

Midterm I Guide for Chem109C
(Kahn, Spring 2005)

Midterm I will be held on Tuesday, April 19th, 5–6:20 PM in Chem1179.

In general, exam questions are based on topics that we covered in the lectures. However, in some cases the textbook provides more detailed examples of these topics and you are expected to be familiar with this material as well. Topics covered in quizzes and vitamin problems may be revisited in the exam. Furthermore, I anticipate that you are familiar with basic concepts of organic nomenclature, stereochemistry, and reactivity that were taught in Chem 109A and Chem109B.

The exam questions are designed to test your knowledge and understanding of the following topics:

Molecular Orbital Theory

- Bonding, nonbonding, and antibonding orbitals
- Drawing molecular orbital diagrams
- Recognizing HOMO and LUMO orbitals in ground state molecules
- Description of chemical reactions as flow of electrons from one orbital to another
- Electron delocalization
- Stability of allyl cation; reactions of allyl halides
- Conjugated vs. non-conjugated π systems
- Properties of the amide bond

Ultraviolet Spectroscopy

- Lambert–Beer law
- $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions
- Effect of conjugation in π system on $\lambda_{\max}$
- Solvatochromic shifts
- MO-based explanation for the blue shift in $n \rightarrow \pi^*$ transition in carbonyl compounds

Pericyclic Reactions

- Distinction between three kinds of pericyclic reactions
- Frontier orbitals and orbital symmetry considerations, excited state HOMO
- Thermal and photochemical reactions.
- MO description of cycloaddition reactions
- Diels–Alder reaction, prediction of product stereochemistry
- Effect of electron-withdrawing substituents in dienophile on reaction rate
- Electrocyclic reactions, prediction of product stereochemistry
- Woodward–Hoffman rules for electrocyclic reactions.
- Sigmatropic rearrangements, recognizing breaking bonds, forming bonds
- Cope rearrangement: writing product structures (no stereochemistry required)
- TE-AC mnemonic for selection rules
- Synthetic utility of pericyclic reactions, simple retrosynthetic analysis

Carbohydrates

Structural aspects:

- General formula and functional groups
- Classification based on number of carbons
- Classification based on the nature of the carbonyl functionality
- Classification based on the extent of polymerization (mono-, di-, oligo-, polysaccharides)
- Classification into D- and L-isomers
- Fisher projections, R, S nomenclature
- Enantiomers, diastereomers, epimers
- Structure of D-glyceraldehyde and L-glyceraldehyde
- Structures of D-ribose, D-glucose, D-mannose, D-galactose and D-fructose (open chain)
- Structures of D-ribose, D-glucose, D-mannose, D-galactose and D-fructose (cyclic hemiacetal form both in Fisher and Haworth projections)
- Aldonic acids and aldaric acids
- Nomenclature of disaccharides: how to specify the linkage
- Be able to recognize simple disaccharides: maltose, cellobiose, trehalose, and lactose

Chemical reactions:

- Oxidative chemistry of the aldehyde functionality: aldonic acids
- Oxidative chemistry of the primary alcohol functionality: aldaric acids
- Tollens test with aldoses and ketoses; enolization of ketoses
- Reductive chemistry of the aldehyde functionality
- Osazone formation
- Nucleophilic addition to carbonyl carbon;
- Chain elongation: Kiliani-Fisher synthesis
- Chain shortening: Ruff degradation
- Formation and properties of hemiacetals
- Formation and properties of acetals
- Intramolecular hemiacetal formation: cyclic structures
- α,β anomers; conformational stability in glucose
- Furanoses and pyranoses
- Formation of disaccharides
- Reducing and non-reducing disaccharides
- Alkylation of free hydroxyl groups with methyl iodide

Analysis and properties:

- Chiral properties of polyhydroxyaldehydes
- Chiral properties of aldonic acids
- Chiral properties of aldaric acids
- Historic importance of osazones
- Identification of monosaccharides (e.g. Fisher's proof of glucose structure)
- Mutarotation as tool to distinguish hemiacetals from acetals
- Determination of ring size via methylation analysis
- Determination of disaccharide structures via methylation analysis

Amino acids

α -aminocarboxylic acids as a special group of amino acids

General structure of α -aminocarboxylic acids

D, L nomenclature

R, S nomenclature

Names and structures of:

glycine,

alanine,

serine,

cysteine,

aspartic acid,

glutamic acid,

asparagine,

glutamine,

phenylalanine,

tyrosine, and

lysine.

Miscellaneous

Favorskii rearrangement

Fenton reagent

Distinction between S_N1 , S_N2 , and nucleophilic addition mechanisms