Chem 3070: Thermodynamics and Kinetics. Spring 2013

Instructors   Valeria Molinero, Associate Professor of Chemistry
Yuqing Qiu, Graduate Student of Chemistry
Timothy Gorey, Graduate Student of Chemistry
Zhe Gao, Graduate Student of Chemistry

Contact information Professor Molinero: Valeria.Molinero@utah.edu; 801-585-9618.
Office: 4623 Thatcher (324 INSCC until move by end of Jan)
Molinero's assistant, Whitney Cox: Whitney.Cox@utah.edu
Include "chem 3070" in the subject of emails.

Schedule: MWF   9:40-10:30 am HEB 2006 and
TH   7:30-8:20 am in JTB 320 or 9:40-10:30 am ST 205
Office Hours: Molinero Wed. 1-3 pm 324 INSCC/ 4623 Thatcher.

Course Description   An introduction to statistical mechanics, chemical thermodynamics and
kinetics with applications to gases, solutions, and phase and chemical
equilibria. A discussion section accompanies the lecture.

Course Goals   The goal of this course is to investigate the physical models,
mathematical approximations and empirical laws to predict the
behaviors of molecules in physical, chemical, and biological systems.
Elements of statistical mechanics, the laws of thermodynamics, and
relationships between the two will be covered with application to gases,
solutions, and phase and chemical equilibria.

Course Objectives   The principal objective of this course is to improve your ability to
critically apply both qualitative and quantitative models of physical
properties and chemical change to deepen your understanding of
chemical phenomenon.

The content and organization of this course are designed to help you:

- Construct various theoretical models by answering a series of
questions designed to lead students through the thought
processes that result in the development of course topics.

- Use simple models for predictive insight and understanding of
physical phenomena.

- Apply a variety of mathematical tools in order to solve problems
using microscopic models to calculate various thermodynamic
quantities.

- Summarize essential concepts and effectively communicate
knowledge of these topics.

- Analyze, interpret, and draw appropriate conclusions from
numerical simulations and experimental data related to

thermodynamics, equilibria, and transport.

Daily Learning Objectives

- Write the total derivative given a set of variables
- Determine whether or not a total derivative is exact
- Explain the significance of an exact derivative
- Identify the basic assumptions of an ideal gas as described by Kinetic Molecular Theory
- Rationalize why the compressibility factor is greater than or less than one for real gases
- Derive expressions for the 2nd virial coefficient based on different gas models
- Recognize the sign convention for work and define work for a constant pressure system
- Differentiate between the various components of internal energy considered in thermodynamics
- Assess how work and heat effect the change in internal energy of a system based on the 1st Law of thermodynamics
- Assess the probability of a specific combination of events
- Define the total multiplicity of a sequence of events and the resulting probability
- Identify the probability of a particular composition based on the number of permutations
- Characterize the equilibrium composition of a system based on the principle of maximum multiplicity
- Describe the relationship between multiplicity and entropy as defined by Boltzmann
- Define a reversible process and calculate the work performed
- Predict the direction of energy transfer using a simple statistical model
- Assess how energy and number of particles affect the probability of energy flow between subsystems
- Define temperature in terms of entropy changes of a system
- Write the fundamental thermodynamic equation for energy and identify the measurable property corresponding to each partial derivative
- Use the fundamental thermodynamic equation for entropy to predict the direction of heat flow or volume changes
- Use equations of state derived based on experimental data that give more accurate results over a larger range of conditions.
- Recognize both the physical and mathematical implications of adding higher order volume terms to a state equation
- Recognize that a change in boundary conditions leads to new extrema principles (equilibrium conditions) and thermodynamic quantities
- Assess spontaneity of a process in terms of Hemholtz free energy
- Use Legendre transforms to switch from one set of independent variables to another
- Differentiate between different variable sets as fundamental and useful **or** useful but not fundamental
- Derive a Maxwell relation based on Euler's reciprocal relation
- Recognize how a Maxwell relation is used in the derivation of a "working equation" for internal energy or enthalpy to assess the total change in the appropriate state function

- Differentiate between the "standard state" internal energy or enthalpy change for an ideal gas and the additional "imperfection" value based on intermolecular interaction
- Identify the appropriate state function that characterizes the heat transfer at constant volume or at constant pressure
- Calculate the difference in enthalpy with temperature depending on the functional dependence of heat capacity with temperature
- Define and write an appropriate enthalpy of formation reaction
- Calculate the enthalpy of reaction using enthalpy of formation data at different temperatures
- Recognize various conditions for gas expansion
- Derive and calculate the temperature change for a gas under adiabatic conditions
- Describe the conditions for a Joule-Thompson expansion, calculate the corresponding temperature change, and compare it to the value obtained for an adiabatic expansion
- Define entropy in terms of the 3rd Law
- Calculate entopy changes with temperature for pure substances and reactions at different temperatures
- Determine the change in Gibbs Free energy and describe a process as spontaneous or at equilibrium
- Demonstrate that the definitions of entropy as a function of multiplicity or as a function of probability are equivalent
- Describe the probability distribution that corresponds to the state of maximum entropy
- Use the Lagrange Multiplier method to find the probability distribution that maximizes entropy
- Derive the Boltzmann distribution using the Lagrange Multiplier method and use it to describe various populations of state
- Define average energy in terms of the partition function
- Write a system partition function as the product of individual particle partition functions
- Write any thermodynamic function in terms of the partition function
- Write a general expression for the rotational energy partition function
- Derive the analytical expression for the 3D translational energy partition function
- Write a general expression for the vibrational and electronic energy partition function
- Derive an expression for the total energy partition function
- Define chemical potential for a pure ideal gas as a function of pressure
- Assess changes in the free energy of a reaction in terms of pressure ratios and indicate the direction of spontaneity towards equilibrium
- Predict how the equilibrium constant changes with temperature depending on the enthalpy change
- Derive expressions to find the temperature dependence of the equilibrium constant based on various assumptions regarding the temperature dependence of enthalpy
- Use changes in Gibbs free energy to predict phase equilibria changes as a function of temperature and pressure
- Derive expressions relating changes in pressure with temperature for two phases in equilibrium

- Describe the relationship between the solution composition and the partial pressure of each component in the vapor phase for an ideal solution
- Derive an expression for the chemical potential of an ideal solution using Raoult's law
- Relate phase equilibria equations to simple phase diagrams for pure substances
- Describe the affect of adding a solute to the boiling point of a solvent.
- Derive a simple expression to calculate boiling & freezing point changes as a function of solvent properties only and identify all necessary assumptions
- Use the lever rule to determine the percentage of a substance in a given phase as opposed to the composition of the phase
- Use the phase rule to define the number of independent variables (degrees of freedom) needed to define the equilibrium state of a multicomponent, multiphase system
- Use phase diagram for two-component systems to assess whether two substances are mutually miscible, whether an equilibrium can exist over a range of conditions, or whether a system must be brought to a definite pressure, temperature, and composition before equilibrium is established
- Identify elementary steps of chemical reactions and their rate constants
- Derive expressions for the rate of chemical reactions from mechanistic information using the steady state approximation
- Interpret the temperature dependence of reaction rates in terms of activation energies of the individual mechanistic steps.
- Use transition state theory and the concept of reaction coordinate to derive rates of reactions from microscopic data
- Interpret the sign and magnitude of the activation enthalpy, entropy and volume of reactions and their implications for the temperature and pressure dependence of the reaction rate
- Derive expressions for the chemical potential of electrolytes as a function of concentration.
- Identify relationships between the activity coefficients of ions in solution.
- Derive expressions for the activity coefficients of dilute ionic solutions using Debbie-Huckel theory.
- Interpret the concentration and temperature dependence of of ionic activity coefficients of concentrated solutions in terms of the structure and interactions between ions.

Class format and assignments

The course is based on the POGIL (Process Oriented Guided Inquiry Learning) method. To learn about POGIL go to: http://www.pogil.org/. POGIL is a student-centered learning method in which the standard lectures and recitations in which an instructor "provide knowledge" are replaced or complemented by in-class student work on guided inquiry-learning activities (*Workbook* below) that were specifically developed to facilitate student learning through a cycle of exploration, concept formation and application. The activities keep the students actively engaged and thinking in the classroom, constructing their own understanding. ***Students must bring to class a printed copy of the workbook*** *(listed below).* The instructors will request the students to turn in their complete workbooks for assessment. Electronic workbooks will not be accepted.

The students will be organized in learning teams of 4 or 3 people that work together on the guided inquiry learning activities in the classroom and on specific assignments. The students in a team have different roles (that will be rotated weekly): manager, spokesperson, recorder and strategy analyst.

- The **manager** actively participates, keeps the team focused on the task, distributes work and responsibilities, resolves disputes, and assures that all members participate and understand.
- The **spokesperson** (or presenter) actively participates and presents reports and discussion to the class.
- The **recorder** actively participates, keeps a record of the assignment and what the team has done, and prepares a report in consultation with the others.
- The **strategy analyst** (or reflector) actively participates, identifi es strategies and methods for problem solving, identifi es what the team is doing well and what needs improvement in consultation with the others, and prepares a group assessment in consultation with the others.

Reports and assessments on the guided inquiry activities will be prepared by the group and collected by the instructors. Exercises and problems will be worked out in class or assigned as homework. In class, the instructors will facilitate the learning of strategies and procedures to address and solve problems and will specify which exercises and problems of the homework must be completed *before* each class and which ones the students have to turn in for grading.

Thermodynamics is a demanding and challenging subject. Most, but not all, the contents of the course will be covered through guided inquiry activities. The instructors will indicate in class the textbook chapters that correspond to each workbook activity. Lectures in which the instructor presents data and knowledge will be scarce because research has demonstrated that is not the most effective method for student learning. **To fully learn the contents, the students will have to study from the textbook and work on exercises and problems outside the classroom for an expected 8 to 12 hs/week.**

Textbooks

Main textbook (<u>required</u>, available in the Campus Store):
Physical Chemistry: A Molecular Approach
Donald A. McQuarrie and John D. Simon, University Science Books (1997)

Secondary Textbook
Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics and Nanoscience
Ken A. Dill and Sarina Bromberg, Garland Science (2010)

Workbook

A Guided Inquiry: Thermodynamics & Statistical Mechanics (Spring 2013)
Tricia D. Shepherd. Available for download with author's permission from:
https://www.dropbox.com/s/cj1ns1gu68dshda/Workbook-Thermo2013.pdf

A printed copy will be available at the Marriott library for photocopying.

The tentative order in which the activities will be completed is indicated below. (Note that this is *not* the same order in which they are printed in the workbook).

Principles
Toolkit.1: Multivariate Calculus
Principle.1: Gas Equations of State
Principle.2: 1st Law
Principle.3: Processes
Toolkit.2: Probability
StatMech.1: Extremum Principle
Toolkit.3   Sterling's Approximation
Principle.4: 2nd Law
Principle.5: Free Energy
Toolkit.4: Legendre Transforms
Toolkit.5: Maxwell Relations
Principle.6: Heat Capacity
Principle.7: Thermochemistry
Principle.8: 3rd Law
StatMech.2: Entropy & Probability
Toolkit.6: Lagrange Multipliers
StatMech.3: Partition Function
StatMech.4: Equipartition

Equilibria Activities
Equilibria.1: Equilibrium Constant
Equilibria.2: Temperature Dependence of the Equilibrium Constant
Equilibria.3: Vapor pressure
Equilibria.4: Solutions
Equilibria.5: Colligative Properties
Equilibria.6: Lever Rule
Equilibria.7: Phase Rule
Equilibria.8: Multicomponent Phase Diagrams

Kinetics Activities
Kinetics.1: Steady State
Kinetics.2: Activation Energy
Kinetics.3: Transition State Theory

Electrochemistry Activities
Electrochem.1: Electrolyte Solutions
Electrochem.2: Debye-Huckel Theory
Electrochem.3: Structure of Ionic Solutions
Electrochem.4: Degree of Dissociation

Evaluation and Grades

Students will be evaluated individually through 5 exams, quizzes and homework and collectively with their groups through their in-class work, reports and assessments on the guided inquiry activities. The best 4 grades of the 5 exams

contribute 20% each to the grade. The other 20% is from activities, in class participation, homework, quizzes and reports. *There will be no make up exams.*