University of Virginia, Department of Materials Science and Engineering

Fall 2009, Tuesday and Thursday, 09:30 – 10:45 am

Wilsdorf Hall, Room 101

MSE 3050: Thermodynamics and Kinetics of Materials

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Office Hours: 11:00 am to 12:00 pm Monday, Friday ***& open***

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Abstract: In this course we start from a brief review of classical thermodynamics necessary for understanding of phase diagrams. We will then apply the thermodynamic concepts to the analysis of phase equilibria and phase transformations in one-component and multi-component systems. We will learn how to read and analyze phase diagrams of real materials and how to construct phase diagrams from thermodynamic data. In the last part of the course we will consider the basic concepts of kinetic phenomena in materials. Most kinetic phenomena in condensed matter involve diffusion and we will focus on the mechanisms of diffusion in materials as well as on the analytical and numerical methods to describe diffusion. By the end of the course we will see how the interplay of thermodynamic driving forces and kinetics of mass transfer is defining the formation of complex microstructures of real materials.

Grading: Homework 25%; Mid-Term Exams 30%; Final Exam 45%

Main (optional) text: D. A. Porter and K. E. Easterling, Phase Transformations in Metals and Alloys, 2^{nd} edition, Chapman & Hall, London, UK, 1992 (TN690.P597 - placed on reserve circulate, Science and Engineering Library).

This textbook was reprinted by CRC Press in 2003 (2^{nd} edition) and in 2009 (3^{rd} edition) - you can buy it from them (http://www.crcpress.com/) for $70, or from amazon.com (http://www.amazon.com) for ~$60.

Lecture notes: Another important source of course material will come from the lecture notes. The lecture notes will appear at the class web page as course progresses. You should print out the lecture notes before coming to class, or make your own notes and combine them with the printed lecture notes.

Optional textbooks (placed on reserve circulate, Science and Engineering Library):

D. R. Gaskell, Introduction to the Thermodynamics of Materials, 4th edition, New York: Taylor & Francis, 2003 (TN673.G33 2003) $96 for 5th edition hardcover at www.amazon.com, ~$70 for used or earlier editions.

In the first part of this course, when we review the fundamentals of thermodynamics, it would be useful for you to read sections of Gaskell's book suggested in the lecture notes. You may also want to look for more compact and sometimes more clear explanations given in Porter and Easterling. Please keep in mind that notation varies from textbook to textbook; nevertheless, looking into different textbooks may help to clarify complicated topics and provide additional examples.

Kinetics is not covered in Gaskell. In the second part of the course the main source of material will come from the lecture notes and from Porter and Easterling.

Topics that are covered include:

Part 1. Review of classical thermodynamics

- **First Law - Energy Balance**
  - Thermodynamic functions of state
  - Internal energy, heat and work
  - Types of paths (isobaric, isochoric, isothermal, adiabatic)
  - Enthalpy, heat capacity, heat of formation, phase transformations
  - Calculation of enthalpy as a function of temperature
  - Heats of reactions and the Hess's law

- **Theoretical calculation of the heat capacity**
  - Principle of equipartition of energy
  - Heat capacity of ideal and real gases
  - Heat capacity of solids: Dulong-Petit, Einstein, Debye models
  - Heat capacity of metals – electronic contribution

- **Entropy and the Second Law**
  - Concept of equilibrium
  - Reversible and irreversible processes
  - The direction of spontaneous change
  - Entropy and spontaneous/irreversible processes
  - Calculation of entropy in isochoric and isobaric processes
  - Calculation of entropy in reversible and irreversible processes

- **The Statistical Interpretation of Entropy**
  - Physical meaning of entropy
  - Microstates and macrostates
  - Statistical interpretation of entropy and Boltzmann equation
  - Configurational entropy and thermal entropy
  - Calculation of the equilibrium vacancy concentration

- **Fundamental equations**
  - The Helmholtz Free Energy
  - The Gibbs Free energy
  - Changes in composition
  - Chemical potential
  - Thermodynamic relations and Maxwell equations

Part 2. Phase Transitions and Phase Diagrams

- **One-component systems**
  - Enthalpy and entropy dependence on P and T
  - Gibbs free energy dependence on P and T
  - Clapeyron equation
  - Understanding phase diagrams for one-component systems
  - Polymorphic phase transitions
  - Driving force for a phase transition
  - First order and second-order phase transitions

- **Introduction to Solution Thermodynamics**
  - Ideal solution: Entropy of formation and Gibbs free energy
  - Chemical potential of an ideal solution
  - Regular solutions: Heat of formation of a solution
  - Activity of a component
  - Real solutions: interstitial solid solutions, ordered phases, intermediate phases, compounds
  - Equilibrium in heterogeneous systems

- **Binary phase diagrams**
  - Binary phase diagrams and Gibbs free energy curves
  - Binary solutions with unlimited solubility
  - Relative proportion of phases (tie lines and the lever principle)
  - Development of microstructure in isomorphous alloys
  - Binary eutectic systems (limited solid solubility)
  - Solid state reactions (eutectoid, peritectoid reactions)
  - Binary systems with intermediate phases/compounds
  - The iron-carbon system (steel and cast iron)
  - Gibbs phase rule
  - Temperature dependence of solubility
  - Multi-component (ternary) phase diagrams

Part 3. Kinetics

- **Basic concepts in kinetics**
  - Kinetics of phase transformations
  - Activation free energy barrier
  - Arrhenius rate equation

- **Diffusion in solids - phenomenological description**
  - Driving force for diffusion in ideal solutions
  - Flux, steady-state diffusion, Fick's first law
  - Diffusion coefficient, Einstein relation
  - Nonsteady-state diffusion, Fick's second law

- **Thermodynamics of diffusion**
  - Driving force for diffusion revisited
  - Diffusion in ideal and real solutions
  - Thermodynamic factor
  - Diffusion against the concentration gradient: Spinodal decomposition

- **Solutions to the diffusion equation**
  - Numerical integration
  - Analytical solution
  - Applications (chemical homogenization, carburization of steel)

- **Atomic mechanisms of diffusion**
  - Substitutional diffusion
  - Interstitial diffusion
  - Temperature dependence
  - High diffusivity paths (grain boundaries, free surfaces, dislocations)

- **Kinetics of phase transformations**
  - Supercooling and superheating
  - Driving force for phase transformation
  - Homogeneous nucleation
  - Critical radius, nucleation rate
  - Heterogeneous nucleation
  - Nucleation in melting and boiling
  - Growth mechanisms
  - Rate of phase transformations
  - Solidification and growth morphologies
  - Kinetics of solid-state transformations