CHEM 103 Molecular Geometry and Valence Bond Theory

Lecture Notes May 2, 2006 Prof. Sevian





Announcements

 The final exam is scheduled for Monday, May 15, 8:00-11:00am
It will NOT be in our regularly scheduled lecture hall (S-1-006). The final exam location has been changed to Snowden Auditorium (W-1-088).



More announcements

Information you need for registering for the second semester of general chemistry

- If you will take it in the summer:
 - Look for chem 104 in the summer schedule (includes lecture and lab)
- If you will take it in the fall:
 - Look for chem 116 (lecture) and chem 118 (lab). These courses are co-requisites.
- If you plan to re-take chem 103, in the summer it will be listed as chem 103 (lecture + lab). In the fall it will be listed as chem 115 (lecture) + chem 117 (lab), which are co-requisites.
 - Note: you are only eligible for a lab exemption if you previously passed the course.



Agenda

- Results of Exam 3
- Molecular geometries observed
 - How Lewis structure theory predicts them
 - Valence shell electron pair repulsion (VSEPR) theory
- Valence bond theory
 - Bonds are formed by overlap of atomic orbitals
 - Before atoms bond, their atomic orbitals can hybridize to prepare for bonding
 - · Molecular geometry arises from hybridization of atomic orbitals
 - σ and π bonding orbitals





Lewis Structure Theory

- The basics
 - Electrons can be located in a molecule (or ion) in only two ways:
 - As a lone pair of electrons that belongs exclusively to one atom
 - As a bonding pair of electrons that is shared between two atoms inside of the molecule (or ion)
 - Electrons form octets around atoms (except hydrogen which can only have one pair to make a complete shell)
- Stretching the Lewis structure theory to explain/predict other structures not predicted by the basic theory
 - Pretend the actual structure is a mix of all possible resonance structures (ch. 8)
 - Allow more than an octet on certain central atoms (ch. 9)
 - Correctly predict observed bond angles





Procedure for drawing a Lewis structure (abbreviated)

- 1. Determine how many total valence electrons
- 2. Decide on central atom and arrange other atoms around it
- 3. Start with single bonds, make octets on all atoms (except H), making double or triple bonds where necessary

Amendment to procedure

4. If it's not possible to draw a simple structure, determine whether central atom can accommodate more than an octet

Which elements can accommodate more than an octet? Any element that has access to un-used *d*-orbitals All elements in period 3 have access to 3*d* orbitals All elements in period 4 have access to either 3*d* or 4*d* orbitals, etc. Summary: all elements at and beyond atomic #13

Examples of more than an octet on the central atom



Only elements in periods 3 and higher (e.g., S, Cl) can do this.



How Lewis Structure Theory Predicts Molecular Shapes



Note: when given the choice, atoms will space apart as far as possible Electron



Where Lewis Structure Theory Breaks Down



- Bond angles predicted by Lewis structure theory are often incorrect
- Another modification to address this: Valence shell electron pair repulsion theory (VSEPR)





How pairs of electrons around a central atom interact



VSEPR results



• Some bond angles are smaller than Lewis structure predicts

Some bond angles are larger than Lewis structure predicts



How do bond polarities sum to determine molecular polarity?



A molecule is a dipole:

1. If it has at least one bond in it that is polar covalent

<u>and</u>

2. If the bond dipoles do not cancel each other out (cancellation happens when bond dipoles are symmetrically located)

Remember how to determine whether a bond is a dipole? Difference in electronegativities of the two atoms in the bond No difference: perfectly covalent Some difference (as between non-metals): polar covalent

Very different (as between a metal and a non-metal): ionic





Let's practice

For each Lewis structure, determine:

- 1. How many pairs of electrons are around the central atom
- 2. What the electron domain geometry must be
- 3. What the molecular geometry is predicted to be
- Whether there are any angles that VSEPR theory predicts to be different from the Lewis structure model
- 5. Whether the molecule is a dipole



Practice #1

XeF₂



Practice #2

SF₄

Two competing theories that predict various properties of molecules

Valence bond theory

- Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
- Lewis structure's electron pairs translated into quantum mechanics
- Electrons in a particular bond are localized to specific valence bond orbitals

Molecular orbital theory

- Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
- Wave functions (molecular orbitals) are formed from all bonding electrons in molecule
- Electrons in all bonds are spread out (delocalized) over all molecular bonding orbitals in molecule

Mathematically, the approaches are different. Results (predictions) are often the same.

Valence Bond Theory



Central ideas:

- Atomic orbitals initially form hybrids to get ready for bonding to form molecules/ions (costs a little bit of energy – less stable)
- 2. Bonds in molecules/ions are formed by the overlap of atomic orbitals (win back a lot of energy much more stable)

Why it costs a little energy to form hybrid orbitals





Four single bonds between one carbon and four hydrogens



- 1. The first bond between two atoms: Overlap occurs on the axis of bond $\Rightarrow \sigma$ orbital
 - Only one σ bonding orbital can form between two atoms





Double bond between two Carbons

- 2. The second (and third) bond between two atoms (if a σ bond has already formed): Overlap occurs outside the axis of a bond $\Rightarrow \pi$ orbital
 - It is possible to form one or two π bonds between atoms



Reserving a p-orbital for making a π bond



Carbon atom with a 2s and three Carbon atom with three sp² 2p orbitals hybridized orbitals and one 2p orbital left over, ready to make 3 σ bonds and 1 π bond 1 1 1 2p 2p 2p 1 1 2p sp² sp² sp² 11 side view 2s top view SO **p**₇ sp² 2py 2s $2p_z$ 2p_x 10m04an1.mov sp²



Double bond between two Carbons

- 2. The second (and third) bond between two atoms (if a σ bond has already formed): Overlap occurs outside the axis of a bond $\Rightarrow \pi$ orbital
 - It is possible to form one or two π bonds between atoms





Reserving two p-orbitals for making two π bonds



Carbon atom with a 2s and three Carbon atom with two sp hybridized 2p orbitals orbitals and two 2p orbitals left over, ready to make 2 o bonds and 2 π bonds 1 1 1 1 2p 2p 2p 2p 2p 1 11 side view sp sp 2s top view p_x sp p₇ sp 2py 2s $2p_z$ 2p_x 10m04an1.mov

09m15an6.m



p_x

Triple bond between two Carbons

- The second (and third) bond between two atoms (if a σ bond has 2. already formed): Overlap occurs outside the axis of a bond $\Rightarrow \pi$ orbital
 - It is possible to form one or two π bonds between atoms .







Consequences of π Bonding



- Atoms can twist around σ bond
- When π bonds are present in addition to a σ bond, the π bond(s) locks the atoms in a specific orientation (molecule is restricted to no twisting around the σ bond)
- Isomer (= same parts) can result
- Simple example: cis- and trans- versions of 1,2-dichloroethylene



 Much of nature works by recognizing specific isomers to the exclusion of others

Resonance and Delocalization of Electrons in π Bonds (example: benzene)



Macroscopic evidence

Laboratory data indicate that benzene has a planar, symmetrical structure

Particle level – valence bond theory prediction

- Delocalized means not localized to a specific location, but instead spread out over many locations
- For example, in benzene, delocalization occurs with bonding electrons in $\boldsymbol{\pi}$ bonds

Symbolic representation





