What shall we cover today?	Concordia         UNIVERSITY         DEPT. OF MECH. AND IND. ENG.         MECH 6661 Thermodynamics of Materials and Phase Equilibria         Lectures: Wednesday H-603-1 at 5:45 to 8:15 pm         Faculty: Mamoun Medraj, Email: mmedraj@encs.concordia.ca, Room: EV4.411         Office Hours: Wednesday from 3:00 to 5:00 pm			
• What is thermodynamics	References:			
• Brief history of thermodynamics	<ol> <li>Phase Equilibria, Phase Diagrams and Phase Transformations – Their Thermodynamic Basis, 2<sup>nd</sup> ed., Mats Hillert, Cambridge University Press (2008).</li> </ol>			
• Why should I study this course	<ol> <li>Introduction to the Thermodynamics of Materials, 4<sup>th</sup> edition, David R. Gaskell, Taylor and Francis, Washington, DC (2003).</li> </ol>			
• Applications of thermodynamics to materials	3. Measurement of the Thermodynamic Properties of Multiple Phases, R.D. Weir and Th.W. de Loos, Elsevier (2004)			
• Definitions	<ol> <li>Chemical Thermodynamics For Metals and Materials, Hae-Geon Lee, Imperial College Press, London (1999).</li> <li>Methods for Phase Diagrams Determinations, JC Zhao, Elsevier (2007)</li> <li>Thermodynamics in Materials Science, Robert T. DeHoff, McGraw-Hill, (1993)</li> <li>Thermodynamics of Materials: A Classical and Statistical Synthesis, John B. Hudson, Wiley (1996).</li> <li>Chemical Thermodynamics of Materials: Macroscopic and Microscopic Aspects, Svein Chemical Thermodynamics of Materials: Macroscopic and Microscopic Aspects, Svein</li> </ol>			
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### **MECH 691D Thermodynamics of Materials**

#### Handouts: are available at

#### users.encs.concordia.ca/~tmg

#### Assessment:

Assignments	
Projects	
Final Exam:	

20 % 30 % 50 %

• Assignments problems will be collected and marked, some of them (or similar ones) will be asked in the final exam.



### **Course Outline**

### The Aim: Understanding Materials through Thermodynamics

- Structure of Thermodynamics
- The laws of Thermodynamics
- Deriving General Relationships
- Equilibrium in Thermodynamics
- Experimental Methods of Determining Thermodynamic Properties
- The Behavior of Solutions: Ideal and Real Solutions
- Phase Diagram of Binary, Ternary and Multicomponent Systems
- Experimental Determination of Phase Diagrams
- Computer Programs for Thermodynamic Modeling:
  - FactSage and Pandat (WinPhaD)
- Examples of Understanding Materials Development and Processing through Computational Thermodynamics



### Course Outline

Review of classical thermodynamics needed for understanding reactions, solution thermodynamics, phase diagrams and their application in materials processing.

Application of the thermodynamic concepts to the analysis of phase equilibria, phase transformations, and phase diagrams in one-component and multicomponent systems.



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# What is Thermodynamics?

Thermodynamics is the field of science that is concerned with the behavior of matter. *Matter* here is anything that occupies space. This matter is called a system.

### Thermodynamics is the study of transformation of energy.

# **Objective of Thermodynamics**

To make predictions about the behavior of matter, based on a **small** number of **general principles**. These principles are the *laws of thermodynamics*. Application of these laws help understand broad range real life applications.

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# Four Laws!

> Systems in mutual thermal equilibrium all have the same temperature – ...... Law

> There exists a property of the universe, *energy*, which cannot change  $-1^{st} Law$ 

> There exists a property of the universe, *entropy*, which can only increase  $-2^{nd} Law$ 

> There exists an *absolute temperature scale* with a minimum (*absolute zero*). At this temperature, all substances have the same entropy  $-3^{rd}$  Law

The power of thermodynamics is that everything follows from these laws. Figuring out how it follows from the laws is the *hard* part ©.



# Scope Thermodynamics

### Thermodynamics is a multidisciplinary field of study



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# Scope of Thermodynamics

There are two approaches to describe properties and behavior of a material:

1. *Microscopic approach:* to describe the material in terms of microscopic variables (positions, velocities, charges, etc.) of all particles in the system. But there are too many particles ( $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ ) and this approach is unpractical in most cases.

2. Macroscopic (*Classical*) *thermodynamics*: to describe the material in terms of average quantities, or **thermodynamic variables**, such as temperature, internal energy, pressure, etc.

*Statistical thermodynamics* provides the connection between the classical thermodynamics and the behavior of the microscopic constituents of matter (atoms and molecules). Although in this course we will focus on classical thermodynamics, we will also consider a few elements of statistical thermodynamics, in particular in our discussion of the physical meaning of *entropy*.

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# A Brief History of Thermodynamics

### The Concept of Temperature:

atomic motion stops.

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✓ Temperature was measured (*but not understood*) by Galileo (17<sup>th</sup> Century).

✓ Fahrenheit (1715): measured temperature by expansion of a fluid (gas or mercury).

✓ Celsius (1742): defined 0°C as the melting point of ice; 100°C as the boiling point of water; scale in between with *linear* expansion of fluid.

✓ Kelvin (mid 19<sup>th</sup> century): Introduced the

✓ Theoretically defensible measurement of

temp. was performed by the gas Thermometer.

notion of *absolute zero temperature* where all



Anders Celsius, a Swedish astronomer



William Thomson, Lord Kelvin (Scotland) Mech 6661 lecture 1/10



# What is Heat?!

• Even in the 18<sup>th</sup> century (Antoine Lavoisier), heat was viewed as a *fluid* called caloric that moves from a body at high temperature to one at low temperature.

- This model didn't last very long (obviously) but the word "calorie" did!

 During the 19<sup>th</sup> century, the correct view of heat was uncovered: it is ...... in motion Antoine Lavoisier 1743-1794 from hot to cold regions

The effects of heat include: heating a body; melting

a body; vaporizing a liquid; producing mechanical





# Work?!

• Known from mechanics since Newton as: force x distance

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• Heat and Work are two aspects of energy in motion.

"It appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in these experiments, except it be motion." **Rumford** 





James Prescot Joule (Scotland) 1818-1889

American) 1753-1814

Thompson (British -

#### Work is completely convertible to heat (Rumford, Joule 1840)

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work .... etc



# Energy and the First Law

• Energy comes in many interconvertible forms: internal (*atomic vibrations*); chemical (*in chemical bonds*); electrical, kinetic; potential.. etc.

- The principle of energy conservation states that energy cannot be created or destroyed.
- Energy is related to heat and work by the *First Law* of Thermodynamics (Helmholz, Clausius, 1850):  $\Delta E = Q W$
- E is a property of a body; Q and W are not, but their difference is.



Herman von Helmholz (Germany) 1821 - 1894



Rudolf Emanuel Clausius (Germany) 1822 - 1888 Mech 6661 lecture 1/13

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James Watt (Scottish) 1736-1819

 Clausius and Kelvin developed the concept of reversible and irreversible processes

- Although Watt did not invent the steam engine, his

improved engine was really the first practical device

for efficiently converting heat into useful work. This

was a key stimulus to the Industrial Revolution.

• Clausius (1850) uncovers a new thermodynamic property, *entropy*, as  $\Delta S = Q/T$  for reversible processes

Development of steam engines (Watt

convertible to work and Carnot (1824)

showed theoretically why this is so.

1778) showed that heat is not completely

![](_page_3_Picture_17.jpeg)

Sadi Carnot (Luxemburg) 1796–1832 Mech 6661 lecture 1/14

![](_page_3_Picture_19.jpeg)

# Entropy and the Second Law

![](_page_3_Picture_21.jpeg)

Kelvin, Planck, and Clausius state the Second Law of Thermodynamics

Max Planck (Germany) 1858-1947

rmany)

 19th Century – Practical cycles for converting (partially) heat to work are developed (Rankine, Otto, Brayton, Diesel ..... etc.)

![](_page_3_Picture_26.jpeg)

Nikol Otto (Gerr 1831-

![](_page_3_Picture_28.jpeg)

![](_page_3_Picture_29.jpeg)

![](_page_3_Picture_30.jpeg)

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### **Chemical Thermodynamics**

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Entropy and the Second Law

 Developed by Gibbs (end of 19<sup>th</sup> Century)

 Deals with the equilibrium of molecular species in a reacting mixture

• Gibbs introduces the *chemical potential* as analogous to thermal potential (temperature) and mechanical potential (pressure difference)

On the other hand Dalton was the first to study chemistry based on the atomic theory of matter

![](_page_3_Picture_36.jpeg)

Josiah Willard, Gibbs (USA) 1839-1903

![](_page_3_Picture_38.jpeg)

John Dalton (England) 1766-1844 Mech 6661 lecture 1/16

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![](_page_4_Picture_0.jpeg)

# Statistical Thermodynamics

Links atomic motions to thermodynamic properties

![](_page_4_Picture_3.jpeg)

![](_page_4_Picture_4.jpeg)

![](_page_4_Picture_5.jpeg)

- Max Planck (Germany) Einstein, Albert 1858-1947 (Germany) 1879-1955
- Boltzmann (late 19th Cent): relates entropy to order
- Planck (1900): quantization of energy states

 Einstein, Debye (1905): atomic explanation of internal energy

· Fermi, Dirac, Bose, Einstein: quantum statistical thermodynamics

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Peter Debye

(Netherlands) 1884-1966

Enrico Fermi

(Italy)

1901-1954

![](_page_4_Picture_14.jpeg)

### Boltzmann

![](_page_4_Picture_16.jpeg)

![](_page_4_Picture_17.jpeg)

 $S = k \log W$ 

By the way, Boltzman never wrote this equation in this format, Plank did!

#### Tombstone of Ludwig Boltzmann

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![](_page_4_Picture_24.jpeg)

# Third Law of Thermodynamics

Walter Hermann Nernst (1864-1941)

GIAUQUE is remembered particularly for his discovery of adiabatic demagnetization as a means to reach very low temperatures as well as for his exhaustive and meticulous thermodynamic studies, over a lifetime of research, which

utilized the third law of thermodynamics while also

developing a large body of evidence for its validity. His

"achievements in the field of chemical thermodynamics and especially his work on the behavior of matter at very

low temperatures and his closely allied studies of entropy"

were cited by the Nobel Committee for Chemistry in the

The entropy of a body is zero at absolute zero temp.

The 3<sup>rd</sup> law has been first formulated by Walter Nernst and also known as the Nernst heat theorem.

![](_page_4_Picture_28.jpeg)

![](_page_4_Picture_29.jpeg)

Giauque, William Francis (1895-1982) American born in Niagara Falls, Ont., Canada 😊

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award of the prize in 1949

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![](_page_4_Picture_36.jpeg)

# MECH691D – Thermodynamics of Materials

#### I did my Thermo course(s) already. Why do I need your Thermo of Materials?

In this course we will study the application of the thermodynamic concepts to the analysis of phase equilibria, phase transformations, and phase diagrams starting from one-component until multicomponent systems.

This is in turn very important for:

- development of new materials
- improvement of the current materials

- and in understanding materials in general.

- processing of materials

![](_page_5_Picture_0.jpeg)

# Application of thermo to materials: Phase diagrams

A **phase diagram** is a graphical representation of the combinations of temperature, pressure, composition, or other variables for which specific phases exist at **equilibrium**.

![](_page_5_Figure_3.jpeg)

![](_page_5_Picture_4.jpeg)

### Application of thermo to materials: Ternary PD

![](_page_5_Picture_6.jpeg)

![](_page_5_Picture_7.jpeg)

# Application of thermo to materials: *microstructure*

Thermodynamics can predict the equilibrium phases and the phase transformation at different conditions.

When or how fast does a phase transformation occur?

- This is not a right question for thermodynamics.

- This is addressed by .....

#### Science is the art of asking the right questions

![](_page_5_Picture_14.jpeg)

 $\checkmark$  If we are able to combine thermodynamics with kinetics, the microstructure can be predicted.

 $\checkmark$  this is very important because properties of materials depend on the microstructure.

![](_page_5_Picture_17.jpeg)

![](_page_5_Picture_20.jpeg)

# Application of thermo to materials: *microstructure*

![](_page_5_Figure_22.jpeg)

In order to predict the microstructure in this example, compositions of  $\alpha$  and  $\beta$  are obtained by ...... *modeling* of the phase diagram, whereas the size and arrangement of the layers in the microstructure are defined by the ...... of solidification.

![](_page_6_Picture_0.jpeg)

### Interfacial Thermodynamics

Surface tension is a force acting on the surface of a liquid. This force tends to minimize the area of the surface and hence it specifies the contact angle between two phases.

![](_page_6_Picture_3.jpeg)

Wettability of liquid on solid surface

#### Applications:

- Composite materials *the interface between the matrix and the reinforcement*
- Welding, brazing and soldering
- Casting *die filling*
- Fabrication of ceramics Liquid phase sintering
- Wetting and spreading in general

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![](_page_6_Picture_14.jpeg)

### Definitions: Components

**Components** are chemically recognized species of fixed composition. - e.g. Fe and C in carbon steel, H<sub>2</sub>O and NaCl in salted water

Systems are primarily categorized by the number of components that they contain

- one component  $\rightarrow$  unary system
- two compontents  $\rightarrow$  binary system
- three components  $\rightarrow$  ternary system
- .. etc

#### Materials consist of phases or mixtures of phases.

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![](_page_6_Picture_26.jpeg)

### Definitions: Phases

A **phase** is a portion of a system that has uniform properties.

• The phase may or may not be in an equilibrium state.

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

- A phase may contain one or more components.
- 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 single-phase system is called **homogeneous**.
- Systems with two or more phases are **mixtures** or ......systems.

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

![](_page_6_Picture_39.jpeg)

### Definitions – Summary and Comparison

#### **Elements:** those from the periodic table

Species: an element or a combination of elements that forms an entity, like  $H_2O$ , CO2,  $Fe^{2+}$ 

A phase is a part of space that has homogeneous properties

**Constituents** are the species that exist in a phase

**Component** is an irreducible subset of the species

![](_page_7_Picture_0.jpeg)

# Definitions: Equilibrium

**Equilibrium** is the state that is achieved by giving 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 .....state.

![](_page_7_Figure_3.jpeg)

![](_page_7_Picture_4.jpeg)

### Extensive vs. Intensive variables

Extensive variables only have a value for a system as a whole. They generally depend on the size/extent of a system Examples: volume, energy

Intensive variables have a value at a *point* in the system. They do not depend on the size of a system.

Examples: temperature, pressure

Intensive properties can be identified through the limit of the ratio of two extensive properties. Example: the molar concentration c is defined as

 $c \equiv \lim_{\delta V \to 0} \frac{\delta n}{\delta V}$ 

where  $\delta V$  is an infinitesimal volume containing  $\delta n$ moles of matter.

Similar definitions can be developed by reporting extensive properties per mole of matter in the system. The most familiar example is the mole fraction  $(x_A, x_B,...)$ 

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![](_page_7_Picture_16.jpeg)

# Classification of variables

State functions do not depend on history, but only on current state of a system. E.g.: *T*, *V*, *U*, *S*, .....

- This property permits one to choose ("make up") an arbitrary process to compute any change in a state function

Process variables only have a meaning for changing systems and depend upon the path from state A to state B

Two primary categories:

- *work*: related to the displacement of matter subject to a force, such as the expansion of a gas in a cylinder
- *heat*: change in the kinetic energy of atoms

The difference in any state function is identical for every process that takes the system from the same given initial state to the same given final state – *it is independent of the path connecting the two states* 

Work and heat are not associated with one given state of the system, but are defined only in a transformation of the system. Hence the work performed and the heat absorbed by the system between the initial and final states depends on the choice of the transformation path linking these two states.

![](_page_7_Picture_26.jpeg)

### Definitions: Internal Energy

**Internal energy** U is a sum of all potential and kinetic energies in the system (*not only of mechanical origin*).

Thermodynamics only deal with change of U. The <u>absolute</u> value of U is not defined by the laws of Thermodynamics, but an arbitrary zero point is often chosen for convenience.

# Work and heat are both functions of the path of the process – *they are not state functions*.

Systems <u>never</u> **possess** heat and work! Heat and work are transient phenomena - describe the energy *being transferred* to the system.

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![](_page_8_Picture_0.jpeg)

# <u>Strategy</u>

![](_page_8_Picture_2.jpeg)

When dealing with thermodynamics problem:

✓ Identify a *thermodynamic system*: nature of its contents, location and properties of its boundaries

✓ Specify *thermodynamic properties*: *T* , *P*, *V*, chemical composition

✓ Use *thermodynamic relationships* to compute the change of these properties in a *process* 

# Next time: First Law of Thermodynamics

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