

CHEC 353 - PHYSICAL CHEMISTRY AND APPLICATIONS III

SUMMER TERM, 2008

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Office Hours: One hour before class each week or by appointment

A. COURSE OBJECTIVE

This is a four credit course covering select topics from the areas of chemical kinetics, simple mixtures and properties of solution, and molecular spectroscopy. It will be taught by supplementing the lecture material with presentations that emphasize specific applications that demonstrate the lecture topics applied to "real world" situations.

B. PREREQUISITE CHEC 352 or equivalent

C. REQUIRED TEXTBOOK

Physical Chemistry, Eighth Edition by Peter Atkins and Julio de Paula, W.H. Freeman and Company (2006)

D. CLASS MEETINGS

Monday from 12:00 noon to 12:50 P.M. in LeBow Room 135

Tuesday and Thursday from 12:30 P.M. to 1:50 P.M. LeBow Room 135

E. COURSE LEARNER OBJECTIVES

Upon completion of this course the student should be able to:

- understand the general concepts of spectroscopy
- utilize Beer's Law as a criterion for measuring concentration
- understand and interpret both microwave and infrared spectra to determine parameters such as equilibrium bond lengths
- understand and accurately predict colligative properties of solutions based on their composition
- understand partial molar quantities and their measure of nonideality
- quantitatively describe the rates of chemical reactions and identify reaction types with respect to their reaction order
- understand the influence of temperature on reaction rates
- understand the consequences of parallel and consecutive reactions on overall rates
- understand the correlation between chemical kinetics and chemical equilibrium
- deduce and verify reaction mechanisms with regard to reaction orders
- correlate kinetics to polymerization reactions and types with specific applications to drying oils such as linseed oil and the potential for spontaneous combustion
- apply the concepts of chemical kinetics to analytical techniques like Differential Scanning Calorimetry (DSC)

F. ACADEMIC HONESTY POLICY

Drexel University is committed to a learning environment that embraces academic honesty. In order to protect members of our community from results of dishonest conduct, the University has adopted policies to deal with cases of academic dishonesty. Please read, understand, and follow the "Academic Honesty Policy" as written in the official student handbook. Instances of academic dishonesty, such as cheating and plagiarism, will be dealt with appropriately.

G. GRADE BREAKDOWN

25% of your grade will come from Exam I which will cover material from weeks 1 through 4 and will be given during the fifth week (week of July 21)

25% of your grade will come from Exam II which will cover material from weeks 5 through 7 and will be given during the eighth week (week of August 11)

30% of your grade will come from the Final Exam (date to be determined), which will be comprehensive

20% of your grade will come from two Problem Sets (10% each) distributed throughout the quarter.

NOTE: THERE ARE NO UNIVERSITY HOLIDAYS THAT AFFECT THIS CLASS THIS QUARTER: INDEPENDENCE DAY IS ON FRIDAY JULY 4. LABOR DAY IS THE MONDAY OF FINAL EXAM WEEK SO IT IS AFTER CLASSES HAVE BEEN COMPLETED.

H. PROBLEM SETS

There will be two problem sets distributed during the quarter. These problem sets are primarily the more time-consuming problems which are less appropriate for an in-class exam having a time limit. Successfully completing these problem sets provides an excellent preparation for the in-class exam. Once the answers to the problem set have been posted, no problem sets will be accepted for credit and you will have forfeited that portion of your course grade. Large discrepancies between an in-class exam and the problem set grade will likely require you having to support/explain your problem set answers and could lead to a reduction of the problem set grade. ALL STUDENTS ARE EXPECTED TO DO THEIR OWN WORK AND SUBMIT THEIR OWN WORK. ANY INSTANCES OF DUPLICATE WORK BEING SUBMITTED WILL RESULT IN A ZERO FOR ALL PERSONS INVOLVED. THE PERSON SUPPLYING THE ANSWERS IS JUST AS GUILTY AS THE PERSON WHO COPIED THEM. NOTE: There are no make up options for the problem sets. You will forfeit that portion of your grade if it is not completed.

TOPICS TO BE COVERED DURING THE QUARTER

CHAPTER 13 - SPECTROSCOPY

General Features of Spectroscopy - Intensities of Spectral Lines - Beer-Lambert Law - Rotational Energies - Spectroscopic Selection Rules - Microwave Spectroscopy - Molecular Vibrations - Harmonic Oscillator Model - Anharmonicity - Infrared Spectroscopy - Vibration/Rotational Spectroscopy

CHAPTER 5 - SIMPLE MIXTURES

Partial Molar Quantities - Thermodynamics of Mixing - Liquid Mixtures - Henry's Law - Colligative Properties: Vapor Pressure Lowering, Boiling Point Elevation, Freezing Point Depression, and Osmotic Pressure - Solute and Solvent Activities

CHAPTERS 22 AND 23 - CHEMICAL KINETICS

General Rate Laws - Rates of Reactions - Order of A Reaction - Integrated Rate Laws - Reversible First Order Reactions - Parallel and Consecutive First Order Reactions - Reactions Approaching Equilibrium - Temperature Dependence of Reaction Rates - Mechanisms of Chemical Reactions - Relation Between Rate Constants of Forward and Reverse Reactions - Reaction Coordinates and Transition State Theory - Chain Reactions - Polymerization Kinetics - SPECIAL TOPIC: Kinetic Studies by Differential Scanning Calorimetry

HOMEWORK PROBLEMS

NOTE: UNLESS OTHERWISE INDICATED, ALL EXERCISES PERTAIN TO THE "A" SET AT THE END OF EACH CHAPTER

CHAPTER 13 Exercises 13.5, 13.6, 13.8, 13.12, 13.22, SP5, SP7, SP8

CHAPTER 5 Exercises 5.1, 5.3b, 5.4b, 5.5, 5.6b, 5.7b, 5.8b, 5.11b, 5.12b, 5.14b, 5.16
Problems 5.1, 5.2, 5.5

CHAPTER 22 Exercises 22.1, 22.2, 22.3, 22.5, 22.7, 22.8, 22.11, 22.14
Problems 22.1, 22.2, 22.5 (also determine k at 30°C), 22.6, 22.8, 22.9, 22.20, 22.29, 22.30

CHAPTER 23 Discussion Questions 23.1, 23.2
Problems 23.2, SP1, SP2, SP3, SP4

NOTE: THESE ASSIGNMENTS MAY BE MODIFIED AS THE QUARTER PROGRESSES
SP = SUPPLEMENTARY PROBLEMS LISTED BELOW

SUPPLEMENTARY PROBLEMS

- SP1 Consider a two step consecutive reaction in which $k_1 = 0.50 \text{ min}^{-1}$ and $k_2 = 0.03 \text{ min}^{-1}$. If a reaction was initiated with $[A] = 0.60\text{M}$,
- How long would it take (in minutes) for B to reach its maximum concentration?
 - What is the maximum concentration?
 - At that same time, what are $[A]$ and $[C]$?
- SP2 Consider chain polymerization in which the rate constants for the various steps have been reported as initiation = 0.15 min^{-1} , propagation = 25.0 min^{-1} , and termination = 0.10 min^{-1}
- Assuming that 60% of the initiator molecules successfully generate free radicals that initiate a chain, what is the average chain length for a polymerization process with a monomer concentration of 0.5M and an initiator concentration of 0.005M?
 - If your objective was to make longer polymer chains, what adjustment(s) would you make to the variables you can readily control?
- SP3 Consider a stepwise polymerization to make Nylon in which a stoichiometric blend of diamine and diacid are used. A reactor is charged with $[\text{diamine}] = 0.25\text{M}$ and the rate constant at the reaction temperature is observed to be $1.45 \text{ M}^{-1} \text{ sec}^{-1}$.
- If you want the average chain length for the Nylon to be in the range of 250-275 repeat units, how long should you allow the reaction to proceed before "dumping" the reactor?
 - Qualitatively, would you expect there to be any difference in the chain length after the same time period if the temperature was increased by about 50°?
- SP4 An isomerization reaction is reversible and first order in both directions. At a certain temperature the rate constant in the forward direction is found to be $9.2 \times 10^{-4} \text{ sec}^{-1}$. Eventually, the composition of the reacting system is found to be constant at 20 mole % of the reactant. Calculate the rate constant for the reverse reaction.

- SP5 The fundamental ($v = 0 \rightarrow v = 1$) vibrational transition for H^{35}Cl occurs at 2885.0 cm^{-1} . Close inspection of a high resolution infrared spectrum of this transition shows the following absorptions (in cm^{-1}) for the $J \rightarrow (J-1)$ branch: 2865.10, 2843.62, 2821.56, 2798.94, 2775.76, 2752.04, 2727.78, 2703.01, and 2677.73. From these data, determine
- the rotational constant, B_e
 - the rotational-vibrational coupling constant, α
 - the bond distance

- SP6 Test Stirling's Approximation with $x = 5, 10,$ and 15 by comparing its predictions with the exact values. Repeat the comparison for a more exact form of the approximation
- $$\ln(x!) = (x + 1/2) \ln(x) - x + 1/2 \ln(2\pi)$$

- SP7 When monochromatic radiation of a specific wavelength was sent through an absorption cell 5.0 cm long, containing a 0.10M solution of an absorbing solute, 23% of the incident radiation was absorbed. Calculate the molar absorption coefficient, a .

- SP8 Chromium can be determined by converting it to a colored species, which is then measured with a spectrophotometer. Standardized solutions of exactly known $[\text{Cr}^{+6}]$ were measured in a 1.00 cm cell and the following results were obtained:

$[\text{Cr}^{+6}] (\text{M})$	<u>PERCENT TRANSMITTANCE</u>
0.0018	61.1
0.0042	38.9
0.0067	19.0
0.0088	12.2
0.0110	6.52
0.0130	4.19

- Using all of these data, determine the molar absorption coefficient
- What is $[\text{Cr}^{+6}]$ in an unknown having an absorbance of 0.390 ? NOTE: This answer requires a calculated mathematical solution, not simply a "ballpark estimate" obtained by casually examining and/or interpolating the data

