Midterm I Preparation Guide

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

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

1) Introductory topics
    a. The importance of kinetics in technology and everyday life
    b. The role of kinetics in understanding reaction mechanisms
    c. The goal and scope of kinetic studies
    d. Connection between reaction energy diagrams, rates, and equilibrium
    e. Qualitative understanding of effect of temperature on reaction rates
2) Rate laws, reaction order and reaction mechanisms
    a. The definition of reaction rate as the rate of change of concentrations with time
    b. Differential and integrated forms of rate laws
    c. Differential and integral methods for determination of reaction order
    d. Initial rates method: advantages and issues
    e. Elementary and complex reactions
    f. Reaction stoichiometry, molecularity, and reaction order
3) Traditional ways to measure rates of not very fast reactions
    a. Sample the reaction in time: Separate and quantitate approaches
    b. Continuous detection as the reaction proceeds: Optical methods
    c. Calculation of concentrations from absorbance in two-component system
4) Characteristic features of the irreversible first-order reaction
    a. Examples of irreversible first-order reactions
    b. Differential and integral forms of the rate law
    c. Single-exponential decay of the reactant to zero, half-life
    d. Linearization via logarithmic transformation
5) Characteristic features of the reversible first-order reaction A ⇆ P
    a. Examples of reactions with $k_1 = k_2$ and $k_1 \neq k_2$
    b. Differential and integral forms of the rate law
    c. Single-exponential decay of the reactant to equilibrium
    d. Relationship between the rate coefficients and the equilibrium constant
    e. A need to measure both [A] and [B] if B is initially present; global fit
    f. Use of empirical exponential rate expression
    g. Chevron plots for protein folding kinetics
6) Temperature and pressure dependence of equilibrium constants
    a. Differential equations for $\mathrm{d}\ln K / \mathrm{d}T$ and $\mathrm{d}\ln K / \mathrm{d}P$
    b. Le Chatelier Principle
    c. Heat capacity and temperature dependence of reaction enthalpy
    d. Heat capacity and temperature dependence of reaction entropy
    e. Linear and non-linear van't Hoff plots
    f. Effects of temperature and pressure of protein folding equilibrium
7) Relaxation methods: principles and applications
    a. How to achieve temperature and pressure jumps
    b. Relaxation methods in studies of protein folding
    c. Detection methods for relaxation methods
    d. Kinetic analysis of relaxation data

8) Characteristic features of the first-order irreversible parallel reactions: $A \rightarrow P$, $A \rightarrow R$
    a. Examples of parallel irreversible reactions
    b. Differential rate laws for first-order irreversible parallel reaction
    c. Exponential decay of reactant; effective half-life
    d. Exponential build-up of products as a function of time
    e. Difficulties with analysis, and possible solutions when initial concentrations are unknown
    f. Temperature-dependence of reaction rate and yield of the desired product
9) Characteristic features of the first-order reversible parallel reactions: $A \leftrightarrows P$, $A \leftrightarrows R$
    a. Examples of parallel reversible reactions
    b. Differential rate laws for first-order reversible parallel reaction
    c. Features of time-dependence of reactant and product concentrations
    d. Kinetic vs. thermodynamic control; temperature-dependence of yield
10) Characteristic features of the second-order irreversible reactions: $A + A \rightarrow P$
    a. Examples of $A + A \rightarrow P$ reactions
    b. Differential rate laws for this second-order irreversible reaction
    c. Inverse-time decay of reactant to zero
    d. Linearization via inverse transformation
11) Characteristic features of the third order and fourth-order irreversible reactions
    a. Mechanism of gas-phase reactions that display third-order kinetics
    b. Differential rate law for $A + A + A \rightarrow P$ reaction
    c. Differential rate law for $A + A + A + A \rightarrow P$ reaction
    d. Linearized inverse forms for these reactions

Paper by Jacob *et al* on protein folding studies: posted discussion questions

Helpful material from textbooks:

- House: pg 1-27, 31-47, 58-64, 79-98
- Metiu: pg 1-32