# Thermodynamics of Materials

3.00 Fall 2002
Department of Materials Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Institute of Technology
Cambridge, MA 02139

## Course Information

3.00 Staff

| Instructor | Teaching Assistant | Administration |
|---|---|---|
| W. Craig Carter | Rajesh Raghavan | Rachel Kemper |
| Associate Professor | Postdoctoral Associate, Course 3 | 13-5026, x3-6936 |
| 13-5018, x3-6048 | Office 13-5114, 258-0222 | rkemper@mit.edu |
| ccarter@mit.edu | rajeshsr@mit.edu | |
| Office Hours: Mon 1-2PM | Off. Hours: Th 2-3PM in 13-5002 | |

Email questions will be answered as much as possible—I will often copy the answer to the entire class.

Please see http://pruffle.mit.edu/3.00 for updates to this document.

Appointments can be made in addition to office hours.

**Exams** There will be two midterm exams, one hour each on Friday, October 4 and Wednesday November 13. There will be a final exam during exam week.

**Homework** Homework assignments will be posted almost every Friday and will usually be due the Monday of the following week (i.e., you will have about 10 days to complete each homework, although on three of those days you will have two different assignments. The intent is allow you a bit of flexibility so that you can budget your time accordingly.) No homework can be assigned that will be due after Friday, Dec. 6. **You are encouraged to work in groups and turn in a single homework for the entire group.** Group homeworks[1] will receive a 5% bonus score. In other words, if the homework score is 73, then everyone in the group will receive a 77.[2] I hope that you will use the group homeworks as a vehicle for cooperative teaching and learning as well as a time-saving device. Regarding the group homeworks—some students fall into a trap of letting other members of their group do the hard intellectual work and think that they can catch up in time to take the exams. Of course, this is not only a mistake and not an effective way to learn—it is also bad manners.

Homeworks will be due the following Monday at 5PM in the designated box outside of Dr. Raghavan's office: 13-5114. If you choose to work in a group, it is each group member's responsibility that the group's homework is turned in on time.

You will be allowed one **and only one** late homework.[3] No exceptions.

[1] Groups are comprised of two or more people.

[2] With the caveat about group participation described below.

[3] You can be associated through your group with only one late homework. Acceptable homeworks expire one week after their due date—i.e., you get one week's grace for a late homework.

**Final Grade** The grade in 3.00 will be determined by:

**10% Class Participation** Records will be kept for good questions and comments during lectures—you must raise your hand so we can maintain some order in the classroom. You will also need to state your name when asking a question. Students will also be asked *randomly* about the current lecture topic. You are allowed to pass on making a comment twice during the semester. Not being present at a lecture in which you are asked a question counts as two passes, unless you have informed the TA or professor that you cannot attend a particular lecture by sending them email.

Students will not get credit for showing off—only productive comments or genuine questions will receive credit.

If you are curious whether you are getting credit—please ask. However, if you are unsure, then you are probably not participating actively.

Asking questions during recitation or coming to office hours also count as participation. If you fear that you are getting very far behind in class participation, it is possible to get some credit for creating web content to add to the 3.00 website.

**20% Homework** You are allowed to turn in one homework up to a week late. Otherwise, homework is due by 5pm on the assigned day with no exceptions except your one free late homework. Homework will tend to test problem solving ability.

You can turn in homeworks as a group—in other words, if you choose to work as a group, you only need to turn in one problem set for the group.[4] There is no limit on the number of people of homework group. However, if you turn the problem set as a group then each member of the group must turn in a *confidential* report of the fraction that each member contributed; the sum of fractions will be unity. We will assign credit based on all the confidential reports.

**20% Exam I Friday, Oct. 4** will cover only material from the beginning of the semester to week before Exam I.

**20% Exam II Wed, Nov 13** will cover only material from the week before Exam I up to the week before Exam II.

**30% Final Exam: Date TBA** will cover all lecture material.

There are exams from last year on the web. It would be wise to look at them as this year's exams will follow a similar format. You should expect conceptual questions on exams—the kind *you should read very carefully* because they can be tricky. For instance, a typical question may be: Explain whether and why the following statements are true or false. "The entropy of an isolated system can never decrease." "If the Gibbs Free energy of two bodies are equal, then the two bodies are in equilibrium at constant pressure." There may simple questions that require symbolic computation—you definitely won't need a calculator, but bring one with you if it helps you feel more comfortable. No notes or open book exams.

Thermodynamics is a subject that must be digested slowly. Please try to keep up and work at a constant rate. Cramming for a thermodynamics exam is usually a recipe for poor performance.

[4] **Late homeworks will be charged to all members of the group.**

# Abridged Notes

Abridged lecture notes will be available on the web the night before each lecture.[5] You can download and print them from http://pruffle.mit.edu/3.00—looking over the notes briefly before the lecture is a good idea. As you will see, they are designed for you to add notes during the lectures. Just printing the notes and reading them in lieu of attending lectures is not a good idea—the notes are designed as an aid to your comprehension and retention of lectures. Also, as described below, printing the lectures and taking notes on them will also provide another means of accruing points towards your final grade.

Copies of the notes will not be provided you—you must download and print them yourselves. Many of the figures are in color. It is not necessary to print them in color, but it may prove to be useful.

# Time Management

This is a 12 unit course. You are expected to spend 4 *waking* ☺ hours a week in lecture and recitation. You should be spending a minimum of eight hours a week reviewing lecture material, reading books on reserve, doing homework, and studying for exams. My advice to you is that you spend at least 3 of those 8 hours reviewing lecture material each week—and that you set aside regular time to study.

Everything that will appear on the exams or the homeworks will be covered in the lectures and lecture notes. However, you will want to supplement the lecture notes with reading from the text or other sources on thermodynamics.

I recommend that you take your own lecture notes on the printed versions of the abridged notes that are available on http://pruffle.mit.edu/3.00 (perhaps with extra paper) and then recopy the notes neatly at a time shortly after the lecture. You could recopy on freshly printed versions of my notes or rewrite it them completely yourself. That way, you are constantly reviewing the important points and will see how everything fits together; I believe you will be surprised at how effective a studying strategy that this is. In fact, I believe it so strongly that I will make the following bargain. *Anyone who shows me that they are carefully re-copying the notes will receive—as a reward—half the difference between their score on one of the midterms and the top score for the class for that midterm.* To receive this bonus, you must show me or Dr. Raghavan your carefully recopied notes at least one day before **each** exam (i.e., three times during the semester). To determine whether you have been sufficiently assiduous to receive this bonus, Dr. Raghavan or I will judge whether you have spent at least one hour per lecture re-copying the notes.

# Outside Reading

Although there is no formal text for this course, you should be doing a couple hours a week of reading. You are all mature enough to find readings on your own that supplement parts of the lecture that are hard to understand. There is a section below that lists some of the thousands of books on thermodynamics. People tend to like the second book on thermodynamics that

[5] At least, I will do my best to get them there on time.

they use more than the first. I think this is because thermodynamics is deceptively subtle and students really need some familiarity with the difficulties before they can understand them.

If you are having trouble finding outside reading for a particular—ask!

This struggle with familiarity creates a dilemma for professors of thermodynamics: should the first course in thermodynamics be taught as formulaic solving of the standard problems—or should one try to teach the more philosophical aspects of the subject. I am not sure which is the best approach. I was educated with the practical first approach, but I have chosen the second for MIT 3.00 because I find it more interesting and hopefully more useful in the long-run. I am pretty sure that this theoretical approach is not the best for *every* student; but, I hope that it is best for the majority.

As a hedge, I have worked with past TA's of this course to create a library of practical solved problems for each week. You can find these on the 3.00 website. I encourage you to study the practical problems.

## About Thermodynamics

Many consider this a "vegetables" class—as in "eating your vegetables first." It is true that thermodynamics is about developing a rigorous understanding of natural processes. And it is true that thermodynamics can become tedious and also true that the useful applications don't begin until a solid foundation is developed. However, I don't think it necessarily has to be boring and I encourage you to keep your minds open about the beauty of developing a subject rigorously. Veggies can be tasty as well.

Much of what you will learn about materials science will rely on your comprehension of thermodynamics. Unfortunately, most of you do not yet know about all the wonderful things you are going to learn over the next three years as you become a professional materials scientist and how they depend on this course. So, there will be times when you will be struggling to learn something without knowing why you should bother to learn it. Had we an infinite amount of time, I would introduce a practical aspect of each thermodynamic concept, then rigorously teach you the concept, and then show how it applies in a particular case. However, there are a large number of concepts that I must teach you in a finite amount of time. Furthermore, some concepts are so basic and essential that any practical example would seem artificial.[6] I have tried to distill the thermodynamics you will need to know into 37 lectures—sometimes you are going to have to trust that I am trying to teach you something useful.

I truly and deeply like thermodynamics and have liked it since the first time I took it. It is elegant and beautiful. I also think that it takes many years to master this subject. I believe that a thorough understanding of the subject—especially of the second law—separates qualified scientists from amateurs and pretenders.

However, I encourage you to be skeptical about what I tell you. Here are some excerpts from what others have said about thermodynamics:

> A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon

[6] Think about how you might try motivate a very young student to learn multiplication, algebra, Newton's laws, or calculus—there are some things that you just need to know to get on with life.

me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

............................ *A. Einstein*

Once or twice I have been provoked and asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: It was also negative. Yet I was asking something which is about the scientific equivalent of "Have you read a work of Shakespeare's?"

............................ *C.P. Snow*[7]

The law that entropy always increases–the second law of thermodynamics–holds I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much worse for Maxwell equations. If it is found to be contradicted by observation—well these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

................... *Sir A.S. Eddington*

Lisa, get in here. In this house we obey the laws of thermodynamics!

...................... *Homer Simpson*

# Text and Reading Materials

Primary Text

The primary source of material will come from the lecture notes. You should print out the lecture notes before coming to class, or make your own notes and combine them with the printed lecture notes.

Last year I used a classical textbook by Denbigh [3] in this course to supplement the lecture material. The students didn't like it because Denbigh is a bit advanced for a first thermodynamics course, but it is the best thermodynamics book that I know of. It is rigorous and descriptive. It will be a useful reference for you in the future as well as this class—I would encourage you to get your hands on a copy.

Additional Reference Material

In the first part of this course, it might also be useful for you to browse through the classic monograph by Fermi [5]. It is a classic introduction to the fundamentals of thermodynamics—it is also a bargain. The coverage in Fermi is generic and applicable to all branches of physics and engineering. Concepts that are specific to materials science will be covered in the lectures.

It is very useful to take a look at one or two of the hundreds of other thermodynamics texts.[8] Everyone learns in different ways and you may find one that is particularly suitable

[7] C.P. Snow (1905–1980) was a physicist and novelist that explored, among other things, the culture of science and the relationship of science to culture. To be fair, this quote is out of context, for in his book *Two Cultures*, Snow is exposing the hypocrisy of company is a group of liberal artists who scoff at what they call the narrow-mindedness of scientists. However, I think that the same question, if applied to a modern group of scientists, might have the same reaction.

[8] Sometimes you will find the entire solution to a troublesome homework question—I think it is perfectly acceptable to transcribe a (homework) solution that you find elsewhere. However, attribution is a moral question that I will leave to you.

for you. Perhaps the reason that there are so many thermodynamics texts is that few people agree on the best way to explain the material. You will find that notation varies considerably from book to book (and sometimes even within a single text). You can often learn just by sorting out differences in notation—after all, it is only the subject material that counts. You will learn even more if you study the different ways that similar subject material is developed. You will begin to master the subject when you start identifying the conceptual errors that exist in nearly every textbook.

Gaskell [6] and Devereux [4] are widely used in Materials Sciences courses at other good universities. Gaskell, in particular, is full of practical worked problems for materials scientists. Keep in mind that notation varies from textbook to textbook; nevertheless, these books may help clarify complicated topics and provide additional practical problems.

*Statistical Physics* from the Landau and Lifshitz [8] series is an excellent advanced treatise on both classical and statistical thermodynamics. It is ponderous, but is a good investment if you find yourself needing more thermo.

Denbigh [3] is perhaps the most complete textbook on chemical equilibrium. It is dense but very well-written. The introductory book by Bent [1] has a number of very clear examples and historical anecdotes, I used it very often while preparing lectures.

Besides Fermi [5], Planck [9] also wrote short and very readable introductory treatises on thermodynamics. Shrodinger has a very nice (but perhaps too advanced for this course) introduction to statistical thermodynamics [10] that is also a bargain. You probably associate these authors with other topics—their interest in the formulation of thermodynamics demonstrates the importance that most professional scientists place on a coherent understanding of thermodynamics as a foundation for advanced study. Chandrasekhar [2] devoted an entire chapter of his book on Stellar Structure to the differential geometry of the second law of thermodynamics. The most complete and fundamental development of thermodynamics is a single paper by J. Willard Gibbs [7]. Even though it is very difficult to read, Gibbs is the quintessential reference in thermodynamics. I've tried to use Gibbs as much as possible when I prepared the lectures.

You should have a good book on multivariable calculus. MIT's 18.02 is a prerequisite for this course.

# References

[1] Henry A. Bent. *The Second Law: An Introduction to Classical and Statistical Thermodynamics.* Oxford University Press, 1965.

[2] S. Chandrasekhar. *An Introduction to the Study of Stellar Structure.* Dover Publications, New York, 1939.

[3] K Denbigh. *The Principles of Chemical Equilibrium.* Cambridge Univ. Press, 3rd edition, 1971.

[4] Owen F. Devereux. *Topics in Metallurgical Thermodynamics.* John Wiley and Sons, NY, 1983.

[5] Enrico Fermi. *Thermodynamics.* Dover Publications, New York, 1936.

[6] David R Gaskell. *Introduction to Metallurgical Thermodynamics.* McGraw-Hill, NY, 2nd edition, 1981.

[7] J. Willard Gibbs. On the equilibrium of heterogeneous substances (1876). In *Collected Works*, volume 1. Longmans, Green, and Co., 1928.

[8] E.M. Lifshitz and L.P. Pitaevskii. *Statistical Physics, 3rd ed, Part 1.* Pergammon Press, New York, 1980. see pages 365ff.

[9] Max Planck. *Treatise on Thermodynamics.* Dover Publications, New York, 7th edition, 1926.

[10] Edwin Shrodinger. *Statistical Thermodynamics.* Dover, 1989.

## Course Calendar (subject to change)

Below is a tentative course schedule. An updated schedule can be found at http://pruffle.mit.edu/3.00. This schedule is a bit ambitious and probably sets too a pace that is too strenuous for effective learning. Because I'd like you to learn a few fundamental things well rather than a great deal of subject material poorly, I will slow things down depending on how the class is keeping up on the average. I'll continuously update the calendar on the web to indicate what lectures will be given at what date.

Sept. 04 2002: Lecture 1:

### Introduction and Course Description

#### Introduction to the Subject

Sept. 06 2002: Lecture 2:

### Course Survey

#### Preview of Entire Course

## Sept. 09 2002: Lecture 3:

# Thermodynamic Variables

### Thermodynamic variables versus microscopic variables

### Intensive and Extensive Variables

### Zeroeth Law of Thermodynamics

## Sept. 11 2002: Lecture 4:

# State Variables and Functions

### State Functions

### Some Example State Functions

### Derived Intensive Variables

### Equivalence of heat and work

Sept. 13 2002: Lecture 5:

## Thermodynamic Systems and Processes

### First Law

### Types of systems

### Types of Processes

### Composition vs Concentration

## Sept. 16 2002: Lecture 6:

# Energy and Work

### Energy

### Internal energy

### Types of Work

### Work of Polarization

### Magnetic Work

### Models for magnetic materials

Sept. 18 2002: Lecture 7:

## Properties of Materials

### Chemical Work

### Elastic Work

### Models for Anisotropic materials

Sept. 20 2002: Lecture 8:

## Stored Energy in Solids, First Law for Fluids

### Summary: Forms of Work in the First Law

### Work performed by Simple Fluids

Sept. 25 2002: Lecture 9:

## Quasistatic Processes

### Reversibility

### Heat Capacities

Sept. 27 2002: Lecture 10:

## Heat Capacities and Gaseous Behavior

### The Difference in Heat Capacities at Constant Volume and at Cons

### Models for Gaseous Behavior

Sept. 30 2002: Lecture 11:

## Internal Energy and Enthalpy for Fluids

### Internal Energy of an Ideal Gas

### A New Thermodynamic State Function: Enthalpy

### Another State Function

## Oct. 02 2002: Lecture 12:

# Thermodynamic Functions for General Systems

### The Unexpected State Function: Entropy

### Another Thermodynamic Function

### Yet Another (and Very Important) Thermodynamic Function

## Oct. 04 2002: EXAM I

## Oct. 07 2002: Lecture 13:

# The Second Law

### The Second Law of Thermodynamics

### An Illustrative Example

### Alternative Statements of the Second Law (There are many)

Oct. 09 2002: Lecture 14:

## Heat Stored during Phase Changes

### The Change of Temperature with the Addition of Heat

### Heat of Transformation

### Phase Fractions

### Hot Ice Melts and Cold Water Freezes

Oct. 11 2002: Lecture 15:

## Gibbs Free Energy

### Nature Prefers Low Enthalpies at Low T and Large Entropies at H

### The Temperature where Unviverse's Entropy Change is Zero

### The behavior of during a phase change.

Oct. 16 2002: Lecture 16:

# Entropy in Materials

## Behavior of Gibbs Free Energy near a Phase Change

## The Third Law of Thermodynamics

## A Survey of Molar Entropies

## Microscopic Origins of Entropy in Materials

Oct. 18 2002: Lecture 17:

# Conditions of Equilibrium

## Equilibrium Thermodynamics

## Unconstrained Equilibrium

## Oct. 21 2002: Lecture 18:

# Describing the State of an Alloy

### Equilibrium for Systems with Internal Degrees of Freedom

### Composition Variation and Phase Fractions

### An Illustrative Example

### A Concrete Example

## Oct. 23 2002: Lecture 19:

# Generalized Conditions for Equilibrium

### Equilibrium for a System with Internal Degrees of Freedom

### Equilibrium with constraints that are more practical

### That which is Minimized at Equilibrium for Constant P and T

### That which is Minimized at Equilibrium for Constant V and T

### The Potential to add a Chemical Species

Oct. 25 2002: Lecture 20:

# The Chemical Potential

## The Chemical Potential in a Closed System

## Models for Chemical Potentials in Solutions

## Equilibrium Compositions in an Ideal Reacting Gas Mixture

## Equilibrium Compositions in an Ideal Reacting Gas Mixture-Part 2

Oct. 28 2002: Lecture 21:

# Mathematics of Thermodynamics

## Mathematics of Exact Differentials in Thermodynamics

## The Other Energy Functionals: The Legendre transformations

## LeChatelier's Principle

Oct. 30 2002: Lecture 22:

## Mathematical Relations and Changing Variables

### Maxwell's Relations

### Change of Variable

Nov. 01 2002: Lecture 23:

## Mathematics and Stability

### Further Considerations of Equilibrium

Nov. 04 2002:

### Equilibrium States With More Than One Variable

### More Mathematical Thermodynamics: Homogeneous Functions

### The Gibbs-Duhem Relation

## Nov. 06 2002: Lecture 25:

# Symmetry and Equilibrium

### Further Restrictions on Material Properties

### Conditions of Multiphase Equilibrium

## Nov. 08 2002: Lecture 26:

# The Gibbs Phase Rule and its Application

### The Gibbs Phase Rule

### Single Component Phase Equilibria

## Nov. 13 2001: EXAM II

## Nov. 15 2002: Lecture 27:

# Gibbs Free Energy and Phase Diagrams

### Addition of a Soluble Species

Nov. 18 2002: Lecture 28:

# Uniformity of Chemical Potential at Equilibrium

## Conditions for the Appearance of a New Phase

## Graphical Constructions for the Free Energy of Solutions

Nov. 20 2002: Lecture 29:

# Important Geometrical Constructions

## Equilibria between Phases

## The Common Tangent Construction

Nov. 22 2002: Lecture 30:

# Phase Diagrams

## Construction of Phase Diagrams from Gibbs Free Energy Curves

## A Menagerie of Binary Phase Diagrams

## Classifying the Invariant Points: Drawing Phase Diagrams

Nov. 25 2002: Lecture 31:

## Using Phase Diagrams

### Interpreting Phase Diagrams

## Nov. 27 2001: Graduate Student Presentation

Dec. 02 2002: Lecture 32:

## Solution Thermodynamics

### Ternary Phase Diagrams

### Solution Free Energies that Generate Phase Diagrams

### Limiting Solution Behavior

Dec. 04 2002: Lecture 33:

## Unstable Solutions

### Non-Ideal Solution Behavior

### Behavior of the Regular Solution Model

### Spinodal Decomposition

### Nucleation and Growth

Dec. 06 2002: Lecture 34:

## Equilibrium Conditions for Solid Solutions

### Equilibria for Reactive Solids and Vapors (Oxidation)

### The Standard Approximation

### An Example of a Gaseous Reaction with Pure Condensed Phase

### Ellingham Diagrams

Dec. 09 2002: Lecture 35:

# Equilibrium Conditions for Charged Species

## Electrochemistry

## Systematic Treatment of the Electrochemical Potential

## An Example

Dec. 11 2002: Lecture 36:

## Introduction to Surface Thermodynamics

### Estimate of the Excess Energy Associated with Surfaces

### Gibbs Treatment of the Interfacial Energy

### Curvatures of Simple Surfaces

### Fundamental relations for surfaces

### The Conditions of Equilibrium where Several Surfaces Intersect

### The Shapes of Things

?? Dec. ?? 2002 :

## FINAL EXAM place:TBA Time:TBA