5.12 Spring 2003
Review Session: Exam #1

I. Review of Lewis Bonding Theory
- A. Ionic Bonding
- B. Covalent Bonding
  - 1. Multiple Bonding
  - 2. Formal Charge
- C. Short-Hand for Chemists
  - 1. Line-Angle Formulas
  - 2. Dashes and Wedges
  - 3. Curved Arrow Formalism

II. Resonance
- A. Drawing Resonance Structures
- B. Energy of Resonance Structures
- C. Structure and Reactivity from Resonance

III. Review of Molecular Orbital Theory
- A. Atomic Orbitals
- B. Sigma-Bonding
- C. Pi-Bonding
- D. VSEPR Theory

IV. Hybridization/LCAO
- A. *sp* Hybridization
- B. *sp*2 Hybridization
- C. *sp*3 Hybridization
  - 1. Rotation of Ethane versus Ethylene

V. Properties of Molecules
- A. Acidity of Organic Molecules
  - 1. Bronsted–Lowry Acidity
    - a) Review of Acid / Base Equations
    - b) Acidity Trends
      - i) Attached Atom
      - ii) Inductive Effects
      - iii) Hybridization
      - iv) Resonance
  - 2. Lewis Acidity
- B. Bond Lengths
- C. Bond Strengths

VI. Alkanes
- A. Molecular Formulas
  - 1. Degrees of Unsaturation
  - 2. Constitutional Isomers
- B. IUPAC Nomenclature
- C. Conformational Analysis
  - 1. Ethane
    - a) Newman Projections
  - 2. Propane
  - 3. Butane

I. Review of Lewis Bonding Theory
- A. Ionic Bonding
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You need to be able to:

- Provide Lewis structures and line angle formulas for given molecular formulas. **Don't forget lone pairs and formal charges!**
- Draw / interpret 3-D structures with dashes and wedges.
- Draw curved arrows to represent simple reaction mechanisms. **Hint: You will frequently start an arrow on a negative charge (electrons!), but never start an arrow on a positive charge (no electrons!).**

1. Provide all of the valid Lewis structures for the following molecules.

CH_2N_2 C_4H_8 CH_3CO_2H

2. Convert the following to line angle formulas.

$(CH_3)_3CCHCH_2$ $(CH_3)_2C(OH)CH_2CH(CH_3)_2$

3. a) Provide a mechanism for the following reaction.

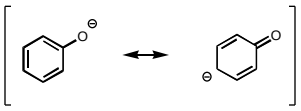
b) Label the electrophile and the nucleophile.

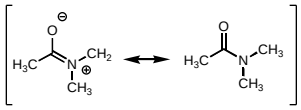
II. Resonance
A. Drawing Resonance Structures
B. Energy of Resonance Structures
C. Structure and Reactivity from Resonance

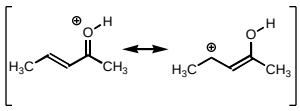
You need to be able to:

- Recognize resonance structures.
- Interconvert resonance structures.
- Predict relative energies and importance.
- Predict reactivity / physical properties using resonance structures.

1. For each pair, circle the most stable resonance structure, and use curved arrows to convert the structure on the left to the structure on the right.





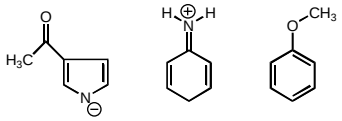


Hint: Generating charges is bad!!

- **When you start with a neutral molecule, don't generate more than two formal charges.**
- **When you start with a charged molecule, don't generate any other formal charges.**

Delocalization = Stabilization

2. Provide all relevant resonance structures for the following molecules, and rank their energies.



III. Review of Molecular Orbital Theory
A. Atomic Orbitals
B. Sigma-Bonding
C. Pi-Bonding
D. VSEPR Theory

IV. Hybridization/LCAO
A. *sp* Hybridization
B. sp^2 Hybridization
C. sp^3 Hybridization
1. Rotation of Ethane versus Ethylene

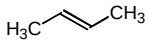
You need to be able to:

- Draw atomic orbitals (*s*, *p*).
- Draw hybrid orbitals (*sp*, sp^2, sp^3).
- Differentiate between σ- and π-bonding.
- Assign hybridization to atoms in a molecule.
- Predict approximate bond angles.
- Draw simple molecular orbital pictures.

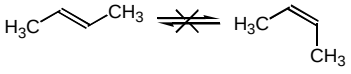
1. Draw the bonding and anti-bonding orbitals resulting from the combination of two p_y orbitals along the x-axis. Label any nodes. Is this σ- or π-overlap?

2. Try to do the same with a p_x and a p_y orbital. Why doesn't this work?

3. a) Draw a molecular orbital picture of the following molecule.



b) Use the picture from part a to explain why the following equilibrium does not occur.



V. Properties of Molecules

A. Acidity of Organic Molecules
  1. Bronsted–Lowry Acidity
    a) Review of Acid / Base Equations
    b) Acidity Trends
      i) Attached Atom
      ii) Inductive Effects
      iii) Hybridization
      iv) Resonance
  2. Lewis Acidity

B. Bond Lengths

C. Bond Strengths

You need to be able to:

- Correlate K_a, pK_a, and acidity.
- Rank relative acidities and explain your reasoning.
- Differentiate between Bronsted-Lowry and Lewis acids and bases.
- Draw mechanisms for acid-base reactions.
- Rank bond lengths and strengths based on bond order.

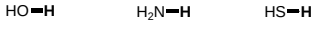
1. Which of the following molecules can act as a Lewis base? Why?

Me_3N **BF_3** **H_2O** **CH_4**

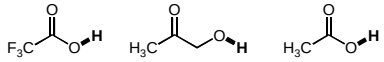
2. The following pair can undergo a Bronsted-Lowry or a Lewis acid-base reaction. Provide the products for both, and use curved arrows to provide the reaction mechanisms.

3. Rank each series by acidity (**1 = most acidic**).

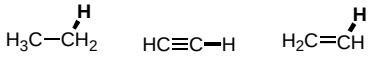
a)



b)



c)



VI. Alkanes

A. Molecular Formulas
  1. Degrees of Unsaturation
  2. Constitutional Isomers

B. IUPAC Nomenclature

C. Conformational Analysis
  1. Ethane
    a) Newman Projections
  2. Propane
  3. Butane

You need to be able to:

- Draw constitutional isomers for a given molecular formula.
- Calculate degrees of unsaturation.
- Draw structures corresponding to IUPAC names.
- Draw Newman projections.
- Determine relative energies of rotational conformers. **Know the rotational energy values on the handout!**
- Draw potential energy diagrams for bond rotations.

1. Draw all of the constitutional isomers of C_5H_{12} and name them using IUPAC nomenclature.

2. For each molecular formula, calculate the degrees of unsaturation and draw two possible constitutional isomers.

C_7H_{12} **C_3H_6** **C_5H_6**

3. a) Approximate the barrier to rotation around the C2–C3 bond of 2,2-dimethylbutane. Draw Newman projections to illustrate your answer.

b) Draw a potential energy diagram for rotation around theC2–C3 bond of 2,2-dimethylbutane.