Exams

There will be three hour exams, each worth 100 points, and a comprehensive final exam worth 200 points, for a total of 500 points for the semester.

Topics to be covered

FUNDAMENTALS
Stereochemistry
Stereeoselective and Stereospecific Reactions
Linear Free Energy Relationships
Hammett (g) equation; \( \sigma^+ \) and \( \sigma^- \) constants; \( \sigma^* \) and \( \sigma^0 \) constants; Application to aliphatic systems—\( \sigma^* \) constants; Grunwald-Winstein equation; Swain-Scott equation; Edwards equation; Thermochemistry; Benson’s Additivity Rules; Application to alkanes, alkenes, aromatics, and cycloalkanes; Entropy considerations

Properties of Solutions
Dielectric constant; Dipole moment and polarizability; Hydrogen bonding; Solvent structure; Protic and dipolar aprotic solvents; Measures of solvating ability

Kinetics
Arrhenius equation; The Hammond Postulate; Reacting bond rules

ACIDS AND BASES
Brønsted definition; Acid and base strength; Levelling effect; Strengths of weak Brønsted bases; Acidity functions; Other acidity scales; Measurements in non-aqueous solvents; Heats of protonation; Strengths of weak Brønsted acids; \( H_- \) acidity functions; Brønsted catalysis law; Kinetic acidity; MSAD scale; Gas-phase acidity; Lewis acids and bases; Strengths of Lewis acids and bases; Hard and soft Lewis acids and bases; Shortcomings and theoretical basis for HSAB principle

WOODWARD-HOFFMANN RULES
Which reactions are concerted?; Intramolecular electrocyclic reactions; Intermolecular cycloadditions; Sigmatropic rearrangements; Meaning of orbital symmetry; \( \sigma \) and \( \pi \) orbitals; Electroyclic ring opening or closure; Woodward-Hoffmann rules; Butadiene and hexatriene examples; Odd-atom conjugated systems; Cyclopropyl-allyl isomerizations

BIMOLECULAR SUBSTITUTION REACTIONS
\( S_n2 \) Mechanisms
Stereochemistry of \( S_n2 \) reaction; Bridged ring compounds; Effect of solvent, substrate structure, nucleophile, and leaving group; Effect of alkyl-group substituents; Heteroatoms in the substrate; Carbonyl-group substitution
**Bimolecular Electrophilic Substitution at Saturated Carbon**
Organomercurials; Stereochemistry; $S_{E2}$ and $S_{E1}$ mechanisms; Attack on carbon-hydrogen bonds.

**Unimolecular Substitution and Related Reactions**

**Limiting Unimolecular Nucleophilic Reactions**
Kinetics and stereochemistry; The $S_{N1}$ mechanism; Ion pairs; Winstein's experiments; Approximations to ionization rate; Special salt effect; Induced common-ion effect

**Effects of Structure and Solvent**
Leaving group $k_{ON}/k_{Br}$ rate ratios; Diazonium ion decompositions; Substitution in alkyl group; Bridgehead compounds; Isotope effects; Entering group; Stability-selectivity considerations of product formation; Solvent effects; Nomenclature for carbocations; Ion-pair mechanism for bimolecular substitution

**Unimolecular Electrophilic Substitutions**
The $S_{E1}$ mechanism; Proton leaving group; Carbanions; Carbon leaving groups

**Carbenes (Methylenes)**
Dichloromethylene; $\alpha$-Elimination; Structure; Reactions; Insertion; Cyclopropane formation

**Intramolecular Rearrangements**

**1,2-Shifts in Carbenium Ions**
Stereoochemistry requirements; Timing of migration in acyclic alkyl systems; Aryl participation and the phenonium-ion controversy; Migratory aptitudes; Carbenium ions on Olah terminology; Bromoallylic carbonium ions—Cholesterol systems and other systems; Migrations to carbonyl carbon; Migrations to electron-deficient nitrogen.