

CHEMISTRY DEPARTMENT COMPREHENSIVE EXAM INFORMATION

Purpose

A student majoring in chemistry is required to pass a comprehensive examination, which must be taken in the final semester. The exam is designed to give majors an opportunity to showcase their knowledge from the different courses they have taken in the department.

Exam Format

There are three parts to the comprehensive exam process: the general competency exam, the chemical literature exam, and the oral exam.

Part I: General Competency Exam. The object of the first written part of the comprehensive exam is to demonstrate general competence in all five sub-disciplines of chemistry (analytical, biochemistry, inorganic, organic, and physical).

Part II: Chemical Literature Exam. The object of the second written part of the comprehensive exam is to demonstrate the ability to analyze the chemical literature via an in-depth understanding of the five sub-disciplines of chemistry. The questions are written with respect to the 2 literature papers chosen by the faculty. These papers will be distributed to comping seniors by the department chair prior to the start of winter break. Students can use their annotated literature papers during the exam. These annotated papers should be turned in with the exam.

Part III: Oral Exam. The object of the oral comprehensive exam is to demonstrate the ability to verbally explain concepts of the five sub-disciplines of chemistry. While the content from the written exams is a potential starting point for questions during the oral exam, faculty can ask questions on any aspect of chemistry. There will be 4 faculty that will participate in a student's oral exam. Students will not be told in advance which faculty will be in their oral exam. A comping senior is allowed to have a non-senior chemistry major observe if desired. It should be stressed, however, that this is not a requirement of the oral exam.

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Exam Timing

The availability and due dates for the parts of the comprehensive exam are as follows:

Exam	Exam Length	Availability Date	Due Date/Time
General Competency (Written Part I)	3 1/2 hours	First Tuesday of spring semester at 9:00 am	First Wednesday of spring semester at 4:00 pm
Chemical Literature (Written Part II)	3 1/2 hours	First Thursday of spring semester at 9:00 am	First Friday of spring semester at 4:00 pm
Oral	1 hour	Second Thursday and Friday of spring semester	

Written exams can be picked up from the department chair when available.

Grading

The entire chemistry department has a role in grading the written exams. Each question is graded by at least two professors using a 5-point scale; each professor assigns a separate score, and these scores are averaged together. Scores will not be provided to students; the department uses these data to determine grades for either Distinction, Pass, and Fail. The faculty will attempt to grade the written parts of the comprehensive exam as soon as possible. Students can expect to have their written exams returned to them for review no later than 48 hours prior to their oral exam (typically by noon of the second Tuesday of the spring semester). Students will return their written exams prior to the oral exam; written exams will not be returned after the oral exam.

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The Comp Review Guide (aka Things That All Chemistry Majors Should Know)

A note about this guide: Since this guide was prepared by compiling the concepts thought to be central to each sub-discipline by the faculty members in that area, some topics may appear more than once.

I. General Concepts

A. Formula, charge and structure of common ions (non-inclusive list):

nitrate	sulfate
phosphate	carbonate
permanganate	chromate
dichromate	halides

B. Balancing equations and reaction stoichiometry

1. Net-ionic equations
2. Acid-base and precipitation
3. Redox including use of half cell potentials
4. Limiting reagent

C. Electronic configuration and periodicity

1. Size
2. Effective nuclear charge
3. Electronegativity
4. Ionization energy
5. Electron affinity

D. Basic bonding models

1. Lewis structures
 - a) formal charges
 - b) resonance
 - c) oxidation number
2. Valence bond theory
 - a) VSEPR
 - b) hybridization
3. Molecular orbital theory

E. Equilibria

1. Calculation of pH
 - a) Strong acids and bases
 - b) Weak acids and bases
 - c) Polyprotic systems
 - d) Buffer systems (Henderson-Hasselbalch equation)
2. Equilibria involving metal-ligand systems
3. Solubility equilibria
4. Graphical methods of representing acid/base equilibria (e.g., alpha diagrams, titration curves)
5. LeChatelier's Principle

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And for each area (in alphabetical order)

- I. Analytical Chemistry
 - A. The analytical method
 1. Criteria for the selection of a particular analytical method (capabilities and limitations)
 2. Importance of sampling and sample preparation
 - B. Statistics and calibration methods
 1. Using significant figures properly
 2. Calculation of mean, standard deviation, and uncertainty
 3. Calculation of concentration (e.g., molarity, molality, ppm, wt%)
 4. Using a calibration curve
 5. Internal standards and standard addition
 6. Limits of detection and quantitation
 - C. Acid-base equilibria (see above items listed under section E for “General Concepts”)
 - D. Spectroscopy
 1. Interpretation of the electromagnetic spectrum
 2. Absorption and emission spectroscopy (UV, visible, fluorescence, IR, Raman, NMR)
 - a) Description of the physical process
 - b) Description of the instrumentation (5 modules)
 3. Using the Beer-Lambert Law ($A = \epsilon bc$)
 4. Interpretation of the Jablonski (energy) diagram (absorption, relaxation, luminescence, etc.)
 - E. Mass spectrometry
 1. Description of instrumentation (mass analyzers: B, E, Q, TOF, and Ion-trap)
 2. Description of common ionization methods (CI, EI, ESI, and MALDI)
 3. Interpretation of mass spectra (fragmentation pathways)
 4. Description of coupling separation techniques to MS
 - F. Separations
 1. Band broadening theory (van Deemter equation/curves)
 2. Interpretation of a chromatogram
 3. Description of the instrumentation for GC, HPLC, IEC, MEC, AC, and CE (5 modules)
 - a) HPLC: Explanation of loop injection
 - b) CE: Explanation of electroosmosis
 4. Description of ways to improve separation for GC and HPLC
 - a) GC: Temperature programming
 - b) HPLC: Isocratic vs. gradient elution
 - G. Electrochemistry
 1. Identification of redox reactions/systems (electron transfer)
 2. Calculation of cell potentials from standard potentials
 3. Calculation of cell potentials using the Nernst equation
 4. Potentiometry

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- a) Description of reference electrodes (e.g., SHE, SCE, Ag/AgCl)
- b) Description of ion-selective electrodes (e.g., glass pH electrode, fluoride electrode)

H. Electroanalytical techniques

1. Description of the instrumentation (5 modules, including three-electrode cell)
2. Description of potential waveforms (e.g., cyclic, square-wave, differential-pulse)
3. Interpretation of a cyclic voltammogram (at macroelectrode and at microelectrode)
4. Description of mass transfer modes (i.e., diffusion, migration, convection)

II. Biochemistry

A. Protein Structure

1. Amino acid structure
2. Examples of 2° structures and basis for formation
3. Folding pathways

B. Catalysis

1. Know organic reactions with biological analogs
2. Understand mechanisms enzymes use to enhance reactivity
3. What is transition state theory and how is it used?

C. Kinetics

1. Understand the derivation of the Michaelis-Menten (or Briggs-Haldane) equation.
2. Understand enzyme inhibition and its effect on kinetic plots
3. Understand the relationship between kinetic constants and free energy diagrams

D. Thermodynamics

1. Understand the basis (H and/or S) for all biochemical events (i.e. protein folding, binding, catalysis, etc.).
2. Understand thermodynamic coupling as it relates to metabolic pathways.

E. Cooperativity

1. How does it arise, general models and molecular mechanisms?
2. What is its significance?

F. Metabolic Pathways

1. Glycolysis.
2. Krebs cycle.
3. Electron transport chain.

G. Acid-base chemistry as it relates to amino acid side chain ionization and reactivity

III. Inorganic Chemistry

A. Basic group theory

1. Assignment of point groups
2. Use of character tables to predict IR/Raman spectra
3. Application of group theory to MO theory

B. Bonding theories for metal complexes

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1. Crystal field theory
 2. Ligand field theory
 - C. Reaction mechanisms
 1. Substitution reactions (associative and dissociative)
 2. Electron transfer (inner and outer sphere including Marcus theory)
 - D. Organometallic chemistry
 1. Stability rules (16/18 electron rule, Wade /Mingos rules)
 2. Important industrial organometallic reaction mechanisms
 - a) Wacker oxidation
 - b) Oxo (hydroformulation) process
 - c) Monsanto acetic acid synthesis
 - E. Bioinorganic Chemistry (active site chemistry of metalloproteins)
 - F. Inorganic spectroscopy
 1. UV-vis of metal complexes
 2. Multinuclear NMR (P, F, S = 1/2 metals)
- IV. Organic Chemistry
- A. Nomenclature for simple organic compounds - IUPAC and common.
 - B. Structure-property relationships such as
 1. Relative acidity/ basicity
 2. Relative nucleophilicity / electrophilicity
 3. Resonance structures for anions, cations, and radicals
 - C. Reaction mechanisms
 1. Carbonyl (Enolates, Enamines/Iminium Ion, Carb. Acid Derivs, Wittig, Hydrates, Acetals)
 2. Nucleophilic substitution (S_N1 and S_N2)
 3. Elimination reactions ($E1$ and $E2$)
 4. Aromatic substitution (Electrophilic and Nucleophilic)
 5. Electrophilic addition to double bonds
 - a) HX
 - b) X_2
 - c) X_2/H_2O
 - d) H_2O/H_3O^+
 - e) Hydroboration
 - f) Simmons-Smith
 - g) Epoxidation (peroxides and peroxyacids)
 6. Pericyclic Reactions
 - a) Diels-Alder
 - b) Claisen Rearrangement
 7. Radical Reactions (X_2 w/ light or heat; NBS; HBr and Peroxides)
 - D. Spectroscopy (basic theory, what information is obtained with each technique, interpreting spectra)
 1. IR
 - a) Frequency ranges (stretches and bends) for functional groups, including hydrocarbons

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2. ^1H NMR
 - a) General chemical shift ranges for protons (methyl, methylene, methine, alcohol, vinyl, etc)
 - b) Splitting patterns versus integrals
 - c) Coupling constant ranges for vinyl protons (cis, trans, and geminal) and aromatic protons ($^3J_{\text{ortho}}$, $^4J_{\text{meta}}$, $^5J_{\text{para}}$)
 3. ^{13}C NMR
 - a) Why are peaks singlets?
 - b) General Chemical shift values and its relationship to Proton NMR
 4. MS
 - a) Base peak versus molecular ion
 - b) Assigning possible structures to peak numbers in the spectrum
- E. Stereochemistry
1. Stereoisomers: enantiomers, diastereomers, meso, and geometric (cis/trans, E/Z)
 2. Fischer, Newman, Sawhorse, and Line-Angle drawings
 3. Reactions that create or destroy stereocenters
 4. Conformational Analysis
 - a) Chair and Boat for cyclohexane
 - b) Axial and equatorial positions on chair as it relates to stability and cis/trans isomerism
 - c) Open Chains: staggered, eclipsed, anti, and gauche and the relationship to stability
- V. Physical Chemistry
- A. Spectroscopy
1. How spectroscopy is used to obtain structural information.
 2. Explain the theoretical background of NMR, IR, and UV-VIS.
- B. Quantum Theory
1. Significance of quantum numbers and how they are related to the properties of the electron.
 2. The wave-particle duality.
- C. Chemical Bonding Theories
1. Lewis structures.
 2. Basic ideas of molecular orbital theory.
- D. Kinetics
1. Describe the kinetic theory of gases and the Maxwell-Boltzmann distribution of molecular speeds.
 2. Determine the order of reaction and the reaction mechanism.
 3. Understand equations and graphs describing zero, first, and second order reactions.
 4. Demonstrate that a proposed mechanism is (or isn't) consistent with an experimentally determined rate law.
 5. Describe collision theory.
 6. Describe transition state theory.

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E. Thermodynamics

1. First, second, and third laws of thermodynamics
2. Hess' Law
 - a) Know the terminology and application to chemical reactions of all types.
 - b) Apply heats of combustion and heats of formation to heats of reaction.
3. Internal energy, enthalpy, Gibbs free energy, and entropy changes
 - a) Manipulate the first and second laws of thermodynamics.
 - b) Evaluate the change in thermodynamic energy for a reaction.
 - c) Explain how temperature effects can be taken into consideration in determining the change in energy for a reaction.
 - d) Relate the equilibrium constant to thermodynamic energies.

F. Phase diagrams and colligative properties

1. Interpret two-component phase diagrams, both P vs. T and G vs. T.
2. Understand phase transitions and apply the Clausius-Clapeyron equation.
3. Understand and diagram the effect of colligative properties on pressure as a function of temperature and on G as a function of temperature.
4. Understand the role of intermolecular forces in pure substances and mixtures.

G. Statistical Mechanics

1. Understand ensembles, both microcanonical and canonical.
2. Interpret thermodynamic functions such as entropy, energy, and chemical potential in terms of the partition function and temperature.
3. Apply the Sackur-Tetrode equation for an ideal gas to determine the standard molar entropy.
4. Describe the intermolecular interactions in a non-ideal gas in terms of the Lennard-Jones potential and understand how these interactions are manifested in an equation of state for a non-ideal gas.