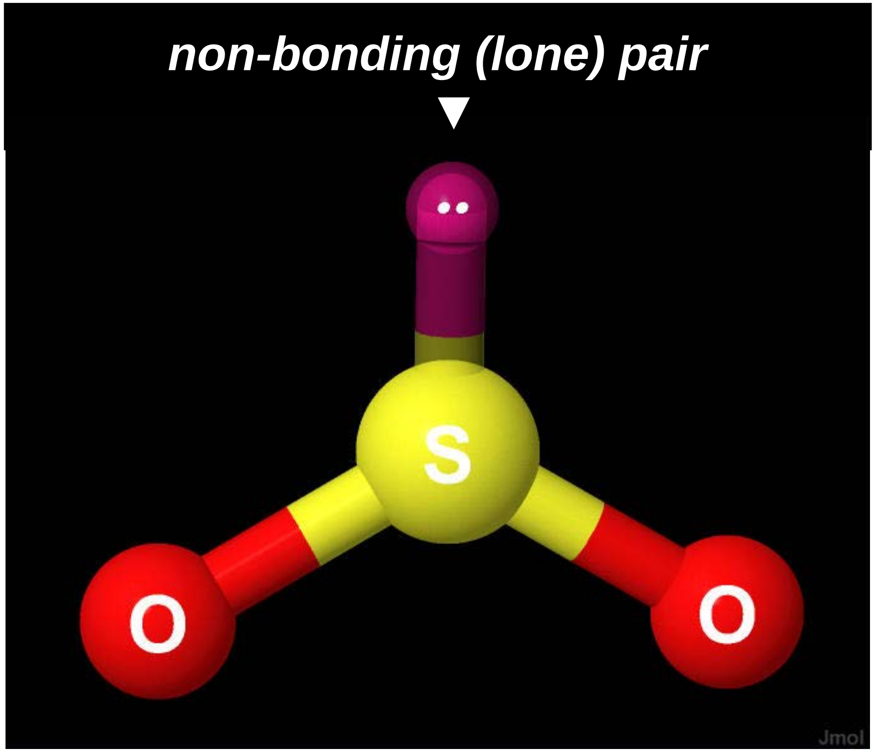
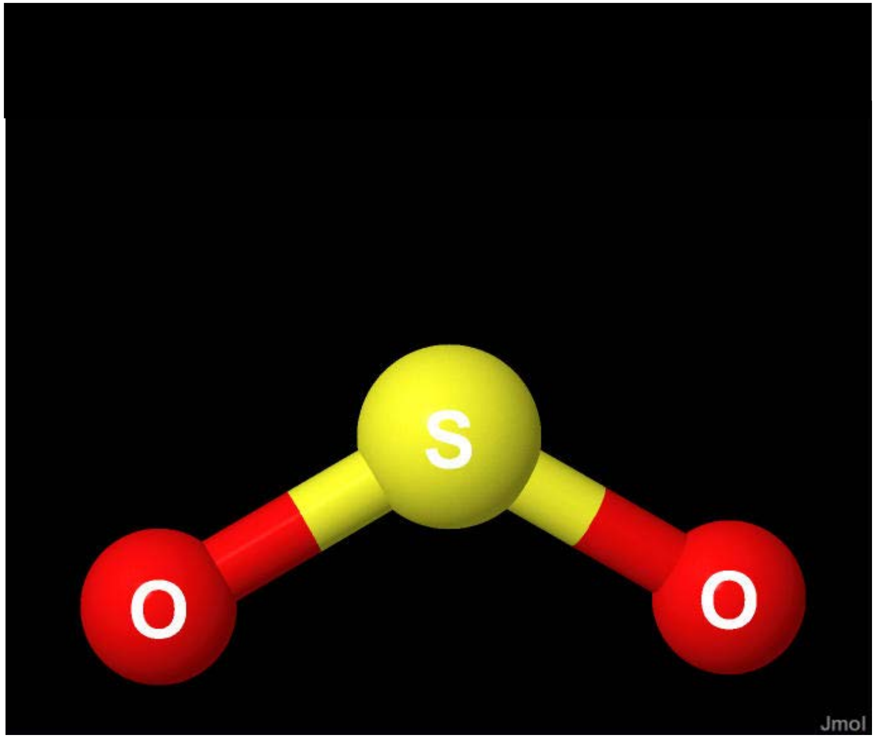


Zumdahl
p. 637

SN=3, 1 LP


non-bonding (lone) pair
S
O
O
Jmol



SO_2 ⇨

electronic geometry
trigonal planar

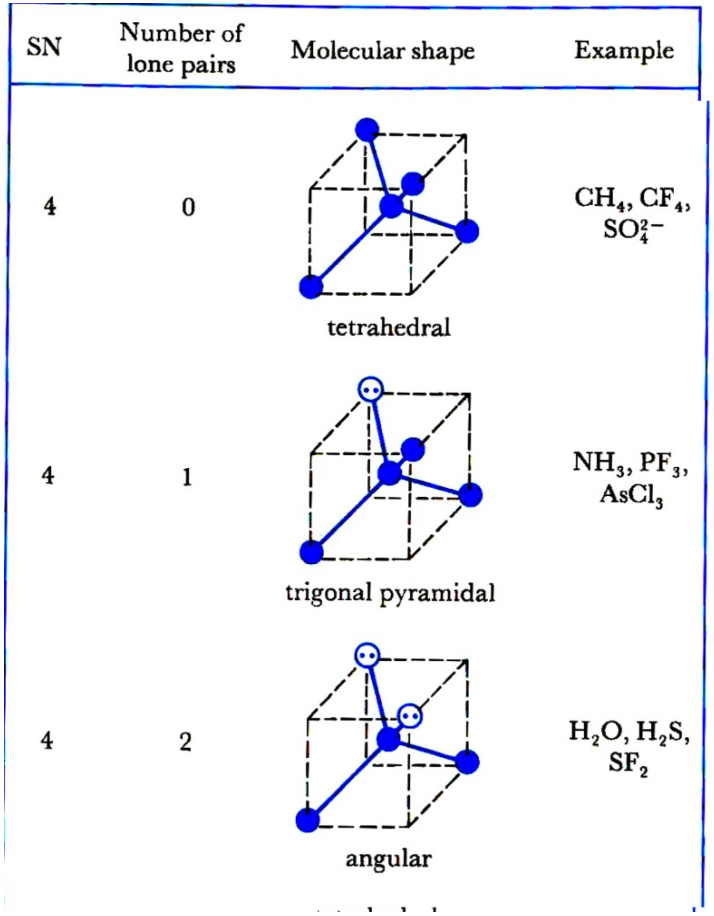
SO_2 ⇨

(molecular) geometry
bent, angular, V-shaped

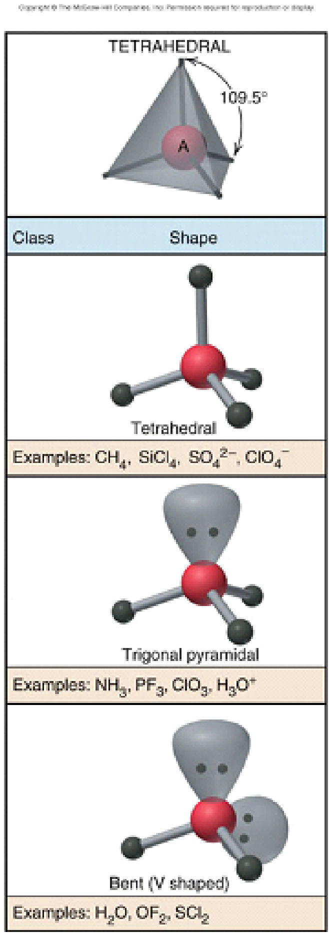
SN=4, electronic geometry is tetrahedral

examples $[SO_4]^{2-}$ NH_3 H_2O

CF_4 ⇨



SN	Number of lone pairs	Molecular shape	Example
4	0	tetrahedral	CH_4, CF_4, SO_4^{2-}
4	1	trigonal pyramidal	NH_3, PF_3, $AsCl_3$
4	2	angular	H_2O, H_2S, SF_2



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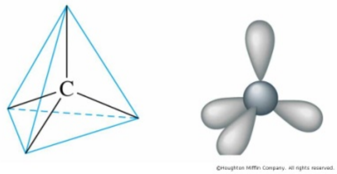
TETRAHEDRAL

Class	Shape
Tetrahedral	
Examples: CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-	
Trigonal pyramidal	
Examples: NH_3, PF_3, ClO_3, H_3O^+	
Bent (V shaped)	
Examples: H_2O, OF_2, SCl_2	



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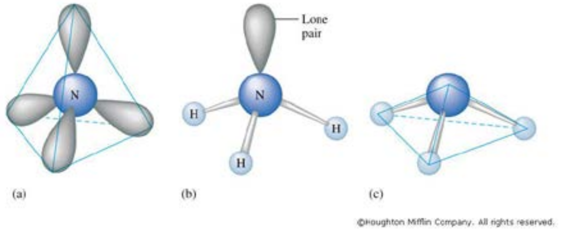

N
(a)
Lone pair
N
H
H
H
(b)
(c)

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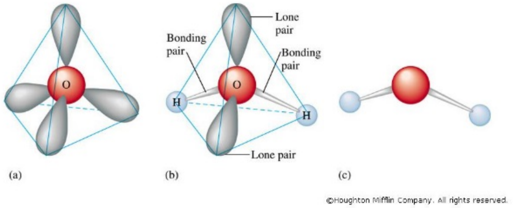

O
(a)
Bonding pair
Lone pair
Bonding pair
O
H
H
Lone pair
(b)
(c)

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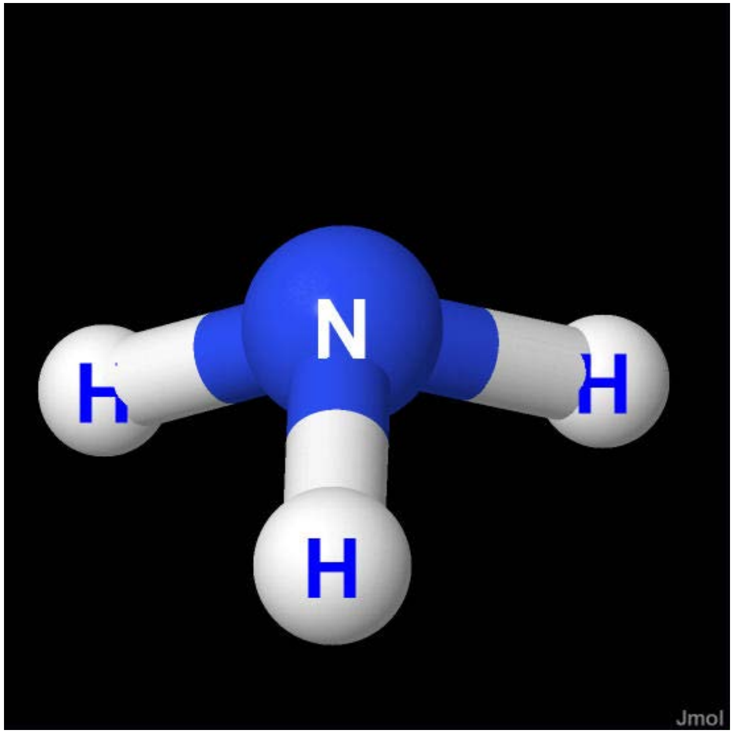
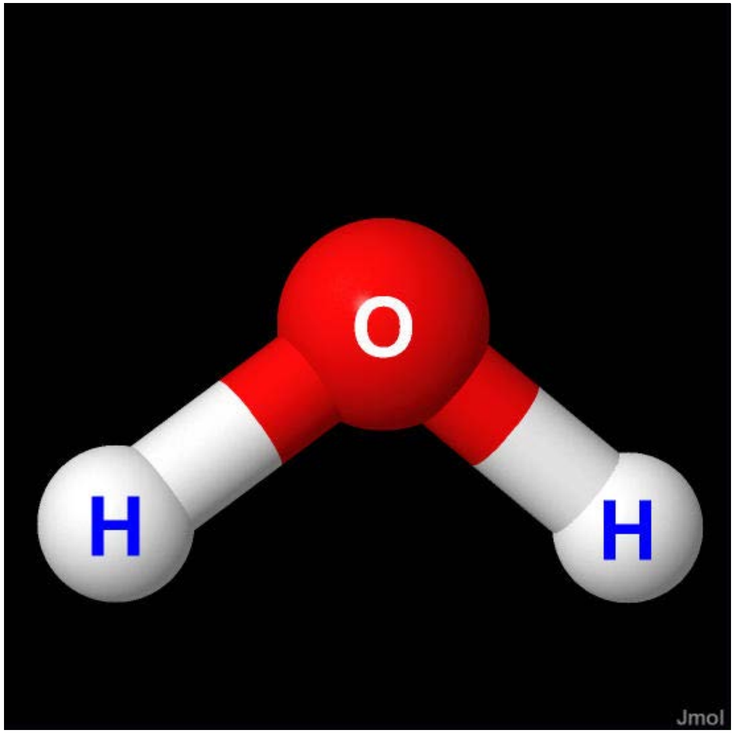
[from Handout #17]

SN=4, tetrahedral electronic geometry





NH_3 ⇨

1 LP

(molecular) geometry

trigonal pyramidal

H_2O ⇨

2 LP

(molecular) geometry

angular, bent, V-shaped

effects of extra lone-pair repulsion

- NH_3 (H–N–H 107.3°) < 109.5°
- H_2O (H–O–H 104.5°) < 109.5°
- H_2S (H –S –H 92°)

  understand using qm ch 14

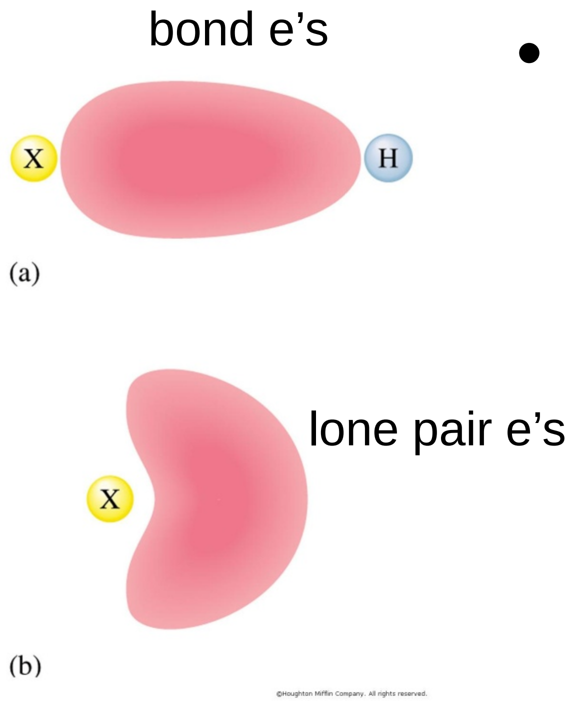

bond e's
X
H
(a)
X
lone pair e's
(b)
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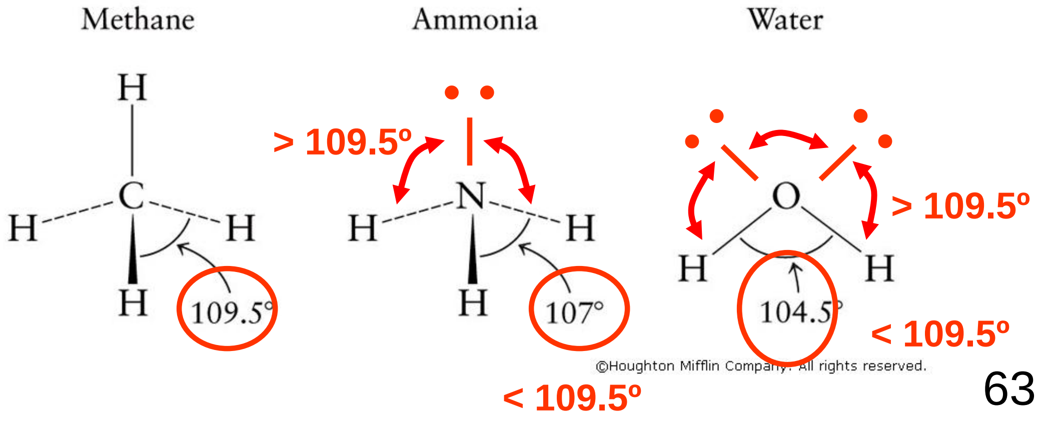
figure 13.19


Methane
H
C
H
H
H
109.5°
Ammonia
> 109.5º
N
H
H
H
107°
< 109.5º
Water
O
> 109.5º
H
H
104.5°
< 109.5º
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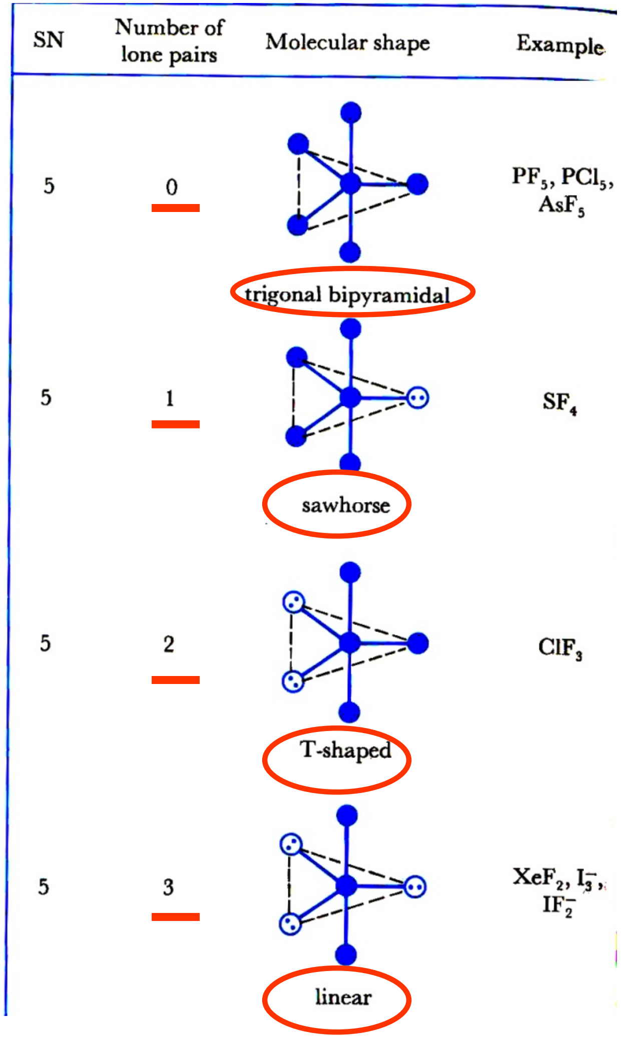
SN=5, electronic geometry is trigonal bipyramidal

[from Handout #17]



SN	Number of lone pairs	Molecular shape	Example
5	0	trigonal bipyramidal	PF_5, PCl_5, AsF_5
5	1	sawhorse	SF_4
5	2	T-shaped	ClF_3
5	3	linear	XeF_2, I_3^-, IF_2^-

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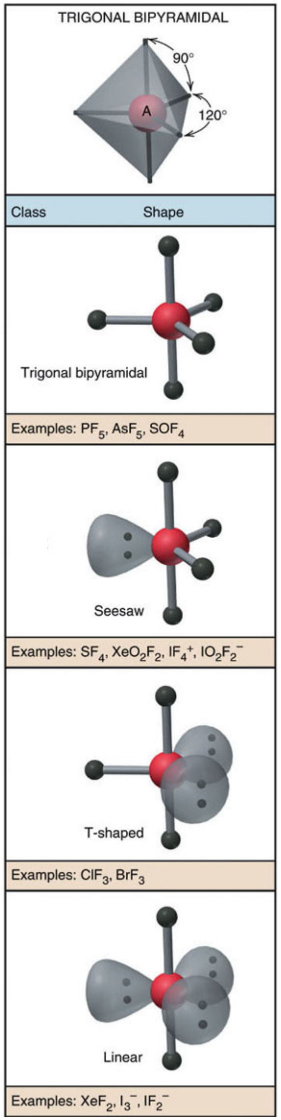


Class	Shape
Trigonal bipyramidal Examples: PF_5, AsF_5, SOF_4	
Seesaw Examples: SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$	
T-shaped Examples: ClF_3, BrF_3	
Linear Examples: XeF_2, I_3^-, IF_2^-	

PF_5 ⇒

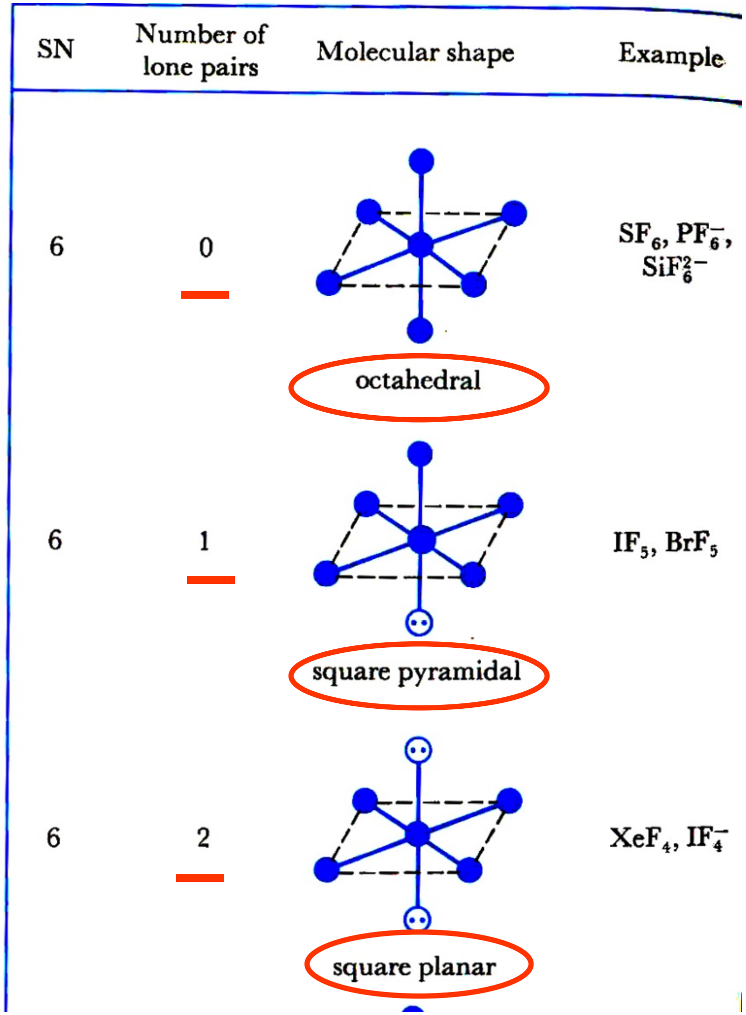
SF_4 ⇒

⇒ **ClF_3** ⇒

⇒ **XeF_2** ⇒

SN=6, octahedral electronic geometry

[from Handout #17]



SN	Number of lone pairs	Molecular shape	Example
6	0	octahedral	SF_6, PF_6^-, SiF_6^{2-}
6	1	square pyramidal	IF_5, BrF_5
6	2	square planar	XeF_4, IF_4^-

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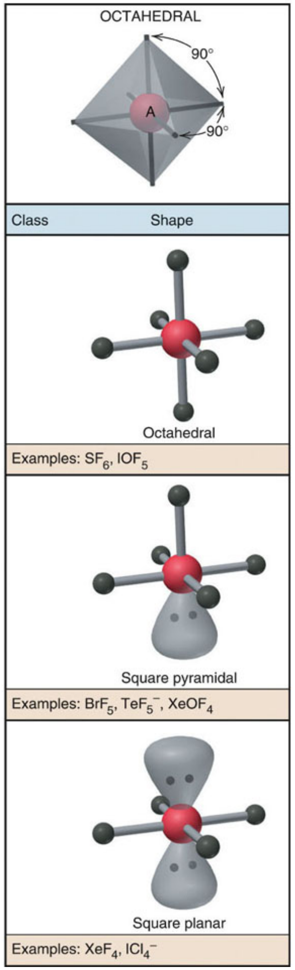


Class	Shape
	Octahedral
Examples: SF_6, IOF_5	
	Square pyramidal
Examples: BrF_5, TeF_5^-, $XeOF_4$	
	Square planar
Examples: XeF_4, ICl_4^-	

SF_6 ⇨

BrF_5 ⇨

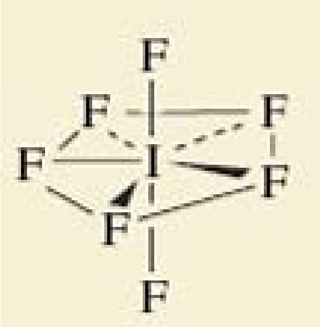
⇨ **XeF_4** ⇨

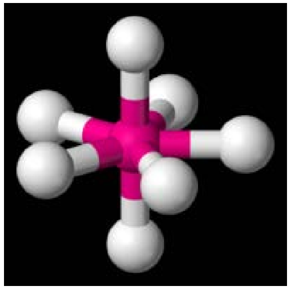
IF_7, XeF_6 SN=7 ????

DON'T FRET

Coordination Chemistry Reviews 252 (2008) 1315–1327

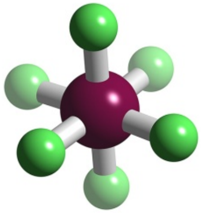
IF_7





pentagonal bipyramid

The other type of molecule in which a lone-pair appears to have no effect on the geometry is AX6E molecules such as BrF_6^- and $SbCl_6^{3-}$ which are octahedral although their Lewis structures have seven electron pairs in the valence shell of the central atom.



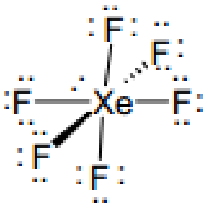
$[BrF_6]^-$

octahedral

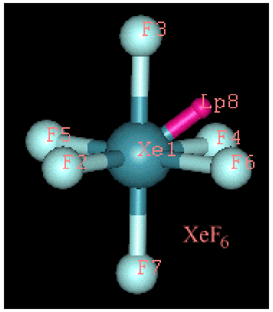
Evidence that this is indeed the case is provided by SeF_6^{2-}, IF_6^-, and XeF_6 where, because the central atom is larger than the Br atom the fluorine ligands are not quite close-packed, allowing room for some of the non-bonding electron density to move into the valence shell to form what has been called a partial or weak lone pair, resulting in a small C_{3v} distortion of the octahedral structure observed for BrF_6^- [23] (Fig. 5).

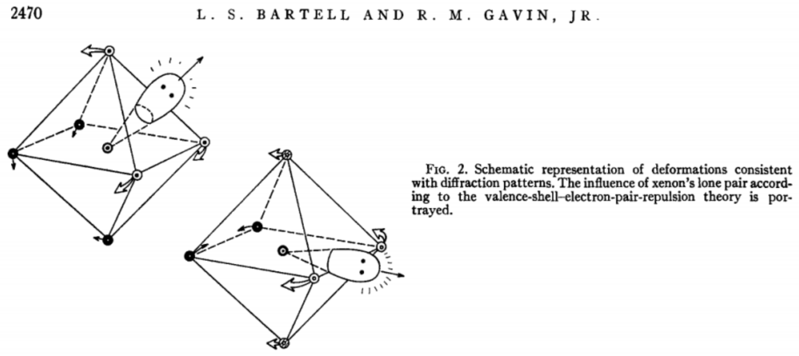
XeF_6

distorted octahedral



distorted octahedral angles <90° because of the lone pair

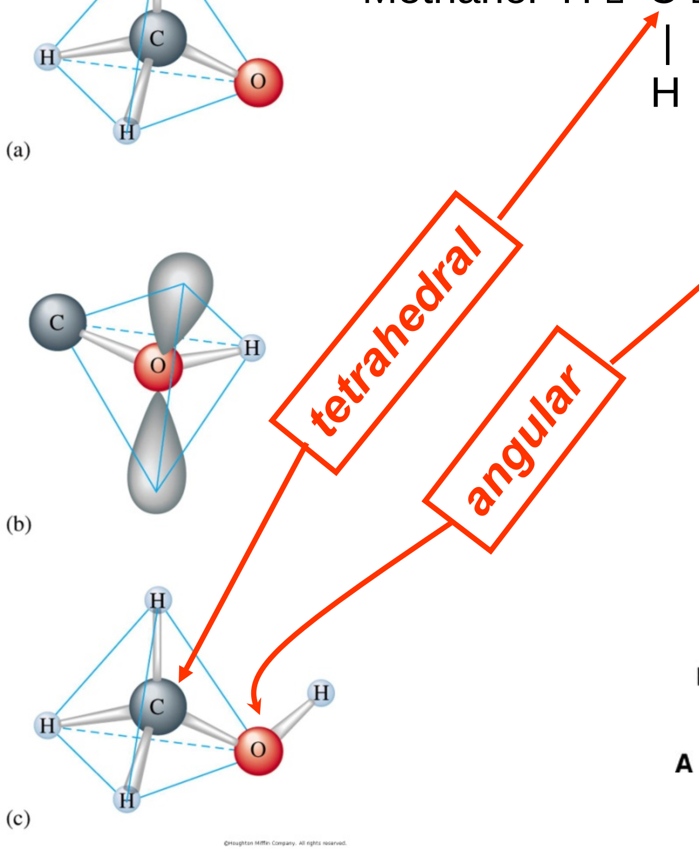




2470 L. S. BARTELL AND R. M. GAVIN, JR.

FIG. 2. Schematic representation of deformations consistent with diffraction patterns. The influence of xenon's lone pair according to the valence-shell-electron-pair-repulsion theory is portrayed.

more than one central atom (figure 13.22 Zumdahl; figure 10.11 Silb)


(a)
(b)
(c)
H
C
O
tetrahedral
angular

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```
                 H
                 |      ··
Methanol  H — C — O — H
                 |      ··
                 H
```

CH_3OH ⇨

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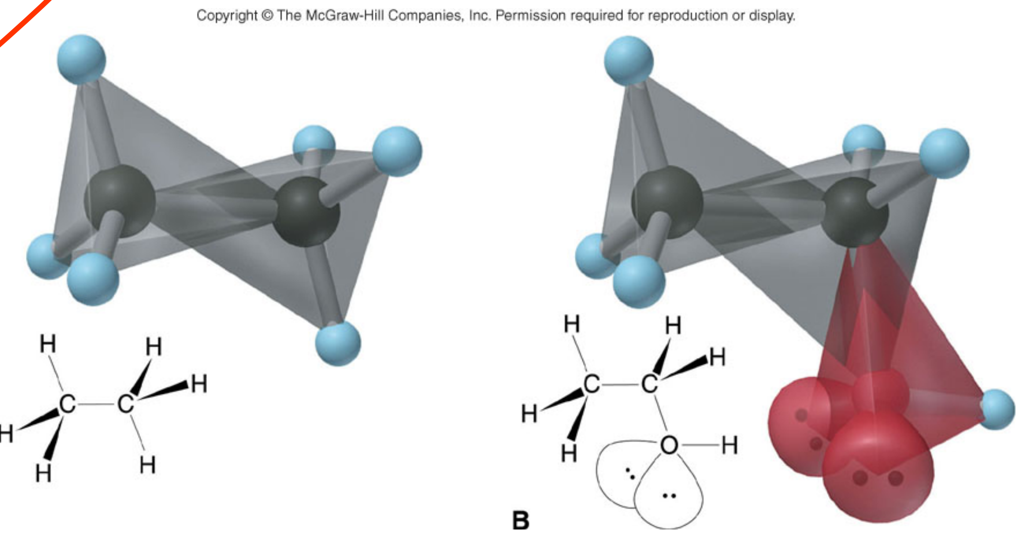
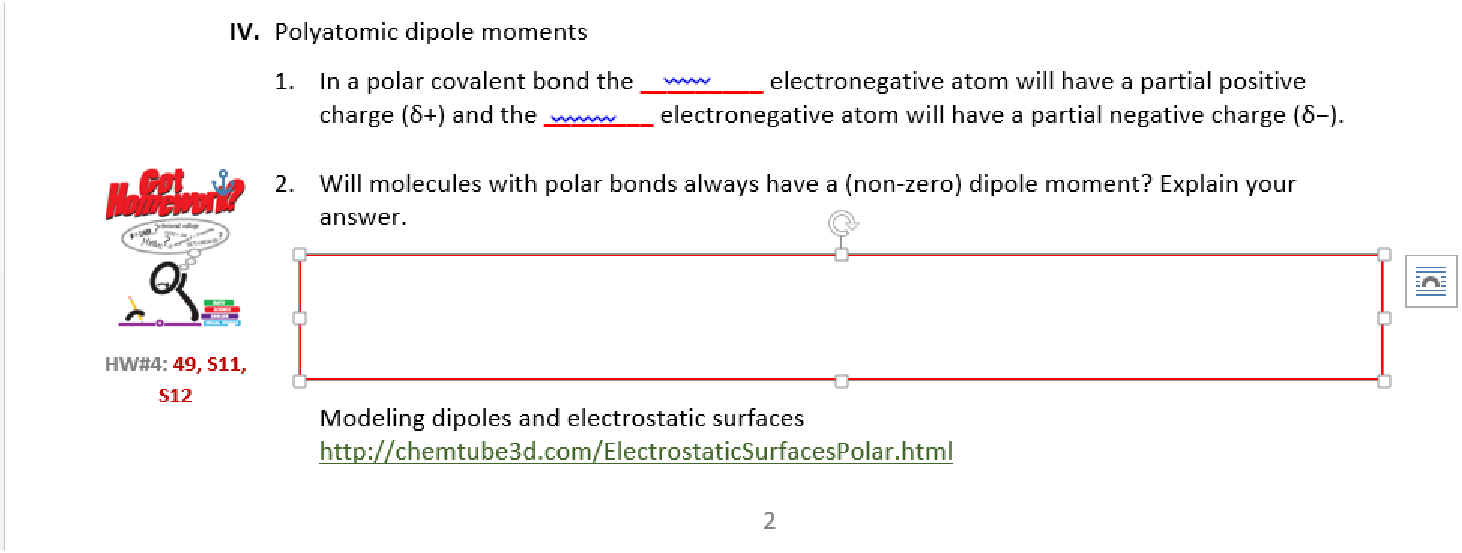


Polar Molecules
Dipole Moments
and
Molecular Geometry

(Pp 600-606)

learning objectives worksheet VII (7): section IV



IV. Polyatomic dipole moments

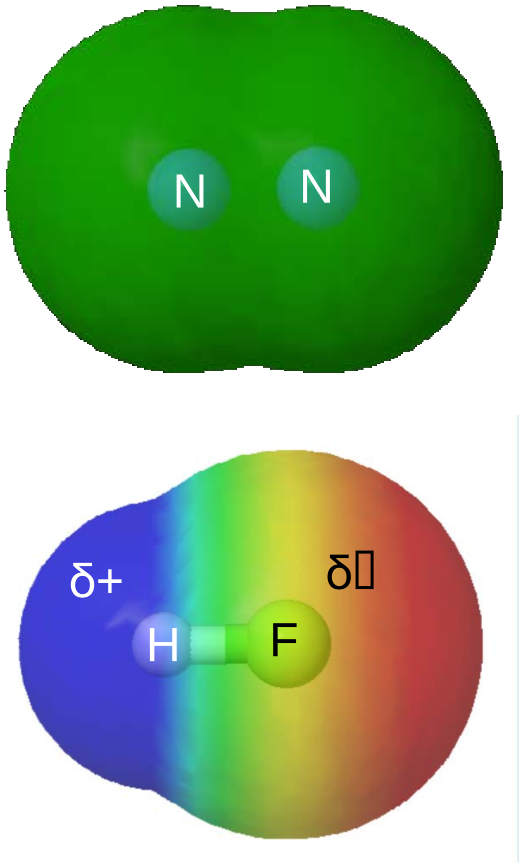
1. In a polar covalent bond the ________ electronegative atom will have a partial positive charge (δ+) and the ________ electronegative atom will have a partial negative charge (δ–).

2. Will molecules with polar bonds always have a (non-zero) dipole moment? Explain your answer.

HW#4: 49, S11, S12

Modeling dipoles and electrostatic surfaces
http://chemtube3d.com/ElectrostaticSurfacesPolar.html

non-polar vs polar bonds

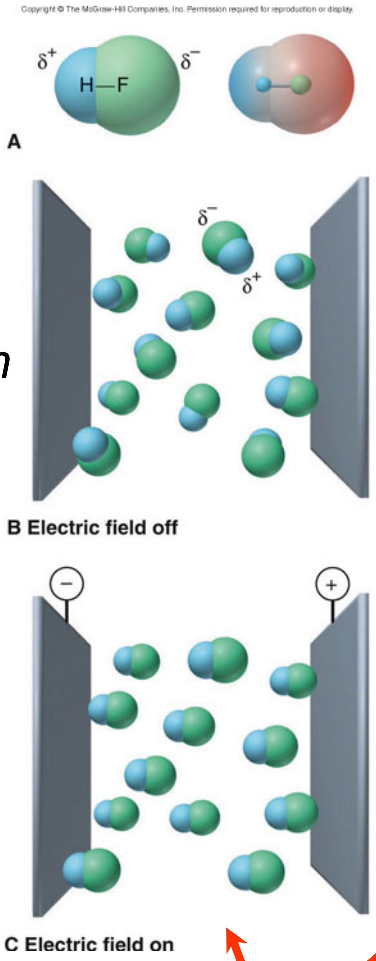


red regions are electron rich and blue regions are electron poor

bond polarity (dipole moment), Section 13.3

off
random

on
alligned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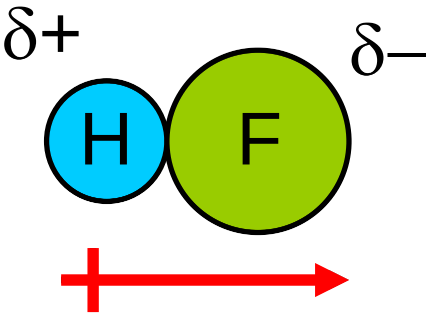
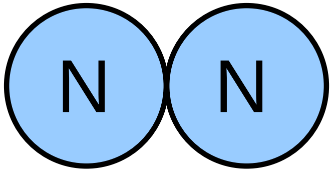
δ+
H—F
δ−
A
δ−
δ+
B Electric field off
−
+
C Electric field on

dipole moment $\vec{\mu}$



$\vec{\mu}$ is large, molecules aligned by electric field



$\vec{\mu}$ is zero, molecules NOT aligned by electric field

degree of alignment is affected by polarity of bond (magnitude of dipole moment)

dipole moments in polyatomic molecules

official formula for dipole moment VECTOR

$\vec{\mu} = \sum \boldsymbol{Q}_A \vec{\boldsymbol{R}}_A$ } don’t fret on this

- Are there polar bonds (bond dipoles)?

- Do the bond dipoles (vectors) cancel-out or reinforce in the polyatomic molecule?

examples

- H_2O
- CO_2
- CCl_4
- $CHCl_3$

Molecular Geometry, Bond Dipoles, and Net Dipole
http://chemtube3d.com/ElectrostaticSurfacesPolar.html

FINISHED For NOW !!

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Sweet
??
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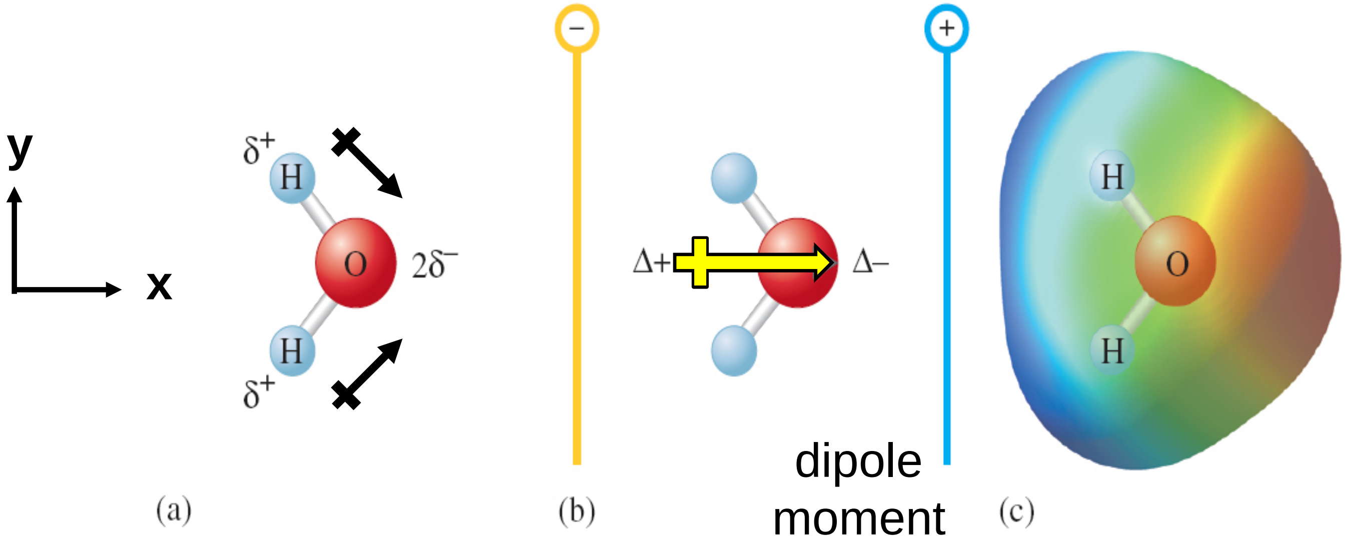
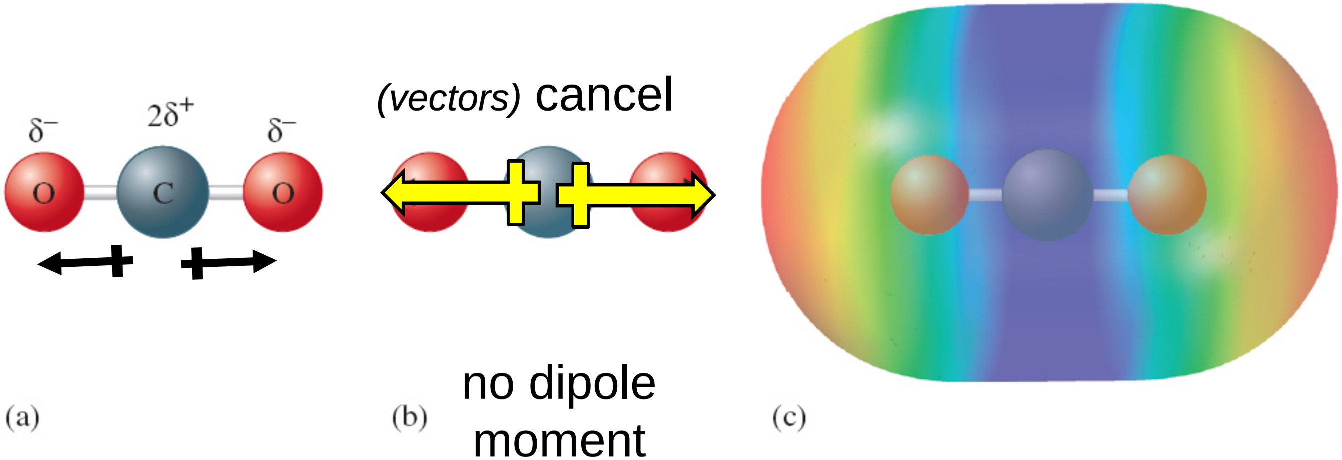
END OF CHAPTER 13

Figure 13.5, 13.7


y
x
δ+
H
O
2δ−
H
δ+
(a)
−
Δ+
Δ−
+
(b)
H
O
H
(c)

dipole moment

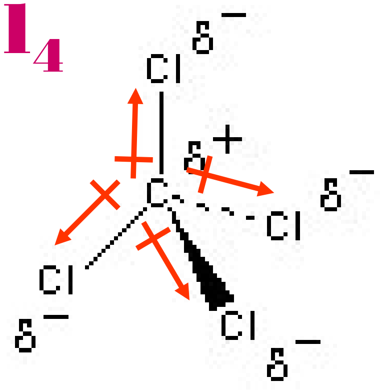

δ−
2δ+
δ−
O
C
O
(a)
(b)
(c)

(vectors) cancel

no dipole moment

CCl_4 and $CHCl_3$

CCl_4



δ−
Cl
δ+
C
δ−
Cl
Cl
δ−
Cl
δ−

nada

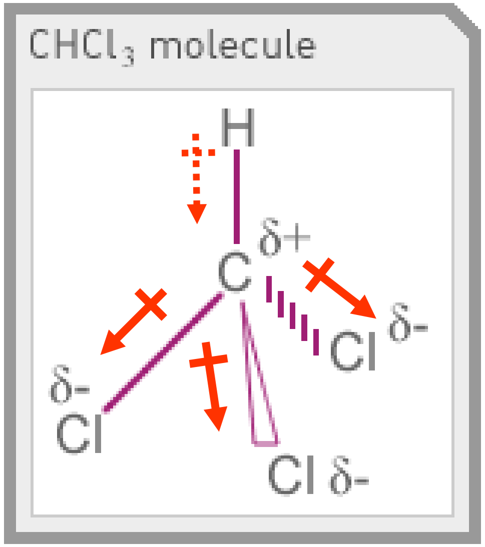
bond dipoles cancel
no dipole moment
non-polar molecule

EN (table 13.2)

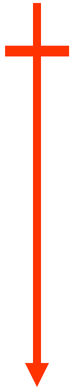
H	2.20
C	2.55
Cl	3.16

(fig. 13.3 ??)

$CHCl_3$



CHCl₃ molecule
H
C
δ+
Cl
δ-
δ-
Cl
Cl δ-

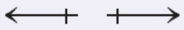
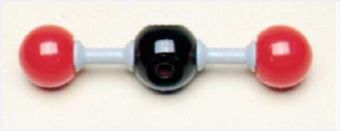
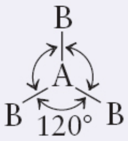
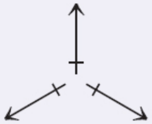
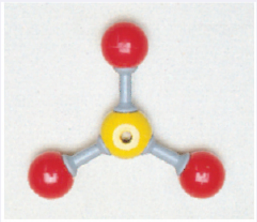
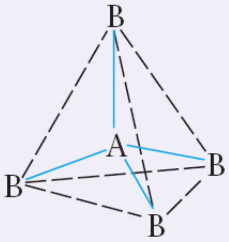
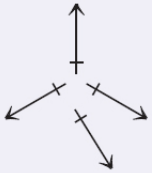


bond dipoles reinforce
dipole moment
polar molecule

geometries where polar bonds MAY cancel (table 13.4)

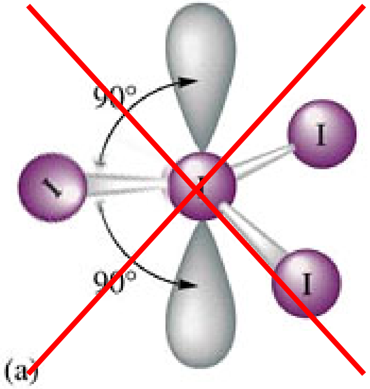
TABLE 13.4

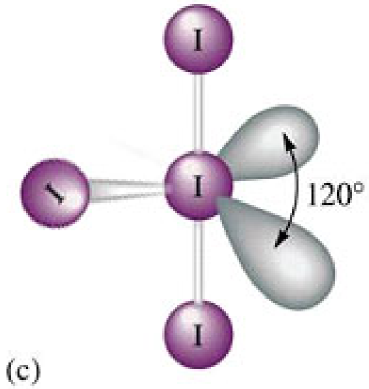
Types of Molecules with Polar Bonds but No Resulting Dipole Moment

Type		Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	B—A—B		CO_2	
Planar molecules with three identical bonds 120 degrees apart			SO_3	
Tetrahedral molecules with four identical bonds 109.5 degrees apart			CCl_4	

SN=5, where to put lone pairs (I_4 and I_3^{-})

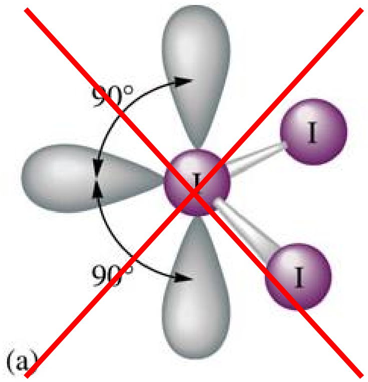
2 lone-pairs

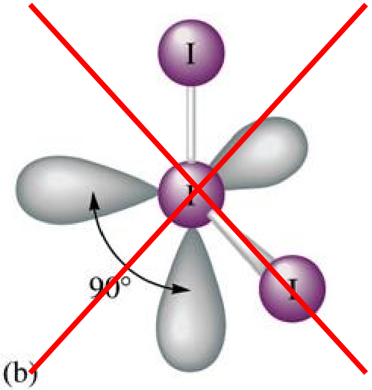


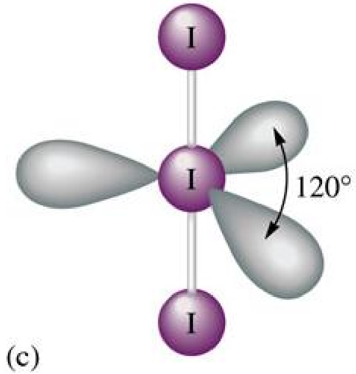


T-shaped molecular geometry

3 lone-pairs

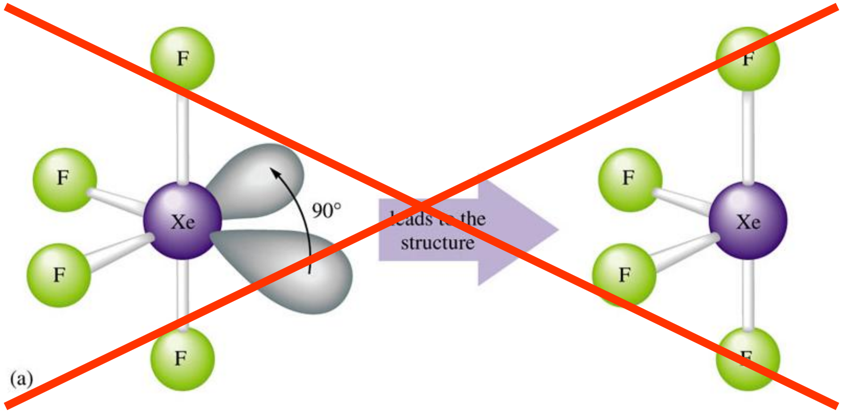


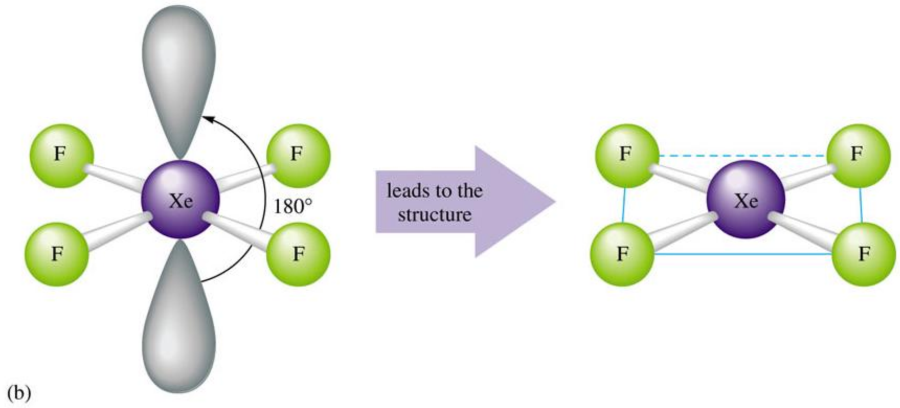




linear molecular geometry

SN=6 adjacent vs across


F
F
F
F
Xe
90°
leads to the structure
F
F
Xe
F
F
(a)


F
F
Xe
F
F
180°
leads to the structure
F
F
Xe
F
F
(b)

square planar molecular geometry

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Silberberg figure 9.13

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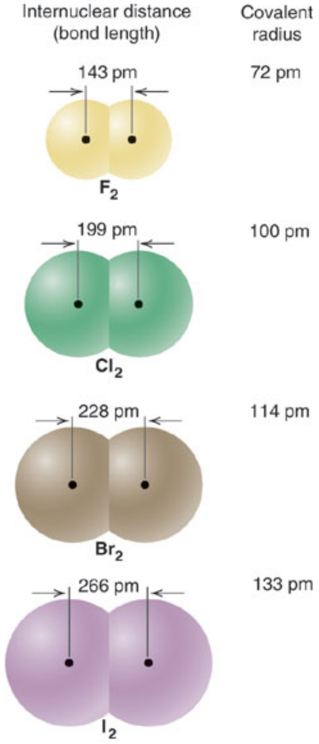
Internuclear distance (bond length)
Covalent radius
143 pm
72 pm
F2
199 pm
100 pm
Cl2
228 pm
114 pm
Br2
266 pm
133 pm
I2

Table 13.7 Zumdahl

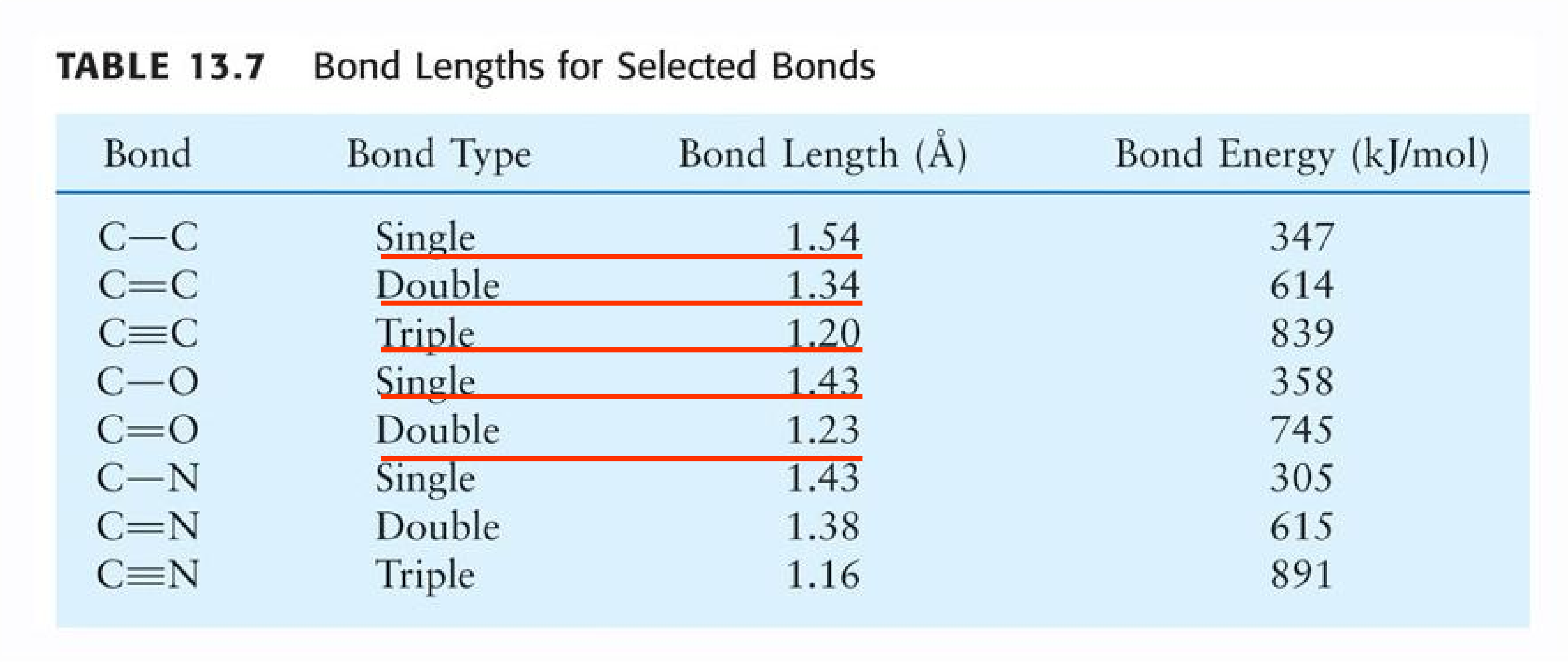

TABLE 13.7 Bond Lengths for Selected Bonds

Bond	Bond Type	Bond Length (Å)	Bond Energy (kJ/mol)
$\mathrm{C-C}$	Single	1.54	347
$\mathrm{C=C}$	Double	1.34	614
$\mathrm{C\equiv C}$	Triple	1.20	839
$\mathrm{C-O}$	Single	1.43	358
$\mathrm{C=O}$	Double	1.23	745
$\mathrm{C-N}$	Single	1.43	305
$\mathrm{C=N}$	Double	1.38	615
$\mathrm{C\equiv N}$	Triple	1.16	891

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Table 13.7 Zumdahl

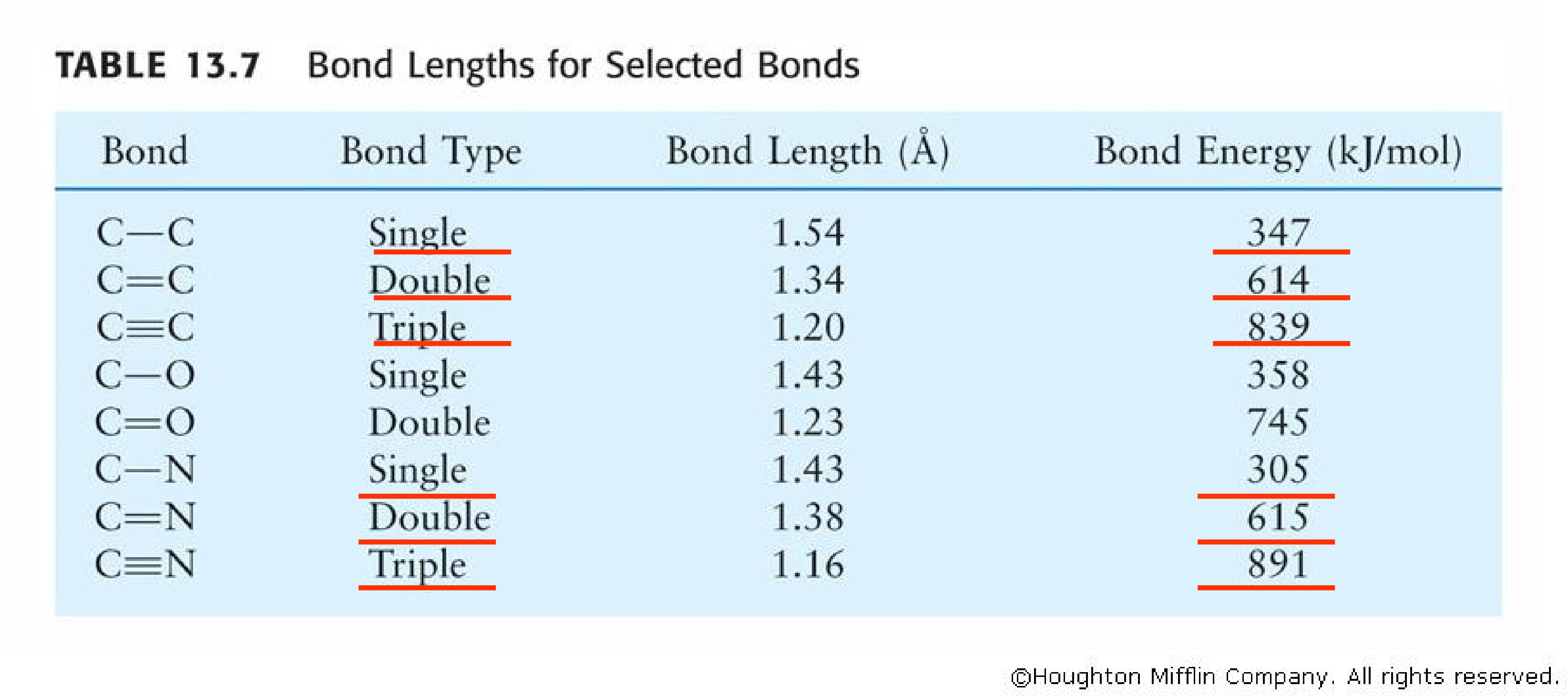

TABLE 13.7 Bond Lengths for Selected Bonds

Bond	Bond Type	Bond Length (Å)	Bond Energy (kJ/mol)
C—C	Single	1.54	347
C=C	Double	1.34	614
C≡C	Triple	1.20	839
C—O	Single	1.43	358
C=O	Double	1.23	745
C—N	Single	1.43	305
C=N	Double	1.38	615
C≡N	Triple	1.16	891

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Zumdahl table 13.6

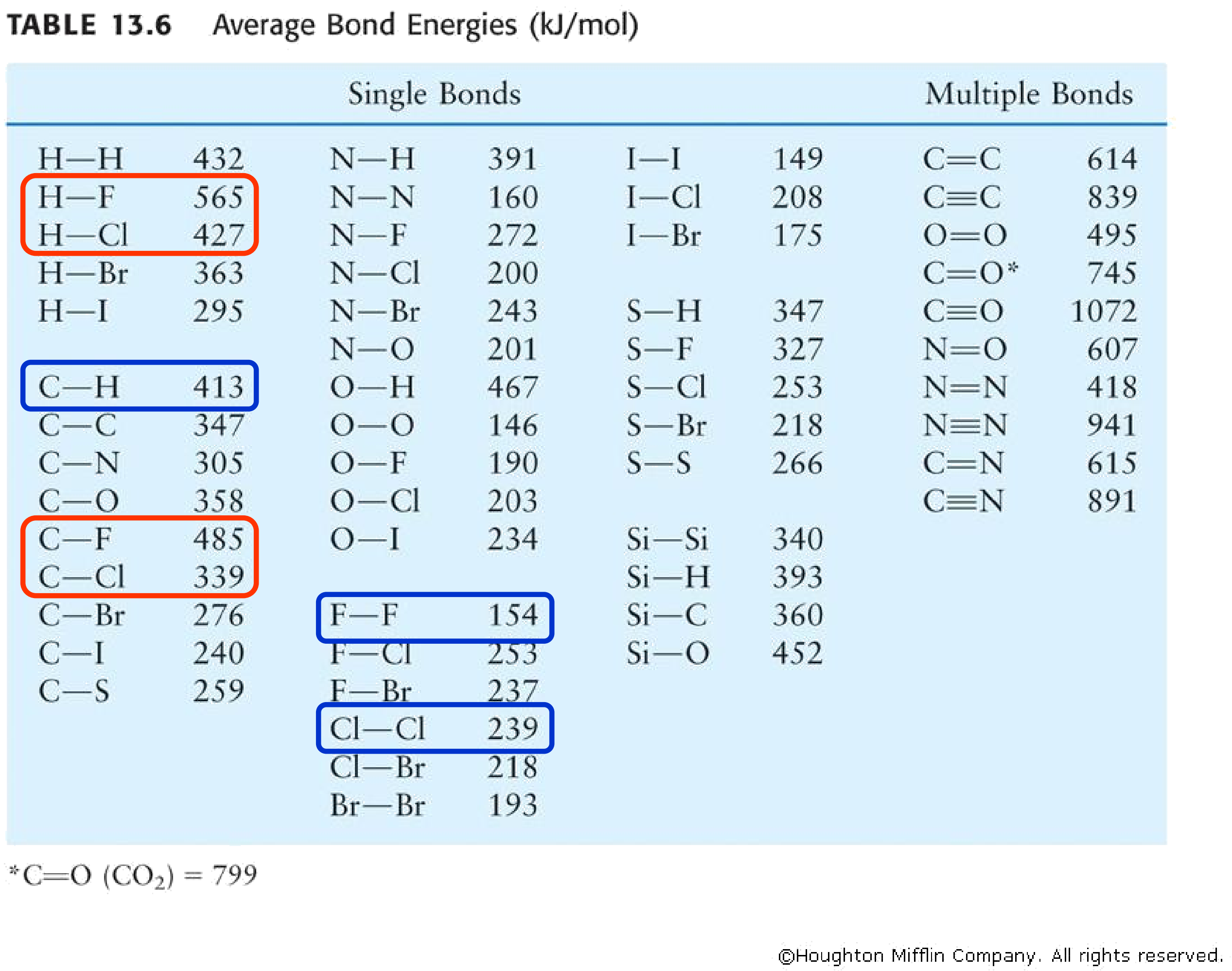

TABLE 13.6 Average Bond Energies (kJ/mol)

Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C=N	615
C—O	358	O—Cl	203			C≡N	891
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O (CO_2) = 799

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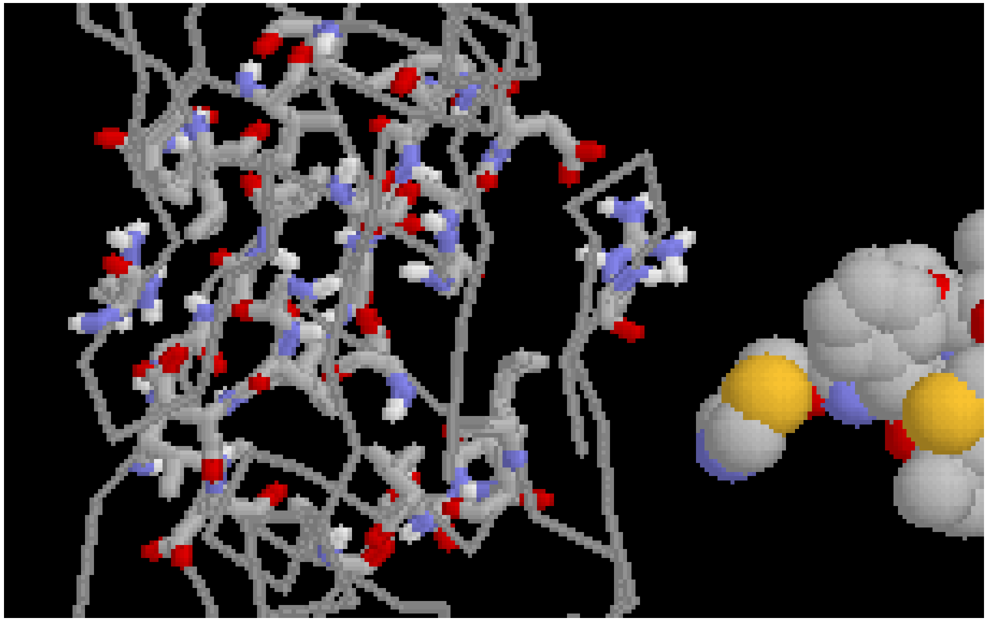
Ritonavir inhibitor "fits into" HIV Protease



HIV protease inhibitor Ritonavir binding to the protease

http://molvis.sdsc.edu/pe1.982/atlas/atlas.htm

Zumdahl Table 2.5 and 13.5, Silberberg figure 9.3

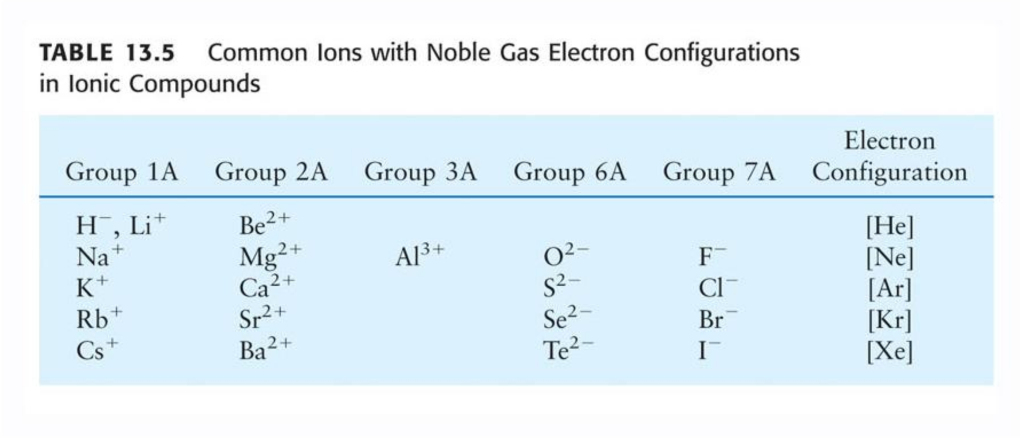
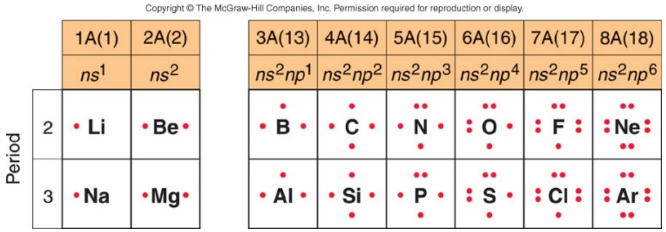


TABLE 13.5 Common Ions with Noble Gas Electron Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]

erved.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1A(1)
2A(2)
3A(13)
4A(14)
5A(15)
6A(16)
7A(17)
8A(18)
ns1
ns2
ns2np1
ns2np2
ns2np3
ns2np4
ns2np5
ns2np6
Period
2
3
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar

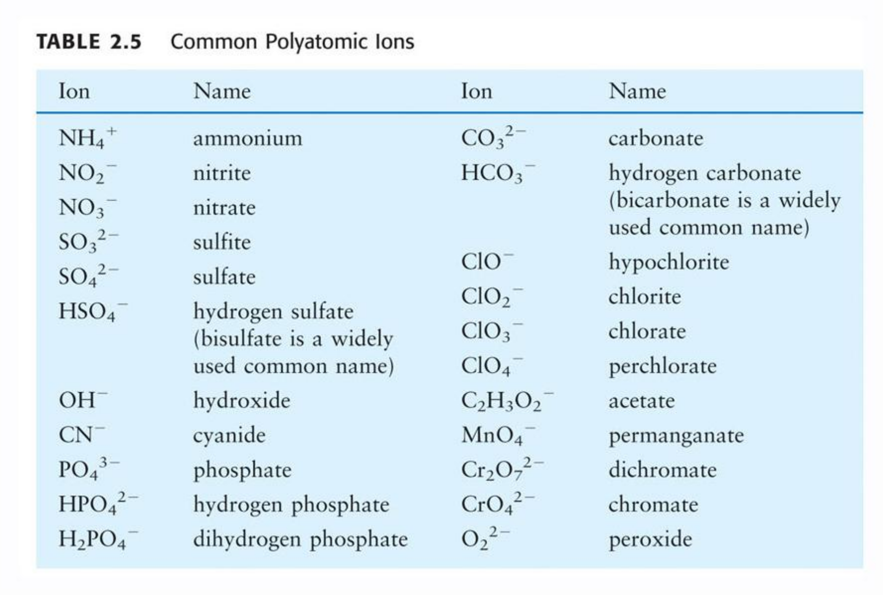

TABLE 2.5 Common Polyatomic Ions

Ion	Name	Ion	Name
NH_4^+	ammonium	CO_3^{2-}	carbonate
NO_2^-	nitrite	HCO_3^-	hydrogen carbonate (bicarbonate is a widely used common name)
NO_3^-	nitrate		
SO_3^{2-}	sulfite	ClO^-	hypochlorite
SO_4^{2-}	sulfate	ClO_2^-	chlorite
HSO_4^-	hydrogen sulfate (bisulfate is a widely used common name)	ClO_3^-	chlorate
		ClO_4^-	perchlorate
OH^-	hydroxide	$C_2H_3O_2^-$	acetate
CN^-	cyanide	MnO_4^-	permanganate
PO_4^{3-}	phosphate	$Cr_2O_7^{2-}$	dichromate
HPO_4^{2-}	hydrogen phosphate	CrO_4^{2-}	chromate
$H_2PO_4^-$	dihydrogen phosphate	O_2^{2-}	peroxide

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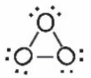
KNOW:

NH_4^+, NO_3^-, SO_4^{2-}, HSO_4^-, CN^- , OH^-, PO_4^{3-}, CO_3^{2-}, HCO_3^-, $C_2H_3O_2^-$, MnO_4^-

triangular cyclic O_3



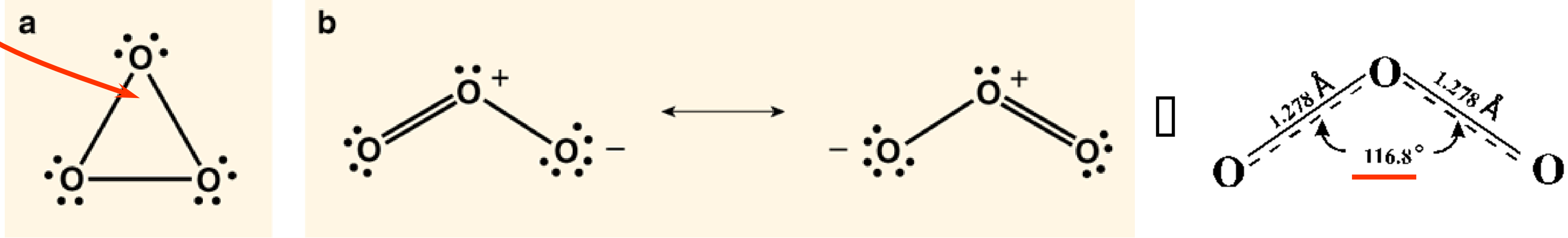
The Story of O
[Roald Hoffmann](http://www.americanscientist.org/issues/pub/the-story-of-o/5)

The Ring

So now we have oxygen chemistry in the atmosphere, in the cell, in a decontamination process. But have we exhausted all of oxygen's secrets?
http://www.americanscientist.org/issues/pub/the-story-of-o/5

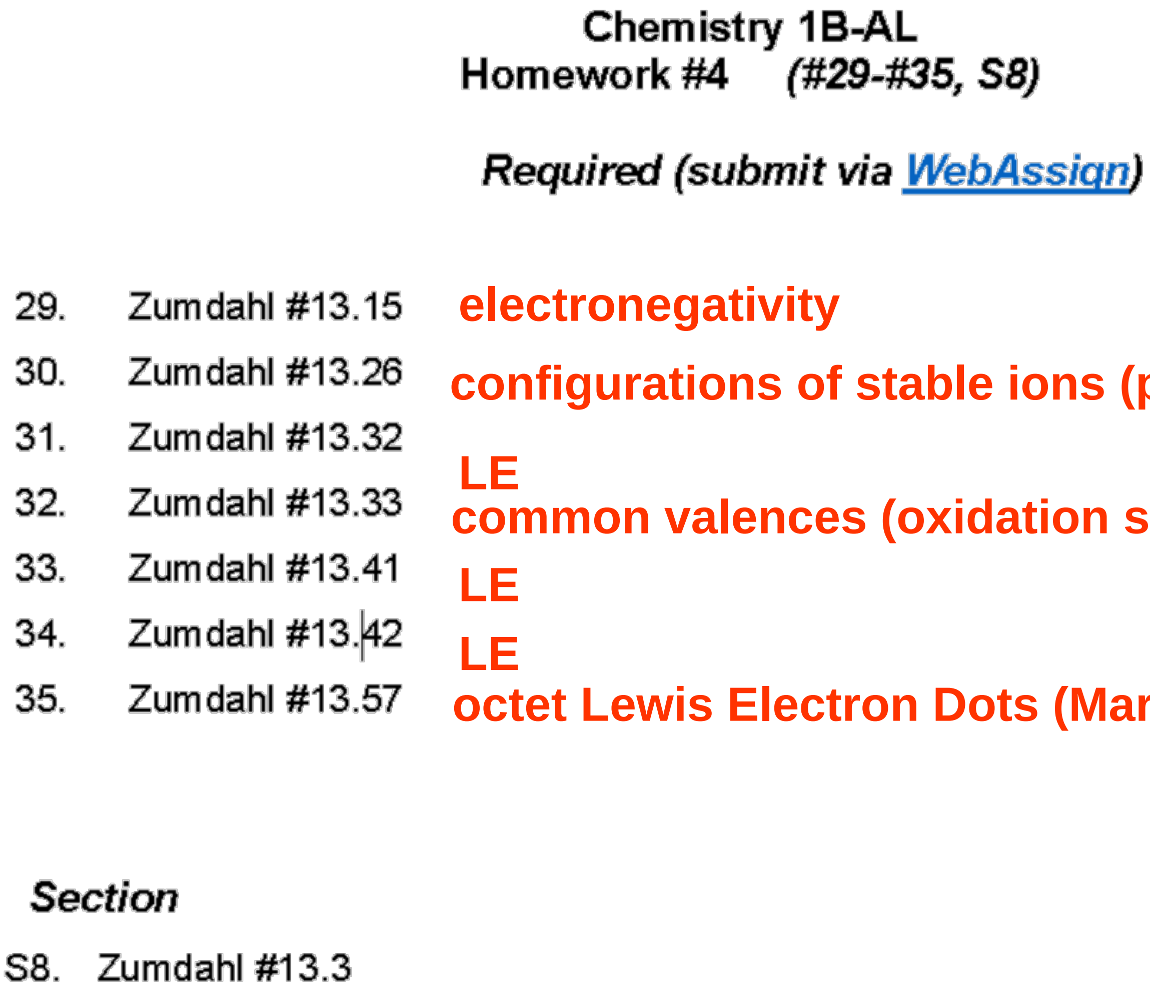
60□ bond angles are “strained” (unstable);

[discuss later in term (quantum mechanics)]



Indeed, the best calculations today confirm the metastability of this ring. Cyclic ozone lies about **130 kilojoules per mole above normal O_3** but has a barrier of no less than 95 kilojoules per mole preventing conversion to the open form.

HW-hints Homework #4, Due 26th October



Chemistry 1B-AL
Homework #4 *(#29-#35, S8)*

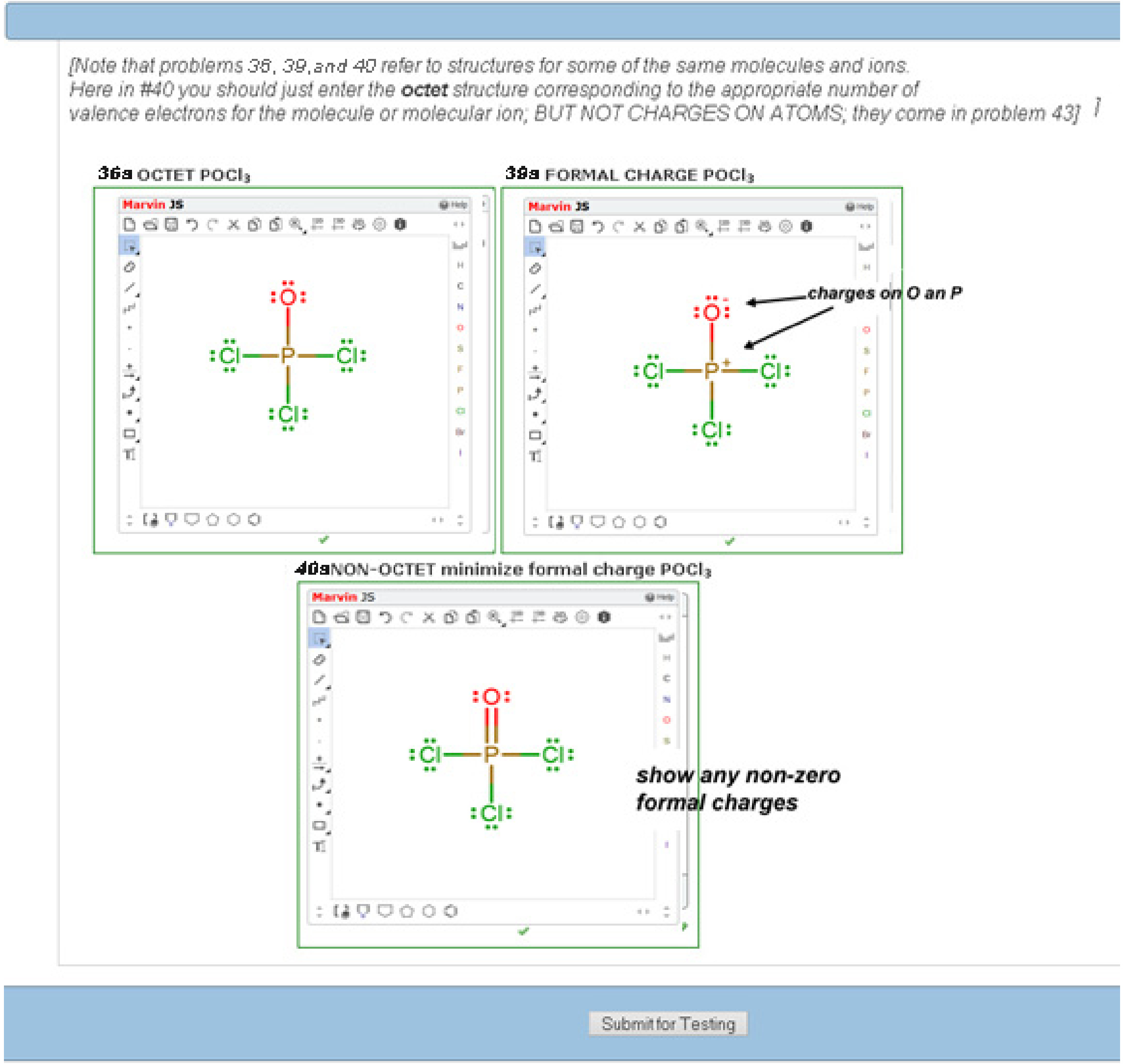
Required (submit via WebAssign)

29. Zumdahl #13.15 **electronegativity**
30. Zumdahl #13.26 **configurations of stable ions (part c: configurations)**
31. Zumdahl #13.32 **LE**
32. Zumdahl #13.33 **common valences (oxidation states) empirical fmlas**
33. Zumdahl #13.41 **LE**
34. Zumdahl #13.42 **LE**
35. Zumdahl #13.57 **octet Lewis Electron Dots (Marvin Sketch)**

Section

S8. Zumdahl #13.3

HW#4 probs 36, 39, 40



[Note that problems 36, 39, and 40 refer to structures for some of the same molecules and ions. Here in #40 you should just enter the ***octet*** *structure corresponding to the appropriate number of valence electrons for the molecule or molecular ion; BUT NOT CHARGES ON ATOMS; they come in problem 43]*

36a OCTET $POCl_3$

39a FORMAL CHARGE $POCl_3$

charges on O an P

40a NON-OCTET minimize formal charge $POCl_3$

show any non-zero formal charges

Marvin JS
Marvin JS
Marvin JS
O
P
Cl
Cl
Cl
+
Submit for Testing

HW#4

36. Zumdahl #13.54 (a) **resonance structures**

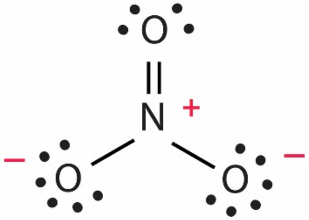
37. Zumdahl #13.57 **resonance structures**

38. Zumdahl #13.71 (a, d, and f) **formal charge (octet)**

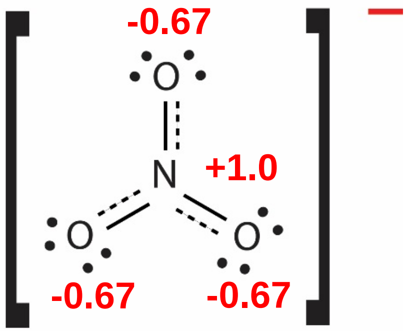
39. Zumdahl #13.72 (for 13.71 a,d,f) **formal charge (non octet)**

nitrate ion NO_3^-

Lewis **Formal** Charge:



+ 2 other equivalent resonance structures =

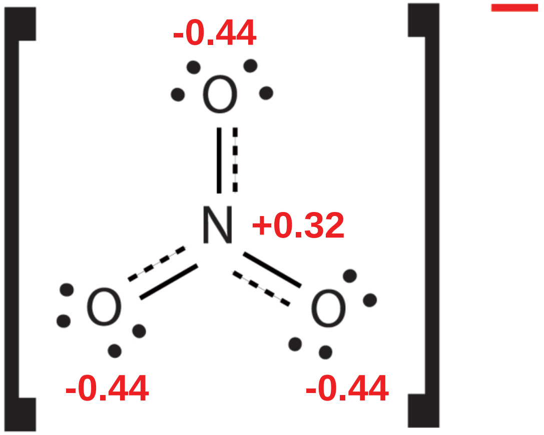


Actual

(calculated by quantum mechanics)

Structure and electron density distribution of the nitrate ion and urea molecule upon protonation

Guus J. M. Velders and Dirk Feil
Chemical Physics Laboratory, University of Twente, PO Box 217, NL-7500 AE Ensche
The Netherlands

Theoretica Chimica Acta
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