University of Virginia, Department of Materials Science and Engineering

Fall 2025, Tuesday and Thursday, 3:30 am - 4:45 pm

Classroom: Olsson Hall 009

MSE 3050: Thermodynamics and Phase Equilibria of Materials

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Abstract: In this course we start from a brief review of classical thermodynamics necessary for understanding the conditions for phase equilibria, phase stability and phase transformations. We will also undertake several forays into statistical thermodynamics to get a solid physical/intuitive understanding of the heat capacity, internal energy, enthalpy, entropy, and free energy. 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. Examples illustrating the connections between the phase diagrams and microstructure/properties of real materials will be discussed. Finally, we will discuss the thermodynamics of interfaces between solid, liquid, and vapor phases, and consider the role the interfaces play in phase transformations and in defining the equilibrium shapes of crystals and elements of material microstructure.

Pre- or Co-requisite: APMA 2120 or MATH 2310 or instructor permission.

Grading: Homework 35%; Mid-Term Exams 30%; Final Exam 35%

Main (optional) textbooks: D. A. Porter and K. E. Easterling, Phase Transformations in Metals and Alloys, 2nd edition, Chapman & Hall, London, UK, 1992 (TN690.P597 in Science and Engineering Library).

This textbook was reprinted by CRC Press in 2003 (2nd edition) and in 2009 (3rd edition) - you can buy it from http://www.crcpress.com/ or http://www.amazon.com

D. R. Gaskell, Introduction to the Thermodynamics of Materials, 3th, 4th and 5th editions, New York: Taylor & Francis, 1995, 2003, 2008 (TN673.G33 in Science and Engineering Library).

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.

In the second and third parts of the course the main source of material will come from the lecture notes and from Porter and Easterling.

Lecture notes: Another important source of course material will come from the lecture notes. The lecture notes will appear under Resources on the course Collab site as the course progresses.

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 and semiconductors – 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 pressure and temperature
  - Gibbs free energy dependence on pressure and temperature
  - 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 Solid Solution Thermodynamics**
  - Ideal solid solution: Entropy of formation and Gibbs free energy
  - Chemical potential of an ideal solution
  - Regular solid 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 solid solutions with unlimited solubility
  - Relative proportion of phases (tie lines and the lever principle)
  - Development of microstructure in isomorphous alloys
  - Binary solid solutions with positive enthalpy of mixing
  - Miscibility gap – derivation for regular solutions
  - Binary eutectic systems (limited solid solubility)
  - Temperature dependence of solubility – derivation for regular solutions
  - Microstructure in eutectic alloys, calculation of fractions of microconstituents
  - Liquid immiscibility and monotectic systems
  - Binary solid solutions with negative enthalpy of mixing
  - Binary systems with intermediate phases/compounds
  - Stoichiometric and non-stoichiometric compounds
  - Solid state reactions (eutectoid, peritectoid reactions)

- Development of microstructure in rapid (nonequilibrium) cooling
- The iron-carbon system (steel and cast iron)
- Gibbs phase rule
- Temperature dependence of solubility
- Multi-component (ternary) phase diagrams

Part 3. Thermodynamics of interfaces

- **Solid-vapor interfaces**
  - Surface free energy and surface stress
  - Dependence on crystallographic orientation
  - Faceting of crystals, Wulff plot and Wulff construction

- **Liquid-vapor and solid-liquid interfaces**
  - Atomic structure and surface free energy
  - Wetting angle, Young equation
  - Capillary pressure, Young–Laplace equation
  - Temperature and composition dependence for liquid-vapor interfaces, Marangoni effect

- **Solid-solid interfaces**
  - Grain boundaries and interphase interfaces
  - Structure and energy of grain boundaries
  - Low-angle and high-angle grain boundaries
  - Special low-energy high-angle grain boundaries
  - Interphase interfaces (coherent, semicoherent and incoherent)
  - Effects of misfit strain and interfacial energy on shape of precipitates

- **Mechanisms of phase transformation, classical nucleation theory**
  - Spinodal decomposition versus nucleation and growth
  - Homogeneous nucleation
  - Critical radius, nucleation rate
  - Heterogeneous nucleation
  - Temperature dependence homogeneous and heterogeneous nucleation rates
  - Nucleation in solidification, melting and boiling

One computer laboratory (on construction of phase diagrams from cooling curves) will be used in the second part of the course. The computer laboratory does not require any programming by students.

Student Disability Access: It is my goal to create a learning experience that is as accessible as possible. If you anticipate any issues related to the format, materials, or requirements of this course, please meet with me outside of class so we can explore potential options. Students with disabilities may also wish to work with the Student Disability Access Center (SDAC) to discuss a range of options to removing barriers in this course, including official accommodations. We are fortunate to have an SDAC advisor, Courtney MacMasters, physically located in Engineering. You may email her at cmacmasters@virginia.edu to schedule an appointment. For general questions please visit the SDAC website. If you have already been approved for accommodations through SDAC, please send me your accommodation letter and meet with me so we can develop an implementation plan together.

Religious accommodations: It is the University's long-standing policy and practice to reasonably accommodate students so that they do not experience an adverse academic consequence when sincerely held religious beliefs or observances conflict with academic requirements.
Students who wish to request academic accommodation for a religious observance should submit their request to me by email as far in advance as possible. Students who have questions or concerns about academic accommodations for religious observance or religious beliefs may contact the University's Office for Equal Opportunity and Civil Rights (EOCR) at *UVAEOCR@virginia.edu* or 434-924-3200.

The UVA Honor Code - https://honor.virginia.edu/statement:
I trust every student in this course to fully comply with all the provisions of the University's Honor Code. By enrolling in this course, you have agreed to abide by and uphold the Honor System of the University of Virginia, as well as the following policies specific to this course.
All graded assignments must be pledged unless otherwise stated.
All suspected violations will be forwarded to the Honor Committee, and you may, at my discretion, receive an immediate zero on that assignment regardless of any action taken by the Honor Committee.
Please let me know if you have any questions regarding the course Honor policy. If you believe you may have committed an Honor Offense, you may wish to file a Conscientious Retraction by calling the Honor Offices at (434) 924-7602. For your retraction to be considered valid, it must, among other things, be filed with the Honor Committee before you are aware that the act in question has come under suspicion by anyone. More information can be found at http://honor.virginia.edu. Your Honor representatives can be found at: http://honor.virginia.edu/representatives.

Support for your career development: Engaging in your career development is an important part of your student experience. For example, presenting at a research conference, attending an interview for a job or internship, or participating in an extern/shadowing experience are not only necessary steps on your path but are also invaluable lessons in and of themselves. I wish to encourage and support you in activities related to your career development. To that end, please notify me by email as far in advance as possible to arrange for appropriate accommodations.

Student support team: You have many resources available to you when you experience academic or personal stresses. In addition to your professor, the School of Engineering and Applied Science has staff members located in Thornton Hall who you can contact to help manage academic or personal challenges. Please do not wait until the end of the semester to ask for help!
Learning: Lisa Lampe, Director of Undergraduate Education; Blake Calhoun, Director of Undergraduate Success; Courtney MacMasters, Accessibility Specialist, Free tutoring is available for most classes.
Health and Wellbeing: Assistant Dean of Students, Student Safety and Support; Elizabeth Ramirez-Weaver, CAPS counselor; Katie Fowler, CAPS counselor. You may schedule time with the CAPS counselors through Student Health (https://www.studenthealth.virginia.edu/getting-started-caps). When scheduling, be sure to specify that you are an Engineering student. You are also urged to use TimelyCare for either scheduled or on-demand 24/7 mental health care.
Community and Identity: The Center for Diversity in Engineering (CDE) is a student space dedicated to advocating for underrepresented groups in STEM. It exists to connect students with the academic, financial, health, and community resources they need to thrive both at UVA and in the world. The CDE includes an open study area, event space, and staff members on site. Through this space, we affirm and empower equitable participation toward intercultural fluency and provide the resources necessary for students to be successful during their academic journey and future careers.