# Screening Exam Topics for Graduate Students
# Organic/Materials Track

## Topic 1. Fundamental Concepts of Bonding

*Students should be able to:*

• Explain molecular structure and models of bonding.

• Apply atomic orbitals, Lewis structures, formal charge, VSEPR, hybridization, dipoles, resonance, bond length/strength, polarizability, stereoelectronics, orbital overlap, and related concepts to explain molecular structure and reactivity.

• Use molecular orbital theory to describe electronic structure and behavior of molecules.

• Describe non-covalent interactions such as ion pairing, hydrogen-bonding, electrostatic (dipole), pi interactions, induced-dipoles, hydrophobicity and their impacts on molecular structure, reactivity, and/or behavior.

## Topic 2. Fundamental Concepts of Strain and Stability (Thermodynamic Driving Forces)

*Students should be able to:*

• Explain types of energy involved in describing a reaction system (favorable, unfavorable, fast, slow): Gibbs free energy, enthalpy, entropy.

• Rationalize reaction design and reactivity using bond dissociation enthalpies, pKa, various types of strain energies, aromaticity, conjugation, hyperconjugation, and related concepts.

• Perform conformational analysis on acyclic and cyclic systems. This includes being able to draw meaningful three-dimensional projections of molecules.

## Topic 3. Acid–Base Chemistry

*Students should be able to:*

• Explain and predict structural impacts on pKa and reactivity.

• Describe the Hammett acidity function.

• Describe Lewis acid/base chemistry, including HSAB theory and how it can inform catalyst selection and/or reaction design.

## Topic 4. Fundamental Concepts of Stereochemistry

*Students should be able to:*

• Explain stereogenicity and stereoisomerism, including the different types of chiral molecules and their relationships to one another (R/S; E/Z; D/L; ent, epi; enantiomers; diastereomers; atropisomers; anomers; etc).

• Apply homotopic, enantiotopic, diastereotopic in reaction design and molecular characterization. This includes transition state analysis to relay stereochemical information.

• Differentiate among possible stereochemical reaction outcomes: stereoselective, enantioselective, diastereoselective, stereospecific, stereoretentive, stereoinvertive, stereoablative, regioselective, chemoselective, resolution, etc.

## Topic 5. Fundamental Concepts of Reaction Kinetics and Thermodynamics

*Students should be able to:*

• Explain transition state theory, including Arrhenius vs Eyring equations, Boltzmann distribution, activated complex, rate-determining step (transition state), and molecularity.

• Apply the Hammond postulate, Curtin–Hammett principle, steady state approximation, microscopic reversibility, kinetic vs thermodynamic control (reversibility), and related concepts to explain/predict reaction design and reactivity.

• Use kinetic analyses and conditions (zero, first, second, pseudo-first, equilibrium, initial-rate, and saturation kinetics + half-life) to understand, develop, and/or optimize reaction systems.

## Topic 6. Applications of Kinetic and Thermodynamic Experiments for Mechanism

*Students should be able to:*

• Explain isotope effects (origins, primary vs secondary, inverse vs normal, kinetic vs equilibrium).

• Apply linear free energy relationships (LFERs) like Hammett plots to reaction systems. This includes understanding the origins of sigma and rho values. It also includes familiarity with other LFERs such as Taft, Grunwald–Winstein, Schleyer, Swain–Scott, Edwards and Ritchie, and other variations.

## Topic 7. Fundamental Concepts of Complex Molecule Synthesis

*Students should be able to:*

• Apply retrosynthesis: disconnect strategic bonds of a given target for facile forward synthesis from smaller building blocks. Highlight key, powerful reactions that rapidly and/or reliably generate chemical complexity.

• Explain idealized retrosynthesis along the line of Corey's logic of synthons, synthetic equivalents, disconnections that optimize simplification (even if a transformation is unknown).

## Topic 8. Fundamental Concepts of Arrow Pushing and Reaction Mechanism

*Students should be able to:*

• Draw arrow pushing mechanisms for common reactions, including the following which contain many basic principles: electrophilic, nucleophilic, and radical aromatic substitutions, cross-aldol reactions, Wittig olefinations, McMurry couplings, pinacol couplings, Appel reaction, Finkelstein reaction, Claisen/Cope rearrangements, Diels–Alder reaction, click reaction, Huisgen reaction, olefin metathesis, Knoevenagel condensation, Prins reaction, Swern oxidation, Fischer indole synthesis, and Piancatelli rearrangement.

• Produce models of transitions states that explain any form of selectivity. This includes use of orbital symmetry and overlap, FMO theory, Woodward–Hoffman rules, Baldwin's rules, and related principles.

• Provide a reasonable reaction mechanism based on fundamentals for any reaction presented given the role of each reagent.

## Topic 9. Structure and Reactivity of Reactive Intermediates

*Students should be able to:*

• Explain molecular structure and reactivity of carbocations.

• Explain molecular structure and reactivity of carbanions.

• Explain molecular structure and reactivity of radicals.

• Explain molecular structure and reactivity of onium ions and ylides.

• Explain molecular structure and reactivity of carbenes/nitrenes, including singlet and triplet states.

### Topic 10. Reactivity of Transition Metals

*Students should be able to:*

• Explain bonding models and structure of transition metal complexes.

• Draw arrow pushing mechanisms and catalytic cycles for major metal-catalyzed processes; including, hydrogenation, catalytic cross-coupling reactions with various electrophilic and/or nucleophilic coupling partners (Suzuki, Sonogashira, Stille, Yamada, Negishi, Buchwald-Hartwig, and Heck reactions, etc), olefin metathesis, C–H bond functionalization.

• Describe elementary steps (oxidative addition, transmetalation, and reductive elimination, for example) involved in major transition-metal catalyzed reactions that are applicable in other metal-catalyzed reactions (cycloisomerization, Pauson-Khand, etc).

### Topic 11. Fundamental Concepts of Polymer Synthesis

*Students should be able to:*

• Define, illustrate, and differentiate step-growth and chain growth polymerizations.

• Define living polymerization and explain the mechanisms and limitations of cationic, anionic, ring-opening (including metathesis), and various radical living polymerizations.

• Draw mechanisms for Ziegler-Natta and Metallocene initiated polymerizations and correlate initiator structure to polymer tacticity.

### Topic 12. Fundamental Concepts of Molecular Characterization

*Students should be able to:*

• Read, understand, and explain typical signals and patterns found in direct detect $^{1}H$ and $^{13}C$ NMR spectra, including common two-dimensional NMR spectra such as COSY, HSQC, and HMBC. This includes chemical shift anisotropy, coupling constants, homo- and heteronuclear couplings, and 1$^{st}$ and 2$^{nd}$ order spin-spin coupling rules.

• Rationally design and interpret nuclear Overhauser effect spectra.

• Read and analyze representative infrared and mass spectra.

• Understand and criticize crystallographic ellipsoid plot diagrams.

• Define and describe the basic principles of NMR, including relaxation times (spin-lattice and spin-spin), dipolar and quadrupolar nuclei, dynamic NMR, polarization and coherence transfer, in vivo NMR, solid state NMR, cross-polarization, and magic angle spinning.