Midterm II Preparation Guide

CHEM 111, Spring 2013 ***Dr. Kalju Kahn, UCSB***

The second midterm (on May 30th, 2013) 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 irreversible reactions: of $A + B \rightarrow P$
   a. Examples of $A + B \rightarrow P$ reactions
   b. Examples of $A + B \rightarrow P + Q$ reactions
   c. Differential rate laws for this second-order irreversible reaction
   d. Connection between the final concentrations and initial concentrations if $A_0 \neq B_0$
   e. Rate of product buildup as a function of excess reagent concentration
   f. Difficulties with analysis, and possible solutions when initial concentrations are unknown
   g. Linearization via logarithmic transformation
   h. Special case of $A_0 = B_0$, connection between exponential and inverse decay expressions
   i. Pseudo-first order reaction: examples and kinetic analysis

2) Characteristic features of the reversible $A + A \rightleftarrows P$ and $A + B \rightleftarrows P$ reactions
   a. Examples of reversible mixed order reactions
   b. Differential forms of rate laws
   c. Nonlinear first order differential equation for the extent of reaction
   d. Riccati equation: importance in kinetics and its characteristic features
   e. General solution for the extent of reaction
   f. Equilibrium constant and equilibrium concentrations: relationships
   g. Equilibrium constant and rate coefficients: relationships

3) Characteristic features of the reversible $A + A \rightleftarrows P + Q$ and $A + B \rightleftarrows P + Q$ reactions
   a. Examples of reversible second order reactions
   b. Differential forms of rate laws
   c. Nonlinear first order differential equation for the extent of reaction
   d. General solution for the extent of reaction
   e. Kinetics of disproportionation of hydrogen iodide
   f. Temperature dependence of equilibrium constant

4) Characteristic features of the irreversible consecutive reaction
   a. Examples of consecutive irreversible reactions
   b. Radioactive decay chains
   c. Differential and integrated rate laws and for A, B, C in $A \rightarrow B \rightarrow C$
   d. Generalization to cases with more intermediate steps
   e. Lag in buildup of C as a characteristic feature of a consecutive process

f. What can we determine from [A] vs. time profile?
g. What can we determine from [B] vs. time profile?
h. What can we determine from [C] vs. time profile?

5) Characteristic features of the reversible consecutive reaction $A \rightleftarrows B \rightarrow C$
   a. Examples of consecutive partially reversible reactions
   b. Differential rate laws and for A, B, C in $A \rightleftarrows B \rightarrow C$
   c. General appearance of concentration profiles
   d. A case of rapid equilibrium first step
   e. A case of rapid irreversible second step
   f. When is a steady-state assumption justified?
   g. Distinguishing between $A \rightleftarrows B \rightarrow C$ and $A \rightarrow B \rightarrow C$ mechanisms

6) 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. Action spectra, assessment of spectral overlap
   d. Analysis of non-overlapping spectral data
   e. 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
      iv. Challenges in calculation rate coefficients from absorbance data when some or all the spectra are unknown

7) Rapid gas phase reactions
   a. Methods to study fast gas phase reactions
   b. Flash photolysis method: principle and limitations
   c. Basic setup of discharge flow apparatus
   d. Advantages and limitations of flow tube method
   e. Considerations for detection methods
   f. Resonance fluorescence detection of atomic species
   g. Laser-induced fluorescence detection of molecular species
   h. Kinetic analysis of flow tube experimental data

8) Rapid reactions in solutions
   a. Challenges in measuring rapid reactions in solution
   b. Stopped flow setup
   c. Quenched flow setup
   d. Continuous flow setup
   e. Considerations for choosing the detection method
   f. Scanning UV-Vis spectrophotometry: advantages and limitations
   g. Diode-array absorption spectroscopy: advantages and limitations
   h. Electron paramagnetic resonance for detection of radical species

9) 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. Basic principles of matrix algebra
    d. Lambert–Beer law in case of two absorbing species
    e. Lambert–Beer law in case of several absorbing species
    f. Calculation of component concentrations from absorbance data of a mixture when the spectra of components in the mixture are known
    g. Moore–Penrose matrix inverse and solution of matrix equations
    h. 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

10) 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. Simulating and plotting spectra as Gaussian curves
    d. Nonlinear regression to estimate numeric values of rate coefficients
    e. Multivariate linear regression to obtain concentration profiles from the absorbance data when all the spectra are known
    f. Using SVD to estimate the number of species that contribute to the change in the absorbance signal

11) Analysis of the paper by Egawa *et al*

12) Pharmacokinetics
    a. Role of pharmacokinetics in drug discovery
    b. Mathematical description of drug distribution: two-compartment model
    c. Dosing in $A \rightleftarrows B \rightarrow C$ model: concentration in the first compartment
    d. Dosing in $A \rightleftarrows B \rightarrow C$ model: concentration in the second compartment
    e. Effective concentration, toxic concentration, and therapeutic index
    f. Special situations: drug overdosing; slow metabolizers

Material from textbooks:

- House: pg 47-58, 94-98, 289-292
- Metiu: Chapter 6