# CHEC 353 - PHYSICAL CHEMISTRY AND APPLICATIONS III

# SUMMER TERM, 2015

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Office Hours: One hour before each class. Additional times 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. PREREQUISITES** (PHYS 211 or PHYS 102 or PHYS 201 or PHYS 153 or PHYS 115) and (CHEM 252 or CHEM 253 or ENGR 210) and (CHEM 356 or CHEC 352)

**C. REQUIRED TEXTBOOK**

Physical Chemistry, Tenth Edition by Peter Atkins and Julio de Paula, W.H. Freeman and Company (2014)

**D. CLASS MEETINGS**

Monday and Wednesday Evenings from 6:00 to 7:45 P.M. in Disque Hall, Room 108

**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 on exams (in any form) and plagiarism, will be dealt with appropriately.

## G. GRADE BREAKDOWN

- 30% of your grade will come from Exam I, which will cover Spectroscopy and Statistical Mechanics/Thermodynamics. It will be given on Wednesday July 15 (tentative date)
- 30% of your grade will come from Exam II, which will cover only Chemical Kinetics. The specific coverage will be the material listed as "Chemical Kinetics – Set #1" under the Answers To Assigned Exercises and Problems on page 7 in this course outline. It will be given on Monday August 10 (tentative date)
- 10% of your grade will come from two assignments to be submitted throughout the quarter: one will be on material for the First Exam and the other will be on material for the Second Exam
- 30% of your grade will come from the Final Exam, which will be comprehensive. The Final Exam will be on Monday August 31 (tentative date)

**NOTE: There will be no classes missed due to holidays for Summer 2015 Quarter. July 4th is on Saturday and Labor Day is September 7 (AFTER the Final Exams).**

During the exams you will be provided with a reference sheet containing constants, conversion factors, and fundamental equations related to the subject matter. NOTHING OTHER THAN THIS REFERENCE SHEET MAY BE USED DURING THE EXAM. **IF YOU ARE FOUND USING ANYTHING ELSE IT WILL BE CONFISCATED AND YOU WILL RECEIVE A GRADE OF "F" FOR THE COURSE.** NO EXAMS WILL BE GRADED OR RETURNED TO ANY STUDENT NOT OFFICIALLY ENROLLED IN THE CLASS.

DURING THE EXAMS THERE WILL BE NO TEXTING, USE OF CELL PHONES, LISTENING DEVICES OF ANY KIND, LAPTOPS, PDAs, AND/OR ANY TYPE OF ELECTRONIC DEVICE OTHER THAN A STANDARD CALCULATOR. CELL PHONES MUST BE TURNED OFF AND STUDENTS CANNOT LEAVE AND RE-ENTER THE ROOM FOR ANY REASON.

ALL COURSE GRADES WILL BE DETERMINED EXCLUSIVELY FROM EXAM AND ASSIGNMENTS GRADES. THERE IS NO EXTRA CREDIT OR OTHER ASSIGNMENTS THAT WILL INFLUENCE THE COURSE GRADE UNLESS OTHERWIDE INDICATED BY THE INSTRUCTOR. ANY OTHER ASSIGNMENTS WILL BE FOR THE ENTIRE CLASS AND NOT ON A BASIS FOR INDIVIDUAL STUDENT(S) EXCLUSIVELY.

## H. 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 at 3:00 on Wednesday August 12 in Room 313 of Disque Hall and it will end at 5:00. This is the only time a makeup exam will be available. If you miss either Exam I or Exam II and do not take the makeup exam you will forfeit 30% of your grade.** The makeup exam 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 and take the make-up exam you will forfeit 30% of your grade. **No make-up exams will be permitted at any other time. THE MAKE-UP EXAM IS TO REPLACE A MISSED EXAM, NOT TO REPLACE A POOR GRADE.**

## I. ATTENDANCE POLICY

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

**J. GENERAL INFORMATION**

The last day to drop this course using an Academic Advisor's assistance is Friday July 3. If you do not need your advisor's permission you can drop it by using Drexel One no later than 11 P.M. on Sunday July 5. The last day to withdraw from this course is Friday August 7. Before you drop or withdraw from a course you should check with your advisor, as there may be consequences. Dropping or withdrawing from a course may affect your academic standing or your financial situation. It may have serious effect on billing at Drexel, financial aid, VA benefits, NCAA athletic eligibility, immigration status for foreign students, and other possible consequences. As a student you are responsible for transactions against your academic record.

http://www.drexel.edu/provost/policies
http://www.drexel.edu/src/financialaid/info/eligibility
http://www.drexel.edu/studentlife/get_involved/international_students_scholars/
http://www.drexel.edu/src/about/veterans

Different policies apply to dropping a course and withdrawing from a course. Dropping a course results in the course being removed from your transcript. Withdrawing from a course results in a grade of W on your transcript. Students should consult their Advisors (both Academic and Financial Aid) and, in some cases, the instructor before dropping or withdrawing from the course.

In order to drop or withdraw from a course, you should have the "Add/Drop/Withdraw" form signed by the course instructor and the student's Academic Advisor. Dropping or withdrawing from the course may affect your billing and academic record. Forms are available in many Department offices, in the lobby of Goodwin College and at

http://www.drexel.edu/src/forms
http://www.drexel.edu/provost/policies/course_drop.asp

Consult "Course Withdrawal Policy", "Course Drop Policy", "Code of Conduct", and other important information at http://www.drexel.edu/provost/policies and
http://www.drexel.edu/provost/

Incomplete Grade (I) or No Grade Reported (NGR) or No Credit. You must take responsibility to meet the University's policies and deadlines for requesting an incomplete grade and completing a course before the deadline passes. If you stop attending a course, you are not automatically removed from the course. It is your responsibility to complete, drop, or withdraw from the course. If you register for a course and do complete, drop, or withdraw from it, eventually an NGR grade will turn to a grade of F. An Incomplete grade will turn to an F grade if the student does not complete the course.

http://www.drexel.edu/provost/policies/grades.asp

If a student has an Incomplete Grade or No Grade Reported, the student should see the instructor for the course and the student's Academic Advisor immediately.

If you do not meet your financial obligations to the University, you will not receive a grade.

Read about Academic Integrity, Plagiarism and other topics at
www.drexel.edu/studentaffairs/community_standards/studentHandbook/general_information/code_of_concuct/

For the "Americans with Disabilities Act" Drexel University has the Office of Disability Services at 3201 Arch Street, Suit 210 and online at

http://www.drexel.edu/oed/policies
http://www.drexel.edu/oed/disabilityResources.

This office is to be contacted by the student if special course accommodations, emergency medical information or building evacuations are need. This office will also verify any special needs and give a form to the student to give to the instructor. The student should make the arrangements with this office and inform the instructor within the first two weeks of the term or when a new situation occurs.

# TOPICS TO BE COVERED DURING THE QUARTER

**CHAPTER 12 - ROTATIONAL AND VIBRATIONAL SPECTROSCOPY**

General Features of Spectroscopy (Line Width, Doppler Broadening, Lifetime Broadening) - Intensities of Spectral Lines - Beer-Lambert Law - Rotational Energies - Rigid Rotor Model of Molecular Rotations - Centrifugal Distortion - Microwave Spectroscopy - Harmonic Oscillator Model for Molecular Vibrations - Anharmonicity - Infrared Spectroscopy - Vibration/Rotational Spectroscopy - Spectroscopic Selection Rules

**CHAPTER 15 - STATISTICAL THERMODYNAMICS**

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

**CHAPTER 21 - 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

**CHAPTER 12** Exercises 12A.2a, 12A.3a, 12A.5a, 12B.5a, 12C.1a, 12C.2a, 12C.3a, 12C.4a, 12D.3a, 12E.1a, 12E.2a, SP1

**CHAPTER 15** Exercises 15A.4a, E15A.6a, E15B.1a, E15B.2a, E15B.4a, E15B.4b (CORRECTION: $H_2O$ IS symmetric with $\sigma$=2). Also, estimate the temperature above which the rotational states are "well populated", E15B.9a ($\sigma$ = 4), E15B.11a, E15E1a, E15E.2a, E15E.5a, E15E.7a, E15F.1a, SP2, SP3

**CHAPTER 21** Exercises 20A.1a, 20A.1b, 20A.2a, 20A.3a, 20A.4a, 20B.2a, 20B.4a, 20D.1a, 20D.2a, 20E.1a (pre-equilibrium condition only), 20F.2a, 20F.,3a

Problems 20A.1, 20A.4, 20B.3, 20B.4, SP2, SP3, 20B.9, 20B.10, 20B.12, 20B.13, 20D.2 (also determine k at 30°C), SP4, SP5, SP6, SP7

**THESE ASSIGNMENTS MAY BE MODIFIED AS THE QUARTER PROGRESSES**

**SP = SUPPLEMENTARY PROBLEMS LISTED BELOW**

# SUPPLEMENTARY PROBLEMS

SP1 The fundamental ($v = 0 \rightarrow v = 1$) vibrational transition for $H^{35}Cl$ occurs at 2885 $cm^{-1}$. 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

a) the rotational-vibrational coupling constant, $\alpha_e$
b) the rotational constant, $B_e$
c) the bond distance

SP2 Calculate the vibrational contribution to the entropy of $Cl_2$ at 500K given that the wavenumber of the vibration is 560 $cm^{-1}$.

SP3 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. Comment the trend in relative error as x increases.

$$\ln (x!) = (x + \tfrac{1}{2}) \ln (x) - x + \tfrac{1}{2} \ln(2\pi)$$

SP4 A second order reaction of the type $A + B \rightarrow P$ was carried out in a solution that was initially 0.075M in A and 0.050M in B. Given that the reaction is first order in each reactant (which makes it second order overall) After 1.0 hour, [B] had fallen to 0.020M.

a) Calculate the rate constant
b) What is the half-life of the reactants?

SP5 One of the hazards of nuclear explosions is the generation of $^{90}Sr$ and its subsequent incorporation in place of calcium in bones. This nuclide has a half-life of 28.1 years. Suppose a newly born child absorbed 1μg. How much will remain after (a) 18 years and (b) 70 years if none is lost metabolically?

SP6 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 $9.2 \times 10^{-4}$ $sec^{-1}$. 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.

SP7 Consider a two-step consecutive reaction in which $k_1 = 0.50$ $min^{-1}$ and $k_2 = 0.03$ $min^{-1}$. Starting with [A] = 0.60M

a) How long would it take (in minutes) for B to reach its maximum concentration?
b) What is the maximum concentration?
c) At that same time, what are [A] and [C]?

SP8 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 $min^{-1}$

a) 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?

b) If your objective was to make longer polymer chains, what adjustment(s) would you make to the variables you can readily control?

SP9 Consider a stepwise polymerization to make Nylon in which a stoichiometric blend of diamine and diacid are used. A reactor is charged with [diamine] = 0.25M and the rate constant at the reaction temperature is observed to be 1.45 $M^{-1}$ $sec^{-1}$.

a) 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?

b) 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°?

## ANSWERS TO ASSIGNED EXERCISES AND PROBLEMS

### SPECTROSCOPY

E12A.2a) 82.9% reduction in intensity

E12A.3a) 5340 $M^{-1}cm^{-1}$

E12A.5a) 449 $M^{-1}cm^{-1}$

E12B.5a) D = 2.073 x $10^{-4}cm^{-1}$, 0.125

E12C.1a) HCl, $CHCl_3$, and $CH_2Cl_2$

E12C.2a) 4.09 x $10^{11}$ $sec^{-1}$, 13.65 $cm^{-1}$

E12C.3a) 127.9 pm

E12C.4a) 4.439 x $10^{-47}$ kg-$m^2$, 166.5 pm

E12D.3a) 329.5 N/m

E12E.1a) HCl, $CO_2$, and $H_2O$

E12E.2a) (a) 3 (b) 6 (c) 12

SP1) (a) $\alpha_e$ = 0.271 $cm^{-1}$ (b) B = 10.89 $cm^{-1}$ (c) r = 126 pm

### STATISTICAL MECHANICS/THERMODYNAMICS

E15A.4a) 524K

E15.A.6a) 354K

E15B.1a) 8.24 pm and 1.79 x $10^{27}$ at 300K

2.60 pm and 5.69 x $10^{28}$ at 3000K

E15B.2a) 0.353

E15.B.4a) 7,967 at 25°C and 1.12 x $10^4$ at 100°C

E15B.4b) $q_{rot}$ = 43.1 at 25°C and 60.4 at 100°C

Temperature is between 23K and 40K

E15B.9a) $q_{rot}$ = 660

E15B.11a) $q_{vib}$ = 2.571

E15E.1a) with fully populated vibrational states $I_2$ = 3.5R, $CH_4$ = 12R, $C_6H_6$ = 33R

E15E.2a) $NH_3$ without vibration = 1.333 $NH_3$ with vibration = 1.111 $NH_3$ actual = 1.311

$CH_4$ without vibration = 1.333 $CH_4$ with vibration = 1.083 $CH_4$ actual = 1.308

E15E.5a) He = 126.1 J/mol-K and Xe = 169.6 J/mol-K

E15E.7a) 43.767 J/mol-K

SP2) 5.19 J/mol-K

E15F.1a) rotational contribution = -13,824 J/mol

vibrational contribution = -205 J/mol

**CHEMICAL KINETICS –SET #1**

E20A.1a) Total pressure will not change during the course of the reaction

E20A.1b) Total pressure will decrease during the reaction, ending at ½ the initial pressure

E20A.2a) A = D = 2.7 mol/L-sec, B = 5.4 mol/L-sec, C = 8.1 mol/L-sec

E20A.3a) A = 2.7 mol/L-sec, B = 1.35 mol/L-sec, D = 4.05 mol/L-sec

E20A.4a) $M^{-1}$ $sec^{-1}$ A = k[A][B] C = 3k[A][B]

E20B.2a) after 50 seconds Pressure = 498 Torr after 20 minutes Pressure = 461 Torr

E20B.4a) t = 1.11 x $10^5$ sec

E20D.1a) $E_a$ = 64.9 kJ/mol, A = 4.32 x $10^8 M^{-1}sec^{-1}$

E20D.2a) 34.94 kJ/mol

P20D.2) $E_a$ = 96.9 kJ/mol, k @30°C = 0.168 $min^{-1}$

P20A.1) second order

P20A.4) (a) rate = k [ICl][$H_2$] (b) k = 0.164 $M^{-1}$ $sec^{-1}$ (c) rate = 2.08 x $10^{-6}$ mol/L-sec

P20B.3) second order rate constant = 0.0596 $min^{-1}$ 2.39 grams of ammonium cyanate left

P20B.4) first order rate constant = 0.054 $hr^{-1}$ = 1.51 x $10^{-5}sec^{-1}$ [$(CH_3)_3CBr$] = 0.00967M

P20B.9) first order rate constant = 0.351 $min^{-1}$ = 5.85 x $10^{-3}sec^{-1}$ half life = 1.98 minutes

SP4) k = 16.2 $M^{-1}hr^{-1}$, $t_{½}$ for A = 1.71 hour and $t_{½}$ for B = 0.71 hour

SP5) 28.1 years = 0.642μg 70 years = 0.178 μg

SP6) $k_{reverse}$ = 2.3 x $10^{-4}$ $sec^{-1}$

**CHEMICAL KINETICS –SET #2**

E20E.1a) rate = $k_2\sqrt{\frac{k_1[A_2]}{k_{-1}}}[B] = k\sqrt{[A_2]}[B]$ in which $k = k_2\sqrt{\frac{k_1}{k_{-1}}}$

P20B.12) first order, k = 0.017 $min^{-1}$

P20B.13) second order, k = 1.19 x $10^7$ $M^{-1}sec^{-1}$, half life = 0.00498 sec (for 0.00012 second point)

P20B.10) 55.4% ketene

SP7) (a) 5.99 minutes (b) 0.50M (c) [A] = 0.03M and [C] = 0.07M

E20F.2a) 0.996

E20F.3a) 0.125

S8) (a) 1,863 (b) decrease [I] and/or increase [M]

SP9) (a) average time = 687 seconds (b) <n> will increase

# CHEC 353 - PHYSICAL CHEMISTRY AND APPLICATIONS III
## SUMMER TERM, 2015

**I have read and understand all of the course requirements that are detailed in this course syllabus. By my signature below I am indicating that I understand each of the following:**

- **When exams are scheduled (at least tentative dates, which are subject to change)**
- **The make up time for a missed exam is on Wednesday August 12 at 3:00 and no make-up exams will be permitted at any other time. Failure to take a makeup exam (for a MISSED exam only) results in forfeiting 30% of the course grade. Also, it is understood that the make-up exam will cover material from both Exam I and Exam II so I may be tested twice on some topics. The make-up exam will replace ONE EXAM ONLY so if I miss both Exam I and Exam II, 30% of my grade will be forfeited.**
- **The policy that all course grades will be determined from exam grades only and extra credit assignments are not available on an individual basis.**
- **The only reference material that can be used during any exam is a sheet containing constants, conversion factors, and select equations that will be provided with the exam. Attempting to use anything else will result in a grade of ZERO for the exam.**
- **It is my responsibility to find out what was missed if I miss a class.**

**NAME (printed)** _____

**SIGNATURE** _____

**DATE**_____