Key Concepts:

Chapter 1
- Know how to draw Lewis structures and resonance structures
- Understand formal charges and electronegativity trends

Chapter 2: know this chapter because it WILL for sure come back in 51B and 51C the most. If you don’t get this chapter ask for help now because you will not pass the later ochem series without knowing this chapter!!!
- Know the four acidity trends
  - Element effect, resonance effect, inductive effect, and hybridization effect
- Differentiate between Bronsted-Lowry acid-base and Lewis acid-base definitions
- Apply pKa values to determine acid/base equilibria

Chapter 3:
- Understand the relationship between intermolecular forces and physical properties (boiling and melting points, solubility)
- Know the names of main functional groups
  - Refer to Tables 3.1, 3.2 and 3.3 on textbook
- Comfortably draw curved arrows in any given reaction
- Understand impact of polarity on functional group reactivity
  - Read section 3.8 on textbook

Chapter 4:
- Know how to draw Newman projections with various conformations
  - Make sure to be able to draw energy diagrams with different dihedral angles
- Understand the definition of isomers and resonance structures
- IUPAC naming will NOT be on exam but is useful to know basic rules since the textbook and professor uses them
- Accurately draw chair conformations
Final Review KEY

Chapter 5: the hardest chapter in my opinion (which most people agree). Ask for help now if you don’t get this because it is not easy

- Identify chiral molecules and stereogenic centers
- Assign R/S configuration accurately
  - Remember the place the lowest priority in the back or dashed
- Be able to classify relationship between different molecules, such as enantiomers, diastereomers, identical and meso

Chapter 6:

- Classify chemical reactions into substitution, elimination or addition
  - Know how the arrow pushing works
- Know radical transformation (homolysis) and use half-headed arrows for those
- Understand the relationship between Gibbs free energy and $K_{eq}$
- Confidently draw reaction coordination diagrams for one and two step reactions
  - Be able to label activation energy, transition states, intermediates, etc

Chapter 13:

- Know the basic principles of IR and mass spectra
- Assign IR absorption values to key functional groups
- Identify fragmentation patterns in MS

Chapter 14:

- Know the basic principles of HNMR spectroscopy
- Determine chemically equivalent protons
- Propose a structure of a molecule from analyzing IR and HNMR spectra
Final Review KEY

Chapter 1

1. Stalevo is the trade name for a medication used for Parkinson's disease, which contains both L-dopa and entacapone.

![Entacapone structure]

a. Draw a Lewis structure for entacapone.

b. Which C-C bond in entacapone is the longest?

c. Which C-C bond is the shortest?

d. Which C-N bond is the longest?

e. Which C-N bond is the shortest?
Final Review KEY

i. Shortest C-C bond is labelled in red and longest C-N bond is labelled in blue. The shortest C-C bond has the greatest s character percentage as it is formed from Csp and Csp^2 bonds. The longest C-N bond has the least s character because it is formed by Csp^3 and Nsp^3 bonds.

f. Used curved arrows to draw a resonance structure that is an equal contributor to the resonance hybrid.
Final Review KEY

Chapter 2

2. Draw the products of each acid-base reaction.

a. Acid

\[
\text{\textbf{b. Base}}
\]

b. Base

3. Answer the following questions about esmolol, a drug used to treat high blood pressure sold under the trade name Brevibloc.
Final Review KEY

a. Label the two most acidic hydrogen atoms in esmolol and explain which H is more acidic

i. The hydrogen atom bonded to oxygen is the most acidic H due to element effect. Remember that protons directly bonded to electronegative atoms will be deprotonated more readily.

b. What products are formed when esmolol is treated with 1 equivalence of NaH?

i. 


c. What products are formed when esmolol is treated with 1 equivalence of HCl?

i. The most basic site on esmolol is the lone pair on nitrogen (think opposite of acidity trends), which can readily act as a base when a strong acid like HCl is present

ii. 


d. Label all carbons that bear a positive dipole.

i.
Final Review KEY

ii. The carbons labelled in red all bear a positive charge because they are adjacent to electronegative atom(s) like nitrogen and oxygen which pulls its electron density away.

Chapter 3

4. Rank the compounds in each group in order of increasing boiling point.

a. Pentan-1-ol > butan-1-ol > 1-bromobutane > pentane. Pentan-1-ol has the highest boiling point because it has the largest surface area (strongest VDW).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intermolecular forces present</th>
<th>Boiling point ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>VDW</td>
<td>4</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>VDW, dipole-dipole, hydrogen bonding</td>
<td>2</td>
</tr>
<tr>
<td>1-bromobutane</td>
<td>VDW, dipole-dipole</td>
<td>3</td>
</tr>
<tr>
<td>Pentan-1-ol</td>
<td>VDW, dipole-dipole, hydrogen bonding</td>
<td>1</td>
</tr>
</tbody>
</table>

b. Cyclobutanol > tetrahydrofuran > cyclopentane

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intermolecular forces present</th>
<th>Boiling point ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentane</td>
<td>VDW</td>
<td>3</td>
</tr>
<tr>
<td>Cyclobutanol</td>
<td>VDW, dipole-dipole, hydrogen bonding</td>
<td>1</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>VDW, dipole-dipole</td>
<td>2</td>
</tr>
</tbody>
</table>
Final Review KEY

5. Many drugs are sold as their hydrochloride salts ($R_2NH_2^+$, Cl$^-$), formed by reaction of an amine with HCl.

\[ \text{acebutolol} \]

a. Draw the product (a hydrochloride salt) formed by reaction of acebutolol with HCl.

\[ \text{acebutolol} \rightarrow \text{hydrochloride salt} \]

i. The most basic site in acebutolol is the lone pair on sp$^3$ nitrogen, thus it will grab a proton from HCl.

b. Discuss the solubility of acebutolol and its hydrochloride salt in water.

i. Both acebutolol and its hydrochloride salt product is soluble in water due to the presence of multiple hydrogen bond donors and acceptors. The product is more soluble in water because the positive charge in nitrogen increases the polarity of the compound.
Final Review KEY

Chapter 4

6. Classify each conformation as staggered or eclipsed around the indicated bond, and rank the conformations in order of increasing stability.

\[ C > A > D > B. \]

B and D are in eclipsed conformation which means they are both unstable than the staggered conformation seen in structures A and C. C is the most stable since it has the anti staggered conformation with the two bulkiest groups in opposite directions. On the other hand, B is the least stable since the two bulkiest groups are stacked on top of each other leading increased steric and torsional strains.

7. Draw the more stable chair conformation for each trisubstituted cyclohexane.
Final Review KEY

ii. All the methyl substituents are in equatorial position.

b.

b. Only one methyl group is in axial position, and all methyl groups are facing away from one another, which prevents steric strains.

i.

Chapter 5

8. Saquinavir (trade name Invirase) belongs to a class of drugs called protease inhibitors, which are used to treat HIV (human immunodeficiency virus).
Recall that a stereocenter is a carbon with 4 different groups (atoms or chains). A chair is more stable when it has groups in the equatorial position. Also, an enantiomer is a non superimposable mirror image. Another way to think of it is that all the stereocenters in an enantiomer pair are opposite. All $R \rightarrow S$ and $S \rightarrow R$. Lastly, a diastereomer has at least one, but not all stereocenters flipped.

a. Locate all stereogenic centers in saquinavir, and label each stereogenic center as R or S.

b. Draw the enantiomer of saquinavir.
c. Draw a diastereomer of saquinavir.

![Diagram of saquinavir molecule]

9. Salicin is an analgesic isolated from willow bark.

![Diagram of salicin molecule]

Recall that a chair is more stable when it has groups in the equatorial position. Also, an enantiomer is a non superimposable mirror image. Another way to think of it is that all the
Final Review KEY

Stereocenters in an enantiomer pair are opposite. All R→S and S→R. Lastly, a diastereomer has at least one, but not all stereocenters flipped.

a. Convert the given skeletal structure to a representation that shows the more stable chair form of the six-membered ring.

\[ \text{more stable ring} \]
\[ \text{all groups equatorial} \]

b. Draw a diastereomer of salicin at C1 and label each substituent on the six-membered ring as axial or equatorial.

\[ \text{diastereomer} \]
\[ \text{re-draw} \]
\[ \text{All other groups on the ring are equatorial.} \]

\[ \text{axial} \]

C. Draw the enantiomer of salicin
Chapter 6

10. The conversion of C(CH₃)₃I to (CH₃)₂C=CH₂ can occur by a one-step mechanism, as shown in Equation [1]. Assume Equation [1] represents an endothermic reaction and draw an energy diagram for the reaction. Label the axes, reactants, products, Eₐ, and ∆H°. Draw the structure for the transition state.

When drawing diagrams, keep the following in mind:
- Endothermic means the products will be higher in energy.
- Transition state is the highest energy point on the graph.
- ∆H° is the total energy change between the products and reactants.
- One step = one “hill” on the graph.
Final Review KEY

11. (a) Draw in the curved arrows to show how A is converted to B in Step [1]. (b) Identify X, using the curved arrows drawn for Step [2].

Recall that when doing these types of problems, you need to use double headed arrows. Single headed ones are when you move a single electron. In this case, we are moving electron pairs. Also, recall that a nucleophile likes to attack an electrophile. The former is electron rich whereas the latter is electron poor. In this example, the oxygen is the nucleophile and the H is the electrophile. This continues in step B, where Br⁻ is the nucleophile and the carbon bonded to the oxygen is the electrophile. Either carbon can be attacked since they are equivalent in their electron distribution to oxygen.
Final Review KEY
Chapter 13

12. Match each compound to its IR spectrum.

For these kinds of problems, it is best to have certain common values memorized. Then, look at each compound one-by-one and note the most characteristic functional group (i.e. and alcohol, C=O, alene, etc). After that, all you need to do is find that functional group in the IR spectrum. Start with the easiest to identify group which is an alcohol. These tend to have broad peaks. You can then eliminate that. After, look for C=O bonds which have sharp peaks at around 1700 cm⁻¹. Continue this process for each group. Below, you will find all the answers.
13. What information is obtained from the mass spectrum and IR spectrum of an unknown compound X? Assume X contains the elements C, H, and O.
Step 1. Use the molecular ion to determine possible molecular formulas. Use an exact mass (when available) to determine a molecular formula.
- Use the procedure outlined in Sample Problem 13.2 to calculate possible molecular formulas. For a molecular ion at m/z = 88:

\[
\begin{align*}
\frac{88}{12} &= 7 \text{ C's} \\
&\quad \rightarrow \quad C_7H_4 \rightarrow C_6O \rightarrow C_5H_{12}O \rightarrow C_4H_8O_2 \rightarrow C_3H_4O_3
\end{align*}
\]

- Discounting C7H4 (a hydrocarbon) and C6O (because it contains no H's) gives three possible formulas for X.
Final Review KEY

• If high-resolution mass spectral data are available, the molecular formula can be determined directly. If the molecular ion had an exact mass of 88.0580, the molecular formula of X is C₄H₈O₂ (exact mass = 88.0524) rather than C₅H₁₂O (exact mass = 88.0888) or C₃H₄O₃ (exact mass = 88.0160).

Step 2 Calculate the number of degrees of unsaturation (Section 10.2).
• For a compound of molecular formula C₄H₈O₂, the maximum number of H’s = 2n + 2 = 2(4)+ 2 = 10.
• Because the compound contains only 8 H’s, it has 10 – 8 = 2 H’s fewer than the maximum number.
• Because each degree of unsaturation removes 2 H’s, X has one degree of unsaturation. X has one ring or one sigma bond.

Step 3 Determine what functional group is present from the IR spectrum.
• The two major absorptions in the IR spectrum above 1500 cm⁻¹ are due to sp³ hybridized C–H bonds (~3000–2850 cm⁻¹) and a C=O group (1740 cm⁻¹). Thus, the one degree of unsaturation in X is due to the presence of the C=O.

Thus, the correct compound is C₄H₈O₂
14. Propose a structure consistent with the data: \( \text{C}_9\text{H}_{10}\text{O}_2 \): IR absorption at 1718 cm\(^{-1} \)

Begin by calculating the degrees of unsaturation.

\[
\text{Degrees of Unsaturation} = \frac{2C + 2 + N - H - X}{2}
\]

\( C = \) # carbons \( H = \) # hydrogens \( N = \) # nitrogens \( X = \) # halogens

In this case, you should get 5 degrees of unsaturation. This could mean there are 5 double bonds or could have 5 rings (or any combination of multiple bonds and rings that add up to 5). Next, consider the IR absorption. In this case, it indicates that it is a C=O (Best to memorize these values). Finally, consider the NMR last and fill a table with what you find.

<table>
<thead>
<tr>
<th>Type of peak</th>
<th>PPM</th>
<th>Hydrogens</th>
<th>Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplet</td>
<td>7.4-8.1 ppm</td>
<td>5 H’s</td>
<td>Complex ~ Benzene</td>
</tr>
<tr>
<td>Quartet</td>
<td>4.4 PPM</td>
<td>2 H’s</td>
<td>Split by 3 H’s</td>
</tr>
</tbody>
</table>
### Final Review KEY

<table>
<thead>
<tr>
<th>Triplet</th>
<th>1.3 ppm</th>
<th>3 H’s</th>
<th>Split by 2 H’s</th>
</tr>
</thead>
</table>

**C₆H₁₀O₂:**
- 5 degrees of unsaturation
- IR absorption at 1718 cm⁻¹: C=O
- **NMR data:**
  - multiplet at 7.4–8.1 ppm, 5 H on a benzene ring quartet at 4.4 ppm, 2 H, split by 3 H’s
  - triplet at 1.3 ppm, 3 H, split by 2 H’s

![Diagram](image)

downfield due to the O atom