

CHEC 353 - PHYSICAL CHEMISTRY AND APPLICATIONS III

SPRING TERM, 2008

Instructor: Ed Thorne
Office: Disque Hall, Room 316
(215) 895-1331

Email: thorneej@drexel.edu

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, statistical thermodynamics, 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 Evenings from 6:00 to 9:30 P.M. in CAT Building, Room 75

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
- recognize the "weaknesses" of classical physics as applied to atomic behavior and evolve that into the statistical treatment of systems
- apply the Boltzmann Distribution to the evaluation of partition functions and ultimately apply it to the statistical and/or spectroscopic determination of thermodynamic functions such as enthalpy, entropy, free energy and heat capacity
- 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 3 and will be given on April 21 (tentative date)

25% of your grade will come from Exam II which will cover material from weeks 4 through 7 and will be given on May 19 (tentative date)

30% of your grade will come from the Final Exam (June 9), which will be comprehensive

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

NOTE: THERE IS ONE MONDAY NIGHT HOLIDAY THIS QUARTER: MEMORIAL DAY IS ON MONDAY MAY 26 (THE NINTH WEEK OF CLASSES)

NOTE: ALL GRADUATING SENIORS ARE RESPONSIBLE FOR ALL WORK WITH THE POSSIBLE EXCEPTION OF THE FINAL EXAM. GRADUATING SENIORS WILL BE EXEMPT FROM A FINAL EXAM ONLY IF THEY HAVE AN AVERAGE OF 75 OR BETTER ON THE FIRST TWO EXAMS. ANY SENIOR FINAL EXAMS WILL BE GIVEN AT A TIME TO BE DETERMINED (WHICH WILL MOST LIKELY BE THE REGULAR FINAL EXAM DATE AND TIME)

H. PROBLEM SETS

There will be two problem sets distributed during the quarter. These problem sets are primarily the more time-consuming problems that 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.

I. MAKING UP MISSED EXAMS

A single make-up exam will be given to replace either Exam I or Exam II. This exam will be given after the second exam and will cover material from both exams. This means that regardless of whether you miss either Exam I or Exam II, the make-up exam you take will cover material from both exams. The make-up exam will replace one exam only, so that if you miss both exams you will forfeit 25% of your grade. To do this, you first have to make an appointment with Marge Fritsche (215-895-2164) at the College of Evening and Professional Studies, located at One Drexel Plaza at 30th and Market Streets. All make-up exams will be administered through the College of Evening and Professional Studies. **If you do not complete the make-up exam by Thursday May 29, your grade for the missed exam will be zero. No make-up exams will be permitted after May 29. THE MAKE-UP EXAM IS TO REPLACE A MISSED EXAM, NOT TO REPLACE A POOR GRADE. THERE IS A TWO HOUR TIME LIMIT ON THE MAKE-UP EXAM SO YOU WILL HAVE TO ARRIVE EARLY ENOUGH TO RECEIVE THE FULL TIME ALLOWED. THE OFFICE WILL NOT REMAIN OPEN PAST THEIR REGULAR HOURS FOR YOU TO COMPLETE THE EXAM IF YOU ARRIVE LATE. IT IS YOUR RESPONSIBILITY TO MAKE A SUITABLE APPOINTMENT TO TAKE THE EXAM.**

J. ATTENDANCE POLICY

Considering the needs of part time students occasionally having to miss class because of employment or familial commitments, attendance will not affect your grade. If you miss a class for any reason, it is your responsibility to call me to find out what work you missed.

TOPICS TO BE COVERED DURING THE QUARTER

CHAPTER 13 - SPECTROSCOPY (WEEKS 1 THROUGH 3)

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

CHAPTERS 16 AND 17 - STATISTICAL THERMODYNAMICS (WEEKS 3 AND 4)

Failure of Classical Physics - Blackbody Radiation and the Ultraviolet Catastrophe - Heat Capacity and Vibrational Energies - Quantization of Energy - Boltzmann Distribution - Partition Functions - Statistical Interpretation of Entropy - Thermodynamic Functions from Partition Functions

CHAPTERS 22 AND 23 - CHEMICAL KINETICS (WEEKS 5 THROUGH 10)

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 16 Exercises 16.2, 16.3, 16.10, 16.11

CHAPTER 17 Exercises 17.1, 17.2, 17.5, 17.6, 17.8b, 17.10, SP6

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 $x = 5, 10, \text{ and } 15$ 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

