AoPS CHEM WOOT
Art of Problem Solving

2023–2024 Syllabus

1. Steady State Kinetics

This class introduces students to chemical reaction kinetics and covers the use of the steady-state approximation to find rate laws for complex reaction systems.

Example Problem: For the reaction $\mathrm{A} \longrightarrow \mathrm{B}$, the rate law is rate = $k[\mathrm{A}]$. If the reaction is 40.0% complete after 50.0 minutes, what is the value of the rate constant, k?

Example Problem: What is the rate law for the hypothetical reaction with the mechanism shown? ($\mathrm{I_1}$ and $\mathrm{I_2}$ indicate intermediates, not molecular formulae.)

$$2\,\mathrm{A} \rightleftharpoons \mathrm{I_1} \text{ (fast equilibrium)}$$

$$\mathrm{I_1} + \mathrm{B} \longrightarrow \mathrm{I_2} \text{ (slow)}$$

$$\mathrm{I_2} + \mathrm{B} \longrightarrow \mathrm{A_2B_2} \text{ (fast)}$$

2. Equilibrium
3. Mass-Charge Balance

These two classes cover chemical equilibria, with a particular focus on how to determine equilibrium concentrations of different species in mixed solutions.

Example Problem: The pH of a saturated solution of $\mathrm{Fe(OH)_2}$ is 8.67. What is the K_{sp} for $\mathrm{Fe(OH)_2}$?

Example Problem: Solution X contains 0.10 M acetic acid and 0.02 M formic acid. Calculate the pH of this solution.

4. Qualitative Inorganic Reactions

This class explores techniques for identifying unknown substances in chemical reactions, with a focus on qualitative properties like color and solubility. Determination of oxidation states and balancing of oxidation states in reactions are also covered.

Example Problem: An aqueous solution contains the ions $\mathrm{Ag^+}$, $\mathrm{Ba^{2+}}$, and $\mathrm{Ni^{2+}}$. Dilute aqueous solutions of NaCl, $\mathrm{Na_2S}$, and $\mathrm{Na_2SO_4}$ are available. In what order should these solutions be added if the goal is to precipitate each of the three cations separately?

Example Problem: When equal volumes of 0.2 M solutions of the following compounds are mixed, which combination forms a red precipitate?

(A) $\mathrm{AgNO_3 + Na_2S}$ (B) $\mathrm{AgNO_3 + K_2CrO_4}$ (C) $\mathrm{NiCl_2 + NaOH}$ (D) $\mathrm{CuSO_4 + NH_3}$

5. Titrations

This class covers techniques for the quantitative determination of amounts of specific substances in solutions or chemical mixtures and the use of these techniques to determine the molecular formulae of substances. Acid-base and redox titrations are a main focus.

Example Problem: 25.00 mL of a solution of a weak monoprotic acid, HX, was titrated with a 0.0640 M solution of NaOH, requiring 18.22 mL. The pH of the solution varied as a function of the HX titrated. These data were collected.

% Titrated	0	33.3 %	66.7 %
pH	3.39	5.14	5.74

(a) Calculate the initial concentration of the weak acid in the 25.00 mL of solution.
(b) Determine the value of K_a.
(c) Calculate the pH at the equivalence point of this titration and write an equation to account for this pH.
(d) Calculate the number of moles of a salt, NaX that must be added to produce a pH of 6.00 in 150.00 mL of the original solution.

6. Quantum Mechanics I
7. Quantum Mechanics II

These classes introduce students to key concepts of quantum mechanics that are relevant to chemistry, including electron wave functions. Students also learn how to mathematically model delocalized electron systems as particles in 1D or 2D boxes or rings and chemical bonds as quantum harmonic oscillators.

Example Problem: Draw an energy level diagram for [18]-annulene as predicted by the particle in a ring model, and calculate the wavelength of light absorbed by its lowest energy transition. Would you predict [18]-annulene to be colored?

Example Problem: Consider the following extremely simple isotope exchange reaction:

$$\mathrm{H_2 + D_2 \longrightarrow 2\,HD}$$

The wavelength of infrared photons absorbed by $\mathrm{H_2}$ as it goes from the $n = 0$ to the $n = 1$ vibrational state is $2.27\ \mu\mathrm{m}$. Use this fact to compute ΔH for this reaction (in kJ/mol).

8. Molecular Orbital Theory

This class covers basic molecular orbital theory, how to draw molecular orbital diagrams, and how to use HOMO and LUMO frontier molecular orbitals to predict reaction products.

Example Problem: Identify the HOMOs and LUMOs of hydroxide and methyl bromide and use this information to predict the product of a reaction between them.

Example Problem: Use the MO diagram for $\mathrm{O_2}$ to explain why it typically behaves in reactions as a diradical.

9. Transition Metal Chemistry

This class covers the structural and electronic properties of transition metal complexes, including crystal field theory and ligand field theory approaches to common structural configurations.

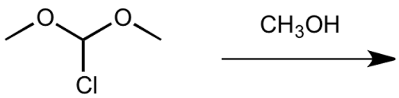
Example Problem: How many atoms are covalently bonded to the chromium atom in $Cr(NH_3)_4Cl_3$?

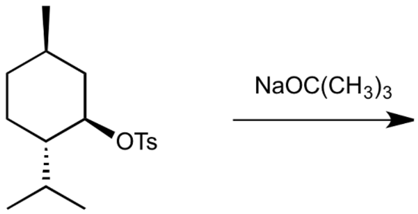
Example Problem: The two complexes $[\mathrm{Mn(H_2O)_6}]^{2+}$ and $[\mathrm{Mn(CN)_6}]^{2-}$ are both octahedral. One has a magnetic moment of 5.9 BM, the other has a magnetic moment of 3.8 BM. Which complex has the 5.9 BM magnetic moment? Explain why its moment is larger than the other complex. Include a diagram of the d molecular orbitals of each complex as part of your answer.

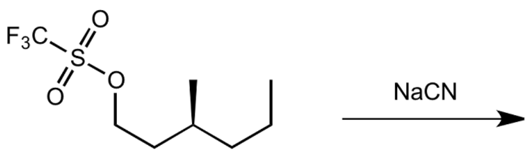
10. SN2/E2 Reactions
11. SN1/E1/Carbocations

These two classes introduce basic principles of organic chemistry, including stereochemistry and reactivity of organic molecules. Important classes of substitution and elimination reactions are explored, and students learn how to predict which reaction type is most likely to occur, as well as relative reaction rates for different reactant combinations.

Example Problem: Draw the product of the following reactions, and name the mechanism that is at work. The possible mechanisms are SN2, E2, SN1, E1, hydration, hydrohalogenation, or no reaction. Be sure to show the correct stereochemistry if applicable.







12. Alkenes
13. Aromatics

The focus on organic chemistry continues with properties and reactions of molecules containing double bonds, both simple alkenes and aromatic compounds. The concept of electron-donating and -withdrawing groups is introduced in the context of effects on reactions of alkenes and aromatics.

Example Problem: For which compound is the OH group most acidic?

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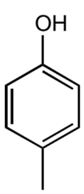

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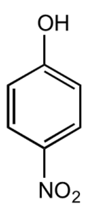

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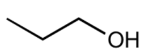

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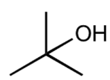


Example Problem: Draw the expected product for reaction of 1-methylcyclopentene with each of the following reagents. Make sure to indicate the correct regioselectivity and stereoselectivity where applicable. Show any intermediates.

1. HBr 2. $\mathrm{H_2O/H_2SO_4}$ 3. $\mathrm{Hg(OAc)_2}$ then $\mathrm{NaBH_4}$ 4.$\mathrm{Br_2}$

14. Spectroscopy

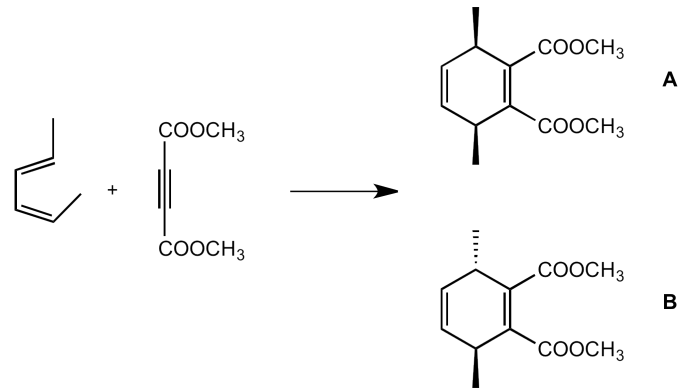
This class describes important modern analytical techniques for the determination of molecular structure, especially mass spectrometry, infrared spectroscopy and NMR spectroscopy.

Example Problem: The following pages contain mass spectrometry, infrared spectroscopy, and proton NMR spectroscopy data for three compounds X, Y, and Z. Determine the structure of all three compounds.

15. Pericyclic Reactions

Returning to organic chemistry, this class teaches students how to apply frontier molecular orbital theory to understanding the mechanism and predicting the products of pericyclic reactions, one of the most complex types of organic reactions.

Example Problem: Which of the following products is produced by this Diels-Alder reaction?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