Chemistry 1B-AL

Fall 2016

sessions ~~Lectures~~ 10-11-12

1

"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)

2

why octets?

---

filling of ns^2np^6 uses atomic orbitals of similar
energy to form covalent bond
(note H requires only 2 electrons)

3

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.

4

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how to get octet Lewis structures

Gene's pathetic method:

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

5

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

- 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

6

3

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)

7

Multiple bonds

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.

8

examples

- C_2H_4

- C_2H_2

- COF_2

9

MASTERING LEWIS STRUCTURES **= PRACTICE   PRACTICE   PRACTICE**

10

WebAssign and Marvin JS (HW4 #35)

HW#4-hints

11

Resonance Structures and Formal Charge

(Pp 626-627, 631-634)

12

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/cPDptoQwUYI

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 Valence Electron Diagrams (LVEDs)
    i. the LVEDs for second and third row atoms are:

· H							He
· Li	· Be ·	· B ·	· C ·	· N ·	· O ·	· F ·	· Ne ·
· Na	· Mg ·	· Al ·	· Si ·	· P ·	· S ·	· Cl ·	· Ar ·

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

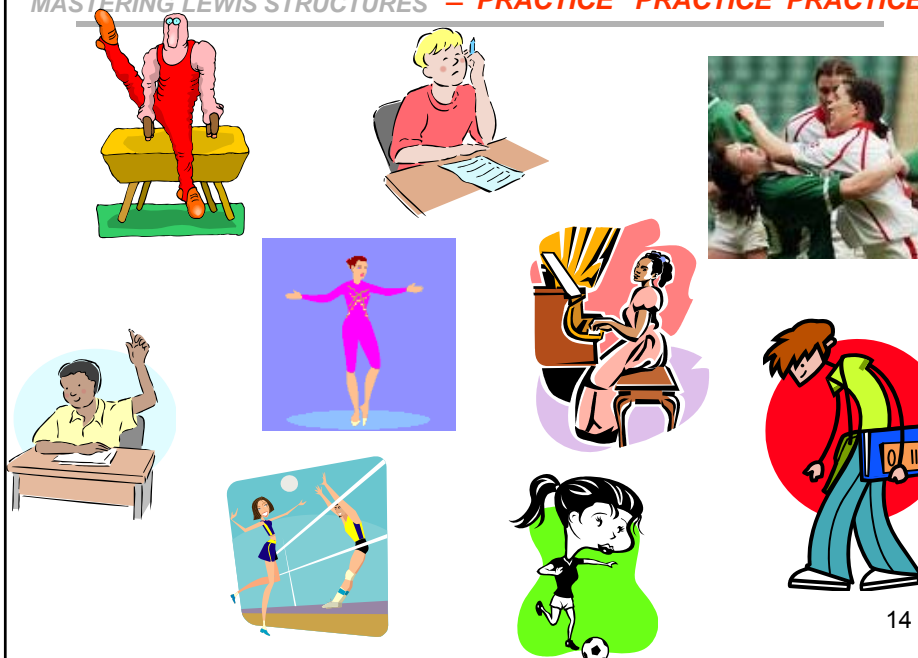5. To become facile with drawing Lewis structures you must:
    _____, _____, _____ !!!!

13

14

Chemistry 1B Fall 2016
Lectures 10-11-12

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?

HOMEWORK
HW#4: 41, 42, 59

2
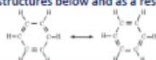
15

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 +____   iv. O +____
    ii. N +____   v. H +____
    iii. F +____

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?

HOMEWORK
HW#4: 43, 44, S10

16
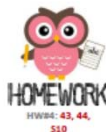
the structure of ozone O_3 *but first: the good and the bad*

absorbs sun's harmful ultra-violet radiation

produced by photochemical smog; oxidizes materials like lungs and tires

Ozone in the stratosphere protects Earth but in the troposphere, it is harmful.
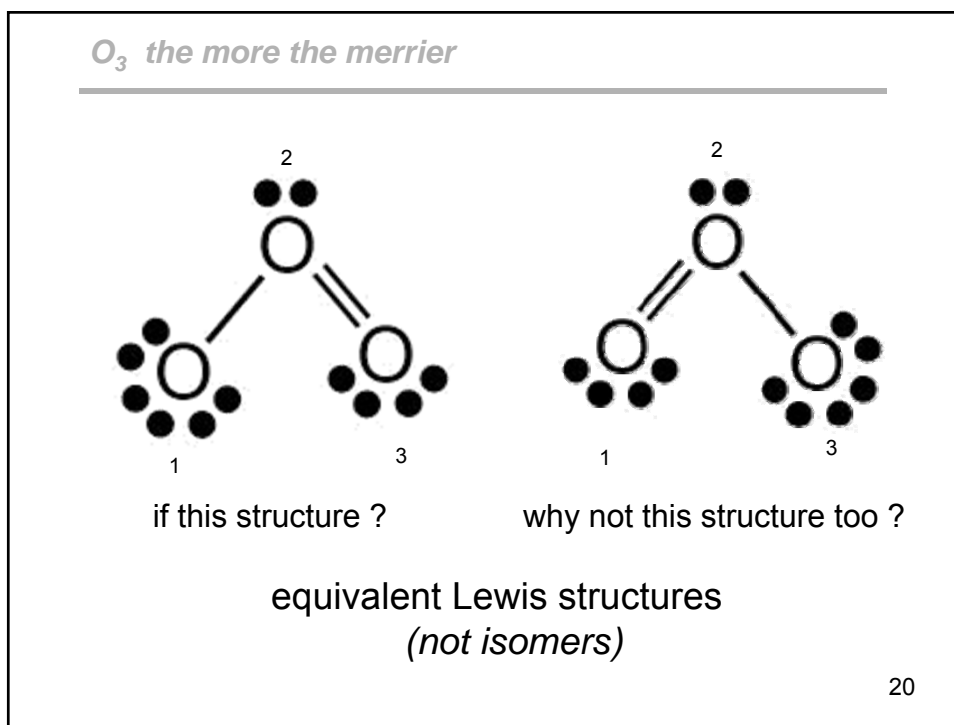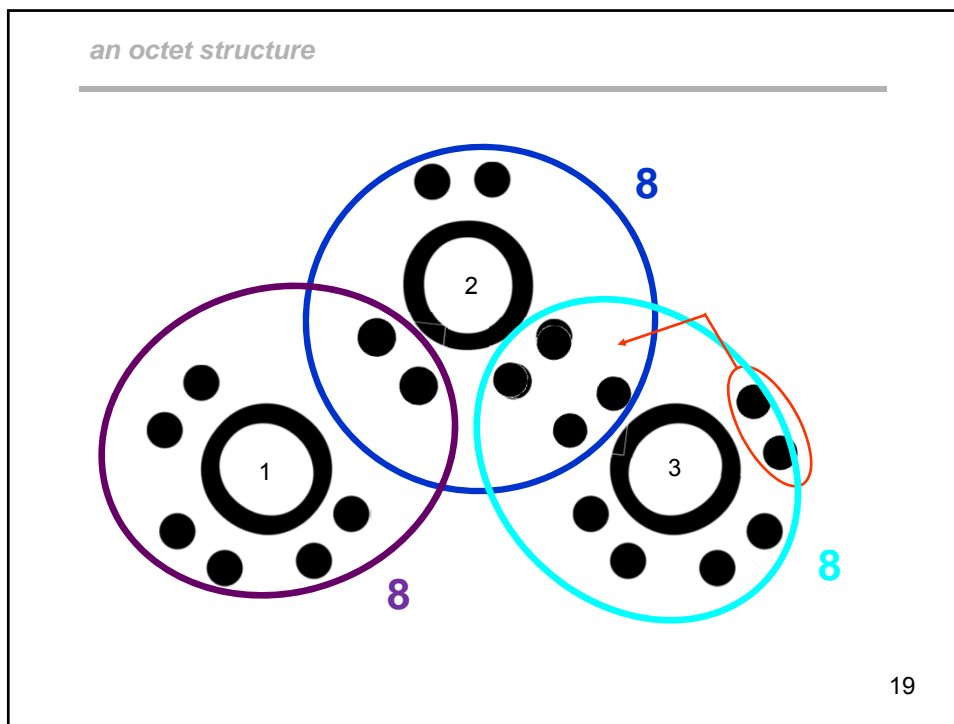
UCAR©2003

17

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ozone (octet structure)

O_3

triangular ??,
however, not the most 'stable' structure of O_3
more later

18

an octet structure

8 **8** **8**

19

O_3 *the more the merrier*

if this structure ?

why not this structure too ?

equivalent Lewis structures
(not isomers)

20

10

non-equivalent bonds

 what do these structures imply?
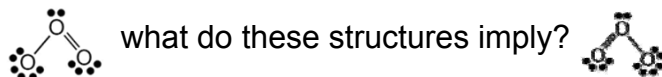
two different O-O bond lengths

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

shorter double bond:
~123 pm (10^{-12} m)
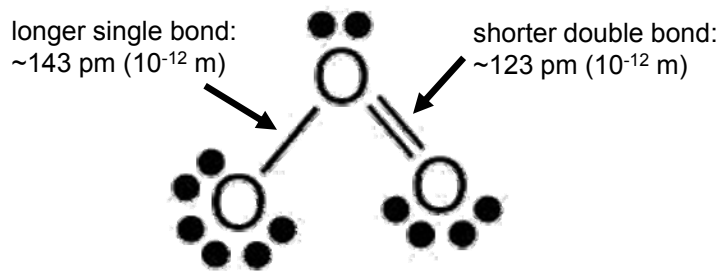
21

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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 ??

22

11
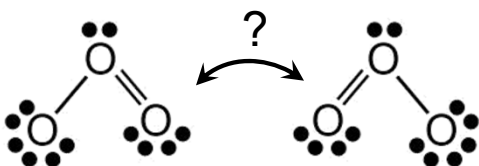
not this (***red donkey*** ⟷ ***blue horse***) *(Sienko and Plane)*

123 pm (10⁻¹² m)   143 pm   ???

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

23

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

123 pm (10⁻¹² m)   143 pm   +

127 pm

Purple mule

24

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

25

(now is later !!) O_3 ring structure
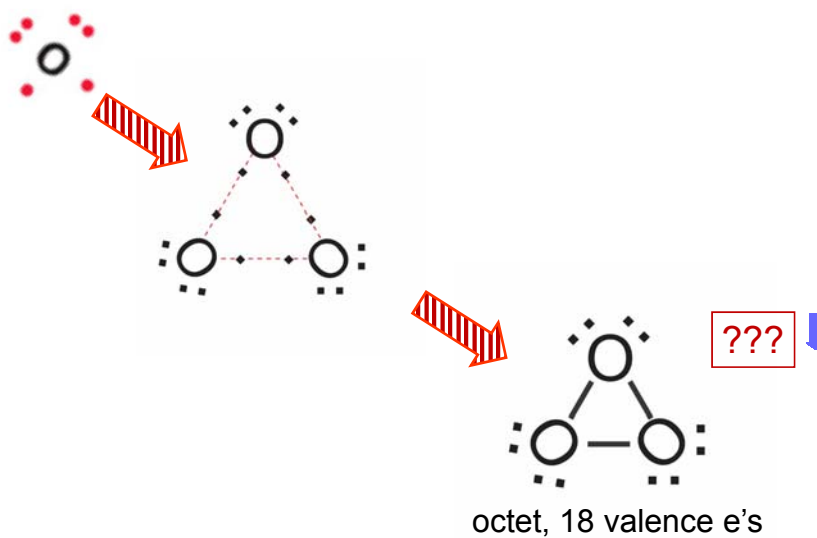
octet, 18 valence e's

26

triangular cyclic O₃

The Story of O
Roald Hoffmann
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 This Article from Issue January-February 2004

60° bond angles are "strained" (unstable);
[discuss later in term (quantum mechanics)]
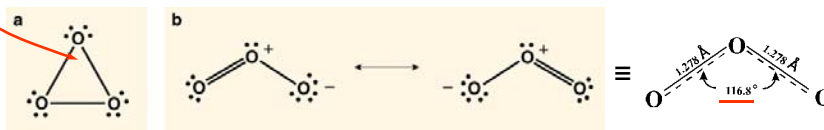
Indeed, the best calculations today confirm the metastability of this ring.
Cyclic ozone lies about **130 kilojoules per mole above normal O₃** but
has a barrier of no less than 95 kilojoules per mole preventing
conversion to the open form.

27

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examples of resonance structures

- $[CO_3]^{2-}$ ➡

- C_6H_6 (in class)

28

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.

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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

30

formal charge

positive core charge

formal charge = **+** # of valence electrons (in neutral atom)

negative charge from electrons assigned to atom

− # of nonbonding electrons

− ½ # of bonding electrons

31

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*

32

16

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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 $COCl_2$

33

$COCl_2$:phosgene

34
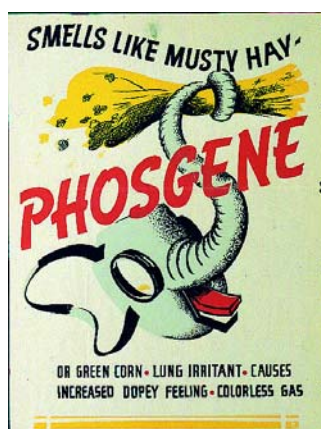
COCl$_2$: non-equivalent resonance forms

octet structures:

I

II

III
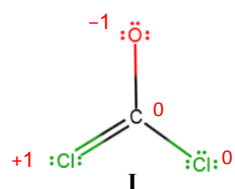
Formal Charge:

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**
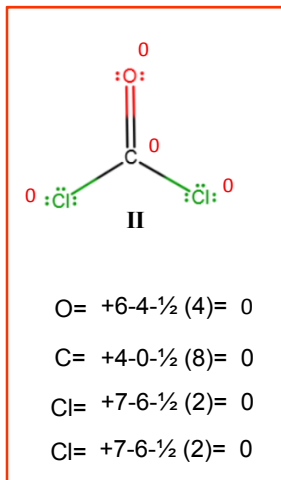
+1 on Cl unfavorable

**II structure with greatest contribution
I and III minor contributions**

35

36

18

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+}		O^{2-}	F^-	[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]

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^-

37

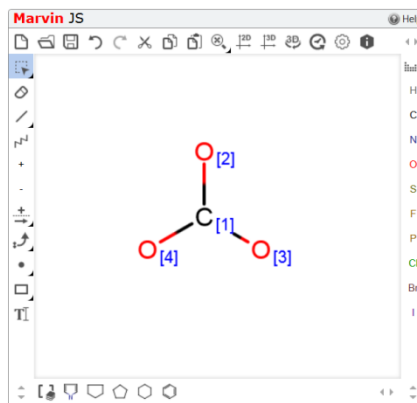*Marvin JS Resonance Structure (HW#5 37, 44)*

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

see additional video06a

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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

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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. $POCl_3$

40

20

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
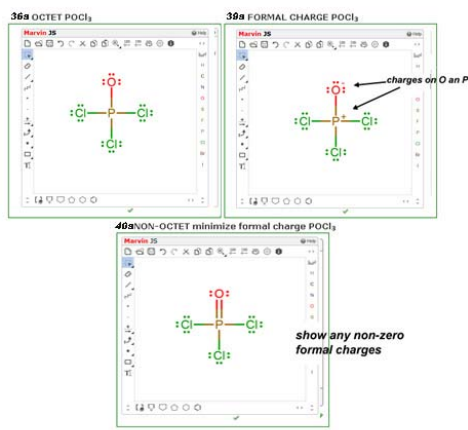
Submit for Testing

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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 rCOMMONS | ON-LINE Q & A |

go to current handouts

look at this for VESPER

	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)

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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

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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)

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Chemistry 1B Fall 2016
Lectures 10-11-12

$$\Delta H$$

$$H_2(g) + F_2(g) \xrightarrow{\Delta H} 2HF(g)$$

breaking bonds
+ BE H$_2$
+ BE F$_2$
ENDOTHERMIC

forming bonds
- 2 BE HF
EXOTHERMIC

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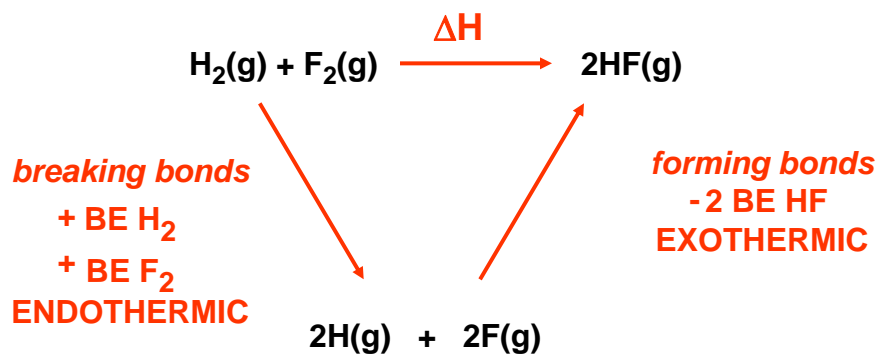
$$\Delta H_{reaction} = BE(H_2) + BE(F_2) - 2BE(HF)$$

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

45

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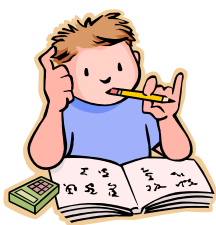
or else

46
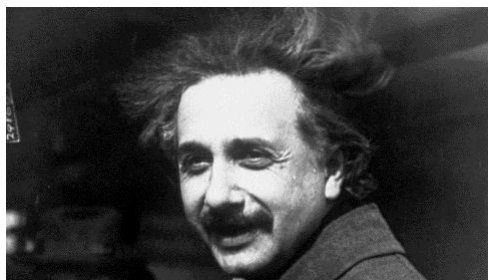
23

Study HINT

47

48

Marie Curie
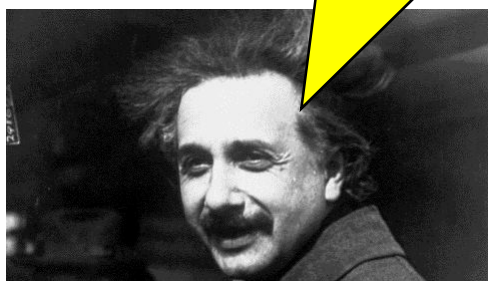
Albert Einstein

VSPER (13.13 pp 637-650; handout for ch. 13)

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

"classical" (electrostatic) theory of
molecular geometry
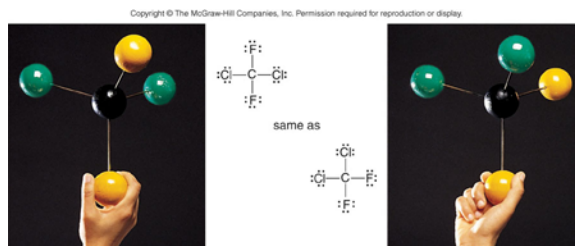
49

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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."

50

25

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a knowledge of molecular geometry is essential in biological chemistry
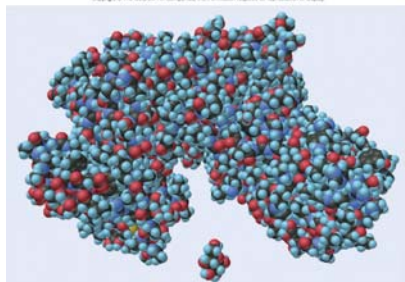
enzyme + sugar

HIV-protease complex

51

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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

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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

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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)

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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

55

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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	

You Tube ➡

WWW Links Ch. 13
VSEPR ➡

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

SN=2
linear

Linear

SN=3
trigonal planar

120°

Trigonal planar

SN=4
tetrahedral

109.5°

Tetrahedral

SN=5
trigonal bipyramidal

90°

120°

Trigonal bipyramidal

SN=6
octahedral

90°

90°

Octahedral

SN≡ number of electron groups
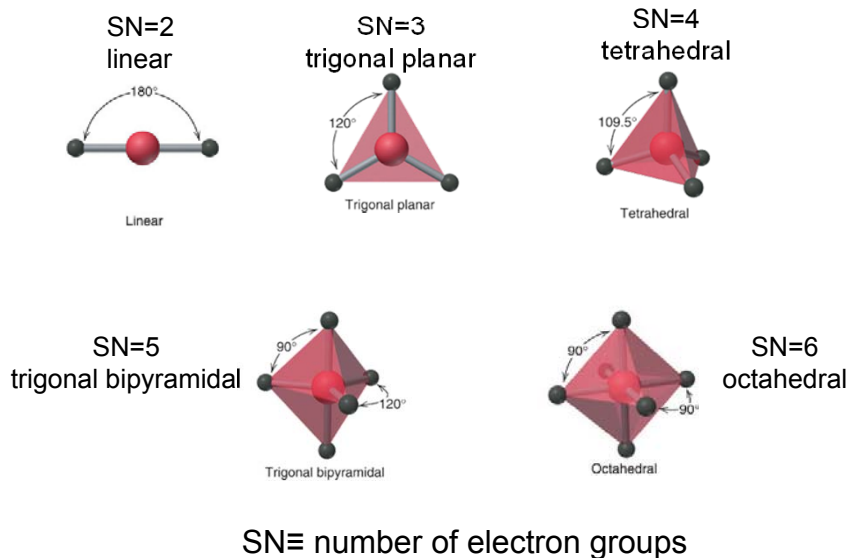
57

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

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

$BeCl_2$ (p. 628)

$BeCl_2$ ⟹
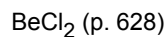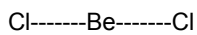
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

LINEAR
180°

A

Class	Shape

Linear

Examples: CS_2, HCN, BeF_2

fig Silb 10.3

58
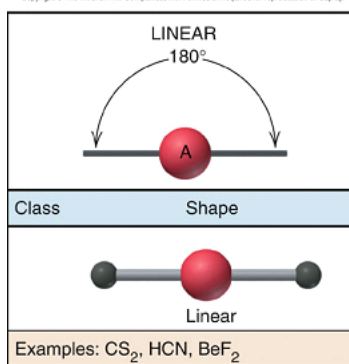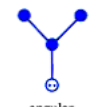
SN=3, electronic geometry is trigonal planar

examples: BF_3 SO_2

BF_3 ⇨
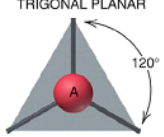
[from Handout #17]

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

TRIGONAL PLANAR

120°

A

Class	Shape

Trigonal planar

Examples: SO_3, BF_3, NO_3^-, CO_3^{2-}

angular=bent=V-shape
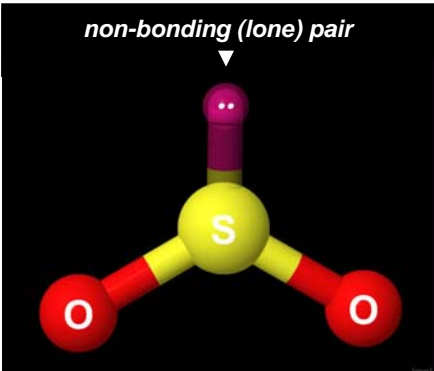
Bent (V shaped)

Examples: SO_2, O_3, $PbCl_2$, $SnBr_2$

F

B

F   F

Zumdahl
p. 637

59
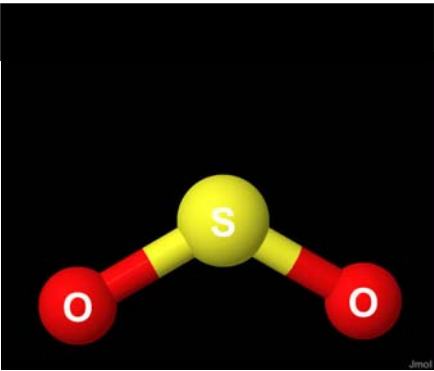
SN=3, 1 LP

non-bonding (lone) pair
▼

S

O   O

SO_2 ⇨

electronic geometry
trigonal planar

S

O   O

SO_2 ⇨

(molecular) *geometry*
bent, angular, V-shaped

60
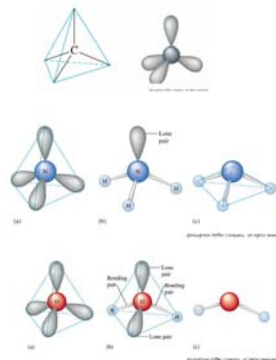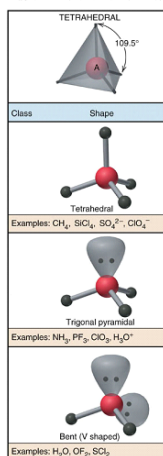
30
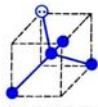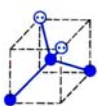
SN=4, electronic geometry is tetrahedral

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

$CF_4 \Rightarrow$

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

TETRAHEDRAL
109.5°

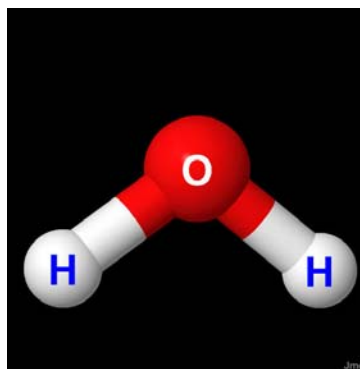| Class	Shape
	Tetrahedral
	Examples: CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-
	Trigonal pyramidal
	Examples: NH_3, PF_3, ClO_3, H_3O^+
	Bent (V shaped)
	Examples: H_2O, OF_2, SCl_2

[from Handout #17]

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SN=4, tetrahedral electronic geometry
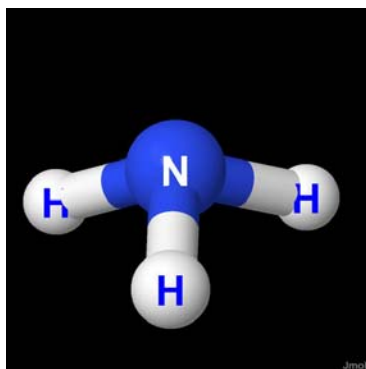
$NH_3 \Rightarrow$

1 LP
(molecular) **geometry**
trigonal pyramidal

$H_2O \Rightarrow$

2 LP
(molecular) **geometry**
angular, bent, V-shaped   62

---

effects of extra lone-pair repulsion

- NH_3 (H–N–H 107.3°)   < 109.5°

- H_2O (H–O–H   104.5°)   < 109.5°

bond e's

- H_2S (H –S –H   92°)
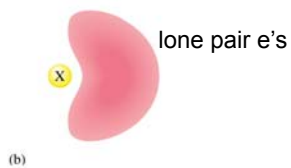 *understand using qm ch 14*
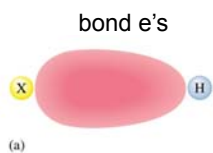
lone pair e's

figure 13.19
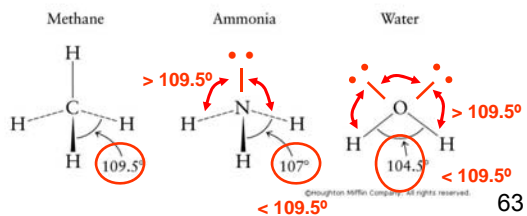
63

SN=5, electronic geometry is trigonal bipyramidal

[from Handout #17]

PF_5 ⟹

SF_4 ⟹

ClF_3 ⟹

XeF_2 ⟹

64
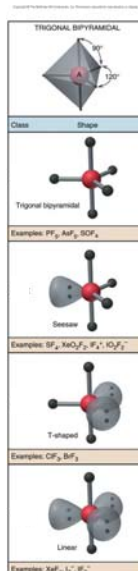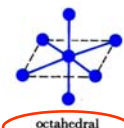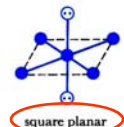
32

SN=6, octahedral electronic geometry

[from Handout #17]

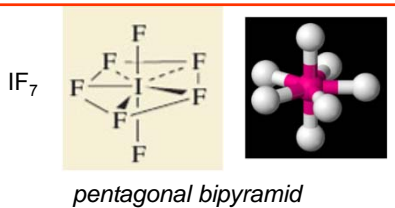| SN	Number of lone pairs	Molecular shape	Example
6	0	octahedral	SF_6, PF_6^-, SiF_6^{2-}
6	1	square pyramidal	IF_5, BrF_5
6	2	square planar	XeF_4, IF_4^-

SF_6 ⟹

BrF_5 ⟹

XeF_4 ⟹
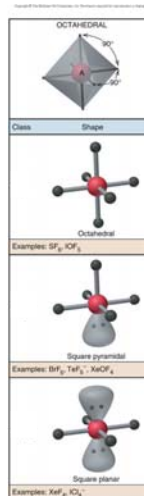
65

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
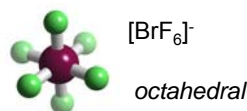
Evidence that this is indeed the case is provided by SeF_6^{2-}, IF_6^-, and XeF_6 where, because the central atom is larger than the Br atom the fluorine ligands are not quite close-packed, allowing room for some of the non-bonding electron density to move into the valence shell to form what has been 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

66

33
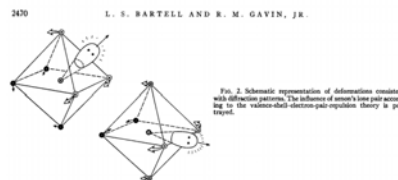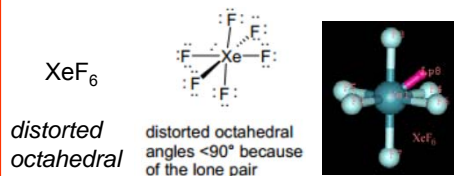
more than one central atom (figure 13.22 Zumdahl; figure 10.11 Silb)

Methanol

CH_3OH ⟹

tetrahedral

angular
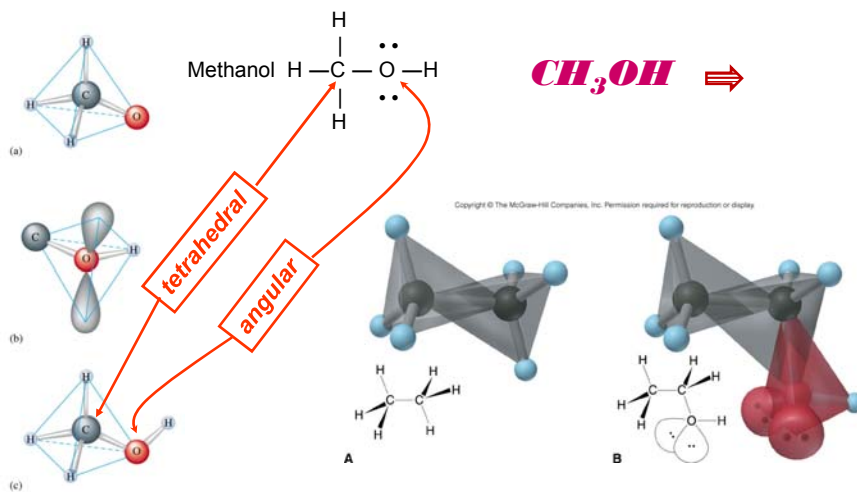
67

Polar Molecules
Dipole Moments
and
Molecular Geometry

(Pp 600-606)

68

34

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.

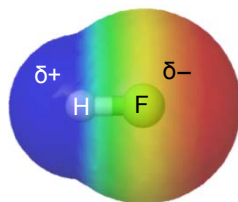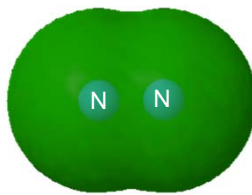HW#4: 49, S11, S12

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

2

69

non-polar vs polar bonds

red regions are electron rich and blue regions are electron poor

70

---

dipole moment $\vec{\mu}$

$\delta+$ $\delta-$

H   F

μ is large, molecules
aligned by electric field

off
random

on
alligned

N   N

μ is zero, molecules NOT
aligned by electric field

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

71

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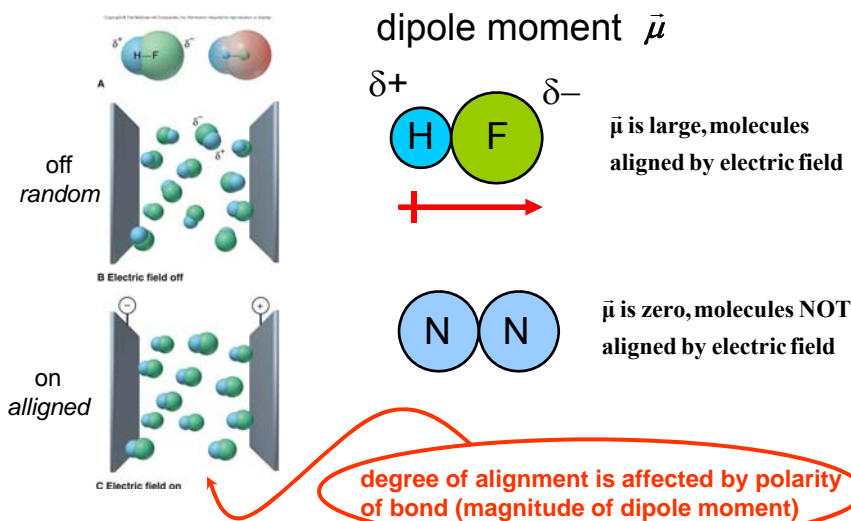
official formula for dipole moment VECTOR

$$\vec{\mu} = \sum Q_A \vec{R}_A$$ } don't fret on this

• Are there polar bonds (bond
  dipoles)?

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

72

36

examples

- H_2O

- CO_2

- CCl_4

- $CHCl_3$

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

73

FINISHED For NOW !!

Short & *Sweet* ??

© The Eclectic Reader

74

END OF CHAPTER 13

75

Figure 13.5, 13.7

dipole
moment

(vectors) cancel

no dipole
moment

76

38
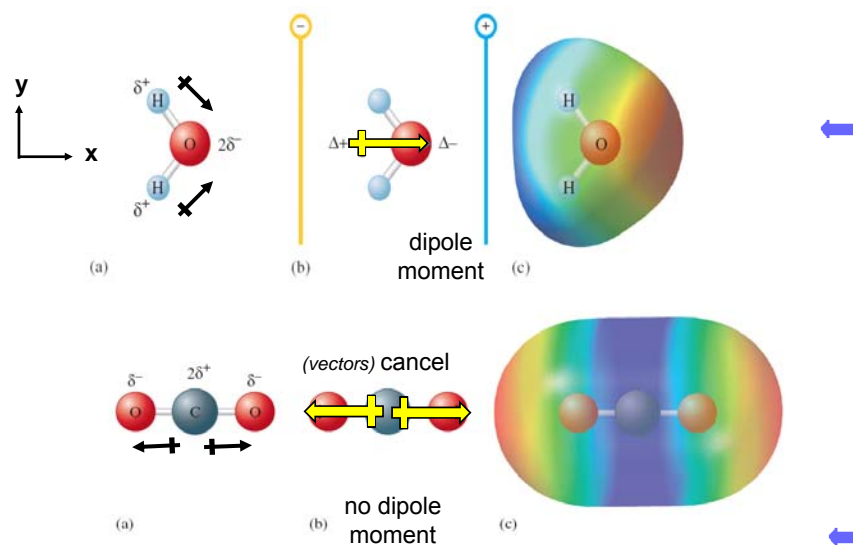
CCl$_4$ and CHCl$_3$

CCl$_4$
⇒

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$_3$ molecule

CHCl$_3$
⇒

**bond dipoles reinforce
dipole moment
polar molecule**

77

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*geometries where polar bonds **MAY** cancel (table 13.4)*

TABLE 13.4

Types of Molecules with Polar Bonds but No Resulting Dipole Moment

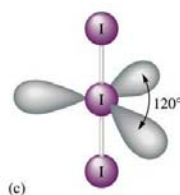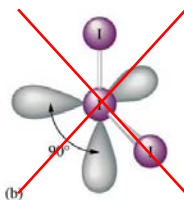| Type		Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	B—A—B	←+ +→	CO$_2$	
Planar molecules with three identical bonds 120 degrees apart	B—A—B 120°		SO$_3$	
Tetrahedral molecules with four identical bonds 109.5 degrees apart			CCl$_4$	

78

39
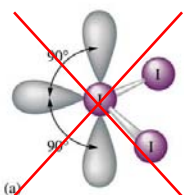
SN=5, where to put lone pairs (I_4 and I_3^-)

2 lone-pairs
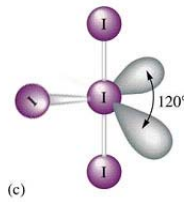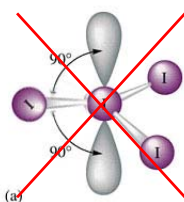
T-shaped molecular geometry

3 lone-pairs

linear molecular geometry

79

SN=6 adjacent vs across

square planar molecular geometry

80

40

Silberberg figure 9.13

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

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
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C≡C	Triple	1.20	839
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C=O	Double	1.23	745
C—N	Single	1.43	305
C=N	Double	1.38	615
C≡N	Triple	1.16	891

83

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

84

42

Ritonavir inhibitor "fits into" HIV Protease
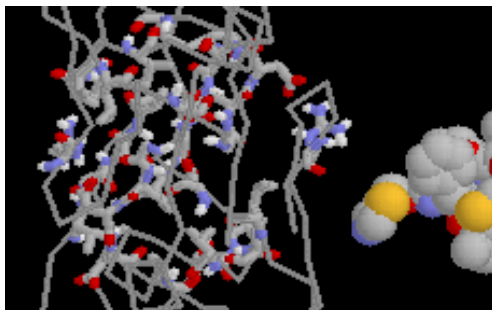
HIV protease inhibitor Ritonavir binding to the protease

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

85

Zumdahl Table 2.5 and 13.5, Silberberg figure 9.3

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

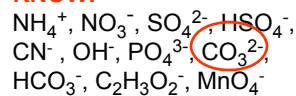| Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}		O^{2-}	F^-	[He]
Na^+	Mg^{2+}	Al^{3+}	S^{2-}	Cl^-	[Ne]
K^+	Ca^{2+}		Se^{2-}	Br^-	[Ar]
Rb^+	Sr^{2+}		Te^{2-}	I^-	[Kr]
Cs^+	Ba^{2+}				[Xe]

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

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^-

86

43

---

triangular cyclic O₃
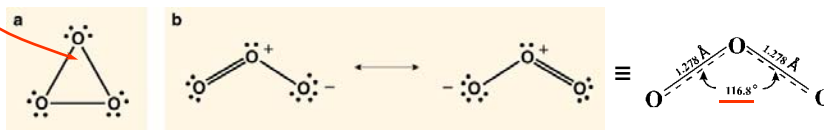
The Story of O
Roald Hoffmann
The Ring
So now we have oxygen chemistry in the atmosphere, in the cell, in a decontamination process. But have we exhausted all of oxygen's secrets?
http://www.americanscientist.org/issues/pub/the-story-of-o/5

60° bond angles are "strained" (unstable);
[discuss later in term (quantum mechanics)]

a   **b**

≡   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 O₃** but has a barrier of no less than 95 kilojoules per mole preventing conversion to the open form.

87

HW-hints Homework #4, Due 26th October

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

Required (submit via WebAssign)

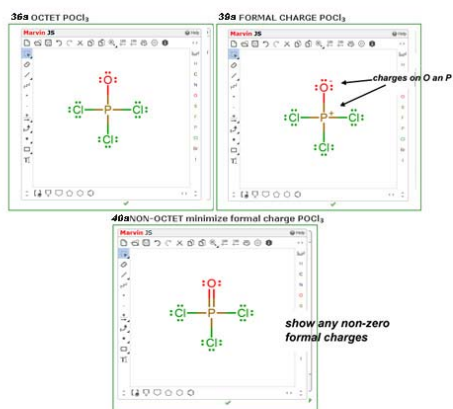|		
29.	Zumdahl #13.15	**electronegativity**
30.	Zumdahl #13.26	**configurations of stable ions (part c: configurations)**
31.	Zumdahl #13.32	**LE**
32.	Zumdahl #13.33	**common valences (oxidation states) empirical fmlas**
33.	Zumdahl #13.41	**LE**
34.	Zumdahl #13.42	**LE**
35.	Zumdahl #13.57	**octet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

Section

S8.   Zumdahl #13.3

88

44

HW#4 probs 36, 39, 40

89

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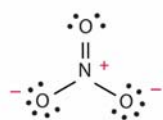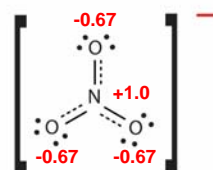39.   Zumdahl #13.72 (for 13.71 a,d,f)   **formal charge (non octet)**

90

45

nitrate ion NO$_3^-$

Lewis **Formal** Charge:

+ 2 other equivalent
resonance structures =

-0.67

+1.0

-0.67   **-0.67**

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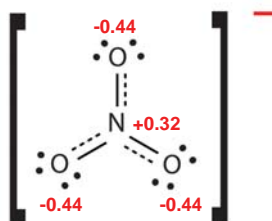and urea molecule upon protonation**

Actual
(calculated by quantum mechanics)

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

**Theoretica
Chimica Acta**

© Springer-Verlag 1992

-0.44

+0.32

-0.44   **-0.44**

91

46