

MSE 305: Phase Diagrams and Kinetics

Tuesday & Thursday, 09:30 – 10:45 am
Wilsdorf Hall, Room 101

Contact Information:

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<http://www.people.virginia.edu/~lz2n/mse305/>

Class e-mail list: MSE305-1@toolkit.virginia.edu

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Grading:

- Homework 25%
- Mid-Term tests 30%
- The final exam: 45%

Homework will be due at the beginning of class on the due date. Homework solutions should be neat and stapled. *Late homework is not accepted.*

Discussions among students are permitted at the conceptual level, but comparing the results and discussing/copying solutions is not allowed.

Discussions through the class mailing list are strongly encouraged.

Mid-term tests and the final exam: pledged, closed-book and closed-notes

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Textbooks:

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

(reserve circulate at Science and Engineering Library).

Reprinted by CRC Press in 2003

~\$40-70 at www.crcpress.com or www.amazon.com

Lecture notes will appear at the class web page (<http://www.people.virginia.edu/~lz2n/mse305/>) as course progresses.

Optional textbooks (placed on reserve circulate):

D. R. Gaskell, Introduction to the Thermodynamics of Materials, 4th. Ed., New York: Taylor & Francis, 2003 (TN673 .G33 2003)

\$104 for 5th edition hardcover at www.amazon.com

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Syllabus:

1. Review of classical thermodynamics needed for understanding of phase diagrams.
2. Application of the thermodynamic concepts to the analysis of phase equilibria, phase transformations, and phase diagrams in one-component and multi-component systems.
3. Basic concepts of kinetic phenomena in materials. Mechanisms of diffusion in materials, analytical and numerical methods to describe diffusion. Effect of kinetics on microstructure.

thermodynamic driving forces
+
kinetics of mass and heat transfer
=
complex microstructure of real materials

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MSE 305: Thermodynamics – Phase Diagrams – Kinetics

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

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MSE 305: Thermodynamics – Phase Diagrams – Kinetics

- **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

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

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MSE 305: Thermodynamics – Phase Diagrams – Kinetics

- **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

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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

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• **Atomic mechanisms of diffusion**

- Substitutional diffusion
- Interstitial diffusion
- Temperature dependence
- High diffusivity paths (grain boundaries, 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

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Application of thermodynamics and kinetics to materials

Definitions: Components and Phases

Component - chemically recognizable species (Fe and C in carbon steel, H₂O and NaCl in salted water). A binary alloy contains two components, a ternary alloy – three, etc.

Materials consist of phases or mixtures of phases. A **phase** is a portion of a system that has uniform properties and composition. The phase may or may not be in an equilibrium state.

Two distinct phases in a system have distinct physical **or** chemical characteristics (e.g. water and ice) and are separated from each other by definite **phase boundaries**. A phase may contain one or more components.

A single-phase system is called **homogeneous**, systems with two or more phases are **mixtures** or **heterogeneous** systems.

Equilibrium – the state in which the system parameters no longer evolve (there are no fluxes of matter or energy, small disturbances decay, ...).

The phases that are **not in equilibrium** can undergo a **spontaneous** phase transformation to an equilibrium phase or mixture of phases.

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Thermodynamics of phase stability and phase transitions

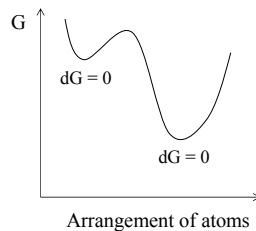
Thermodynamics can be used to predict whether the system is in equilibrium and to analyze the **phase stability and phase transformations**.

Questions thermodynamics can answer: Is a particular process possible? Is a spontaneous evolution in a particular direction possible? What is the final/equilibrium state of the system?

For example, for transformation occurring at constant T and P the relative stability of the phases in a system is determined by their Gibbs free energies, $\Delta G = G_{\text{final}} - G_{\text{initial}} = \Delta H - T \Delta S$

- $\Delta G < 0 \Rightarrow$ process is allowed
- $\Delta G > 0 \Rightarrow$ process is forbidden
- $\Delta G = 0 \Rightarrow$ equilibrium

Understanding of phase stability is very important in material science – all properties of a material - optical, electronic, magnetic, thermal, mechanical depend on its phase composition.



Equilibrium is the state that is achieved given *sufficient* time. But the time to achieve equilibrium may be very long (the kinetics can be slow) and a state along the path to the equilibrium may *appear* to be stable. This is called a **metastable state**.

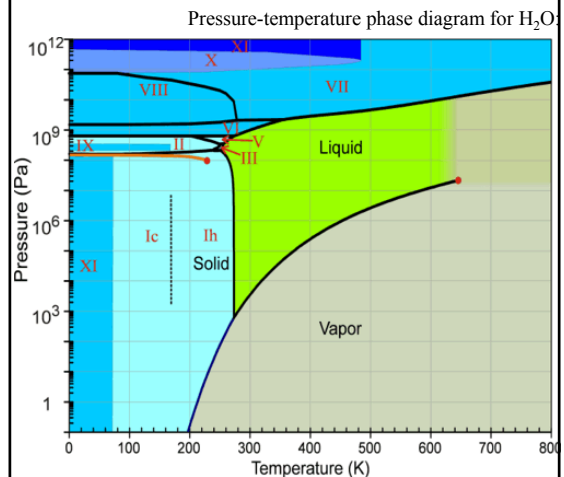
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Phase diagrams

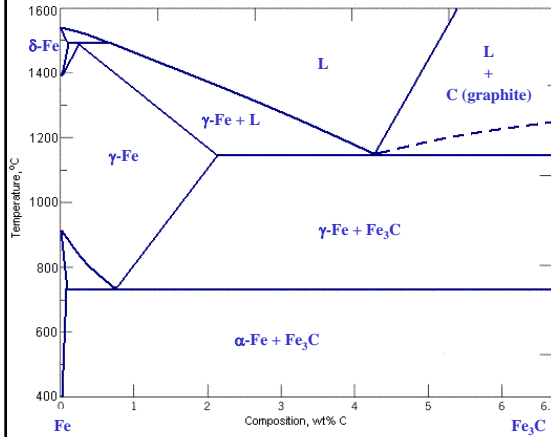
A **phase diagram** is a graphical representation of all the **equilibrium** phases as a function of temperature, pressure, and composition.

Phase diagrams arise from minimizing free energies for each phase. They can be used to describe gas - liquid - solid transitions, polymorphic solid-to-solid transitions, stable phases in alloys of different composition, etc.



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Example of a binary phase diagram: steel
iron-iron carbide (Fe-Fe₃C)

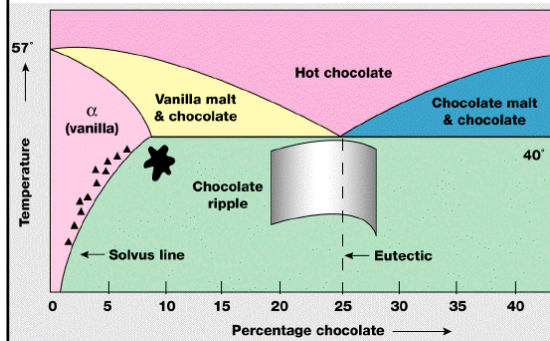


In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe-C phase diagram is a fairly complex one, here we are only looking at the steel part of the diagram, up to around 7% Carbon.

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Another example: phase diagram for chocolate and vanilla

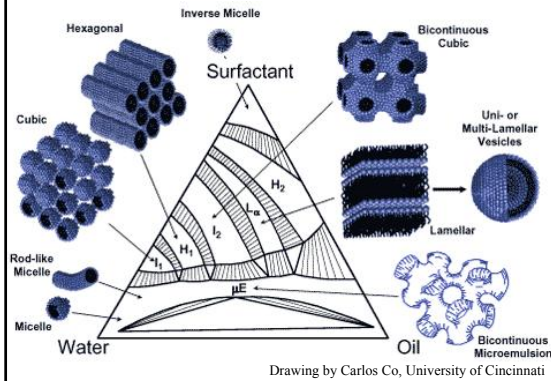


Credit: Kenneth A. Jackson, University of Arizona.

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Example of ternary phase diagram:
oil - water - surfactant system



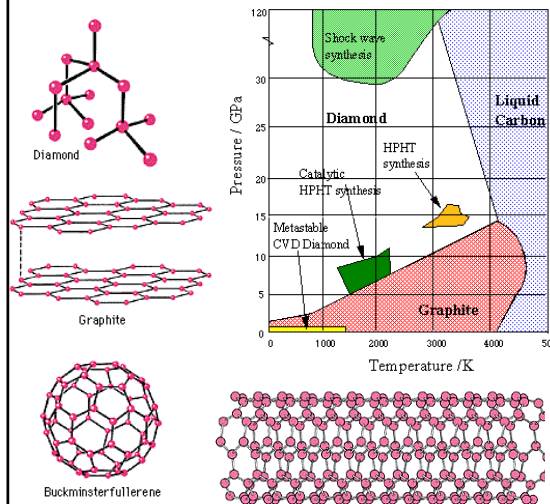
Surfactants are surface-active molecules that can form interfaces between immiscible fluids (such as oil and water). A large number of structurally different phases can be formed, such as droplet, rod-like, and bicontinuous microemulsions, along with hexagonal, lamellar, and cubic liquid crystalline phases. Ternary phase diagram shows compositional ranges for different phases.

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Phase diagrams do not predict all the possible structures

Pressure-temperature phase diagram for carbon:



We can see graphite, diamond, liquid carbon on the phase diagram... but where are fullerenes and nanotubes?

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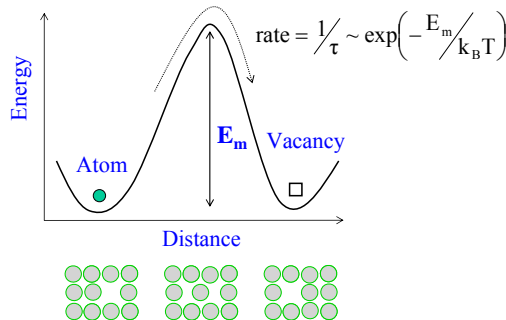
Kinetics

Thermodynamics can be used to predict the equilibrium phases for different conditions as well as the phase transformations that **can occur**.

“When or how fast does a phase transformation occur?” is not a right question for classical thermodynamics.

Thermodynamics tells us what can happen - not how fast it will happen. “How fast?” is the question addressed by **kinetics**.

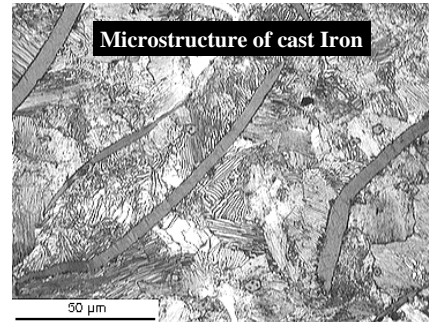
Most kinetic phenomena in materials involve **diffusion**. Therefore we will consider mechanisms of diffusion in materials before discussing kinetics of the nucleation and growth of a new phase.



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Analysis of both the equilibrium phase diagrams and the kinetics of phase transformations will help us to understand and predict complex microstructures like the one shown below



<http://www2.umist.ac.uk/material/research/intmic/>

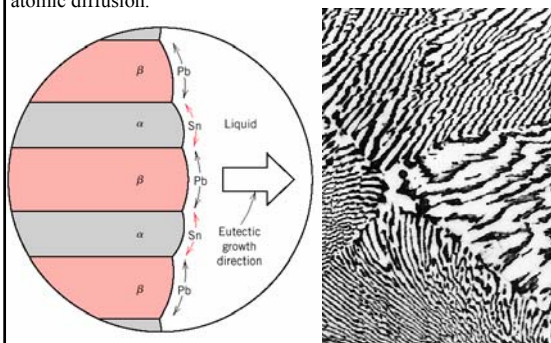
The long gray regions are flakes of graphite.

The matrix is a fine mixture of BCC Fe and Fe₃C compound.

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Formation of eutectic layered microstructure in the lead-tin system during solidification **at the eutectic composition**. Compositions of α and β phases are very different \rightarrow solidification involves redistribution of Pb and Sn atoms by atomic diffusion.



In the micrograph, the dark layers are lead-rich α phase, the light layers are the tin-rich β phase.

Compositions of α and β phases are defined by **thermodynamics** and can be determined from the **phase diagram**, the size and arrangement of the layers in the microstructure is defined by the **kinetics** of solidification.

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