

Midterm II Preparation Guide (Chem 111, Spring 2008)

The second midterm will test your knowledge and understanding of topics and techniques that we have covered since the first midterm. Some of the important topics that you should know are:

- 1) Characteristic features of the second order reaction $A + A \rightarrow P$
 - a. Differential and integrated forms of rate laws
 - b. Inverse linear plot for estimation of rate coefficient
- 2) Characteristic features of the third- and higher-order reactions: $nA \rightarrow P$
 - a. Differential and integrated forms of rate laws for $n=3$
 - b. How to determine the rate coefficient for third-order reaction
 - c. Why are higher-than third-order reactions uncommon
- 3) Characteristic features of the irreversible second order reaction $A + B \rightarrow P$
 - a. Differential rate law
 - b. Pseudo-first order approximation
- 4) Characteristic features of the reversible $A + B \rightleftharpoons P$ and $A + B \rightleftharpoons 2P$ reactions
 - a. Differential forms of rate laws
 - b. Nonlinear first order differential equation for the extent of reaction
 - c. General solution for the extent of reaction
 - d. Equilibrium constant and equilibrium concentrations: relationships
 - e. Equilibrium constant and rate coefficients: relationships
 - f. Temperature dependence of equilibrium constant
- 5) Rapid gas phase reactions
 - a. Basic setup of discharge flow apparatus
 - b. Resonance fluorescence detection of atomic species
 - c. Laser-induced fluorescence detection of molecular species
- 6) Collision theory in chemical kinetics
 - a. Basic assumptions and principles of collision theory
 - b. The kinetic theory of gases: principles and main results: $\langle \epsilon \rangle$, $\langle v^2 \rangle$
 - c. The Maxwell-Boltzmann speed distribution and the average speed $\langle v \rangle$
 - d. Predicted temperature dependence of rate coefficient
 - e. Physical interpretation of the Arrhenius rate law
 - f. The limitations of collision theory, steric factor
- 7) Transition state theory
 - a. The potential energy surface and the saddle point
 - b. Basic assumptions and principles of transition state theory
 - c. The properties of the molecular partition function
 - d. The Eyring equation
 - e. Thermodynamic interpretation of transition state theory
 - f. Activation enthalpy and activation entropy
 - g. Kinetic isotope effect and tunneling

- 8) Characteristic features of the irreversible consecutive reaction
 - a. Differential and integrated rate laws and for A, B, C in $A \rightarrow B \rightarrow C$
 - b. Lag in buildup of C as a characteristic feature of a consecutive process
 - c. What can we determine from [A] vs. time profile?
 - d. What can we determine from [B] vs. time profile?
 - e. What can we determine from [C] vs. time profile?

- 9) Analysis of kinetics when the reaction is monitored by UV-Vis spectrophotometry
 - a. No overlap between spectra of reactants, intermediates, and products
 - b. Spectra of reactants, intermediates, and products are identical
 - c. Partial overlap between spectra of reactants, intermediates, and products
 - i. The essence, value and limitations of the isosbestic point method
 - ii. The essence, value and limitations of singular value decomposition
 - iii. How to calculate rate constants from absorbance data when all spectra are known

- 10) Statistical data analysis and linear algebra
 - a. The basic idea behind the least-squares regression
 - b. How do you know when the model chosen for fitting is wrong?
 - c. Matrix algebra and multivariable linear least-squares regression
 - d. Singular value decomposition:
 - i. The matrix of basis spectra
 - ii. The diagonal matrix of singular values
 - iii. The matrix of basis profiles
 - iv. SVD as a noise-reduction method

- 11) Use of *Mathematica* in solving problems in chemical kinetics
 - a. Solving differential equations to obtain integrated rate laws
 - b. Simulating and plotting concentration profiles based on integrated rate expressions: first-order and consecutive mechanisms
 - c. Nonlinear regression to estimate numeric values of rate coefficients
 - d. Multivariate linear regression to obtain concentration profiles from the absorbance data when all the spectra are known
 - e. Using SVD to estimate the number of species that contribute to the change in the absorbance signal

- 12) Analysis of the paper by Egawa *et al*

The Midterm II has two parts. The first, one-hour in-class part tests your knowledge of the material. The second, at-home part tests your ability to analyze data and solve practical problems in kinetics. You are allowed to use any existing literature or Internet source and software of your choice when answering “at-home” questions. However, students should abide by ethical standards of conduct, including individual work without substantial help from other students in the class or other individuals not associated with the course.