Lecture 1

- logistics
- objectives
- introductory remarks
- scope of the course
- organization of the course
- approaches
- preliminaries

Read: Chs 1-3 Sandler, Chs 1, 2 Callen

Logistics

- TAs –Andrew Friedman
- check syllabus on CANVAS
- class attendance – please come to class!
- homework – encourage thinking through problems before collaboration
- organization of the course
- diagnostic quiz

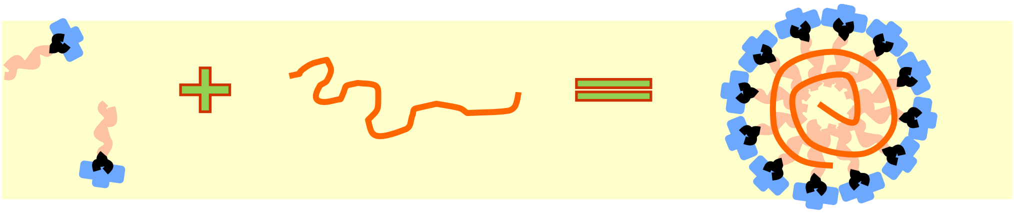
Objectives

• gain deeper understanding of conceptual structure of thermodynamics

  e.g., ideal gas from fundamental equation perspective

• develop better problem solving skills

• learn to view things thermodynamically

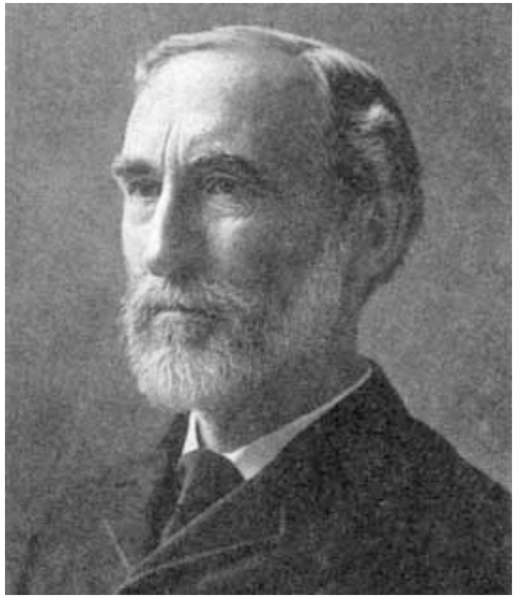


<u>General Remarks</u>

- <u>usefulness</u> and <u>beauty</u> of thermodynamics
- usefulness
  - chemical industry (mixing/separation, phase change, chemical rxns)
  - energy applications (heat pump, waste heat harvesting,nonstoichiometric oxides for hydrogen production)
  - biology (viral packaging, membraneless organelles)
  - climate (global warming, hurricane)

General Remarks

• beauty – simple yet profound, provides conceptually unifying principles, generally applicable to a wide range of phenomena and processes



One of the principal objects of research … is to find the point of view from which the subject appears in the greatest simplicity.

J. W. Gibbs

States of Water

0 ^{0}C

cool

100 ^{0}C

heat

- adding sugar raises boiling temperature
- adding sugar lowers freezing temperature
- water boils at lower temperature on a mountain
- skating blades cause melting of ice
- … …

How do we *understand* these?

What is Understanding?

Accumulation of facts	$\neq$	understanding
Description of phenomena	$\neq$	understanding
Quantification of effects	$\neq$	understanding

Understanding requires theory!

Different levels (types) of understanding/theory

- phenomenological/correlative (but predictive)
- mechanistic/microscopic

Conceptual Role of Theory

Water example:
Phase equilibrium condition

$$\mu^{a}(T,P) = \mu^{\beta}(T,P)$$

Chemical potential and equality of chemical potential provide unified conceptual understanding of phase transition

- Clapeyron equation $\quad \dfrac{dP}{dT} = \dfrac{\Delta h}{T\Delta v}$
- colligative properties $\quad \Delta T_f = -Kx_s$
- osmotic pressure $\quad \Pi = c_s kT$

Predictive Power Provides Rational Guide for Applications

- antifreeze fluids
- reverse osmosis for water purification
- mixing fresh and salty water to generate power
- distillation
- solubilization/extraction of chemicals
- many others…

Einstein on Thermodynamics

A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown.

Attitude and Ways

- not as a passive receptor but as an active participant in the rediscovery process (i.e., put yourself in the position of the pioneers of thermodynamics)
- read slides and text before class
- ask questions
- provide feedback

Thermodynamics

• science dealing with macroscopic properties/behaviors of systems at equilibrium

- macroscopic: evokes length scale
- equilibrium: evokes time scale

• describes relationship between macroscopic properties and their changes and sets limits to possible changes of state

• origins back in 1600s, crystallized in 1900s

• generality both its virtue and its limitation

• molecular content provided by stat. thermo.

Organization

• *fundamentals* – laws of thermodynamics, fundamental equations, equilibrium conditions, stability criteria, …
• *properties* – PVT behavior, model and empirical EOS, heat capacities, derived properties (fugacity, fugacity coefficients, compressibility factor)
• *calculus* – manipulation of derivatives, cp – cv relations, Maxwell relation, calculation of property changes
• *applications* – heat engines and power cycles; phase equilibria; chemical equilibria; interfacial phenomena…

Approaches

• historical vs. postulatory – induction vs. deduction
• engineering vs. physicist's approach

Engineering Approach

- Tester and Modell (1997): “almost all problems of thermodynamic importance can be classified into one of three types:

1. For a given problem with prescribed (or idealized) internal constraints and boundary conditions, how do the properties of the system vary?
2. To cause given changes in system properties, what external interactions must be imposed?
3. Of the many alternative processes to effect a given change in a system, what are the efficiencies of each with respect to the resources at our disposal?

Physicist’s Approach

- Callen (1997): “the single all encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system”

Preliminaries

- Systems: open, closed, insulated, isolated, …
- Processes: isothermal, isobaric, adiabatic, …
- Processes: reversible, irreversible, quasi-static, steady state, cyclic
- Variables: extensive vs. intensive
- Elementary mass balance

Read: Chapters 1,2 of Sandler

<u>Postulate</u>

An isolated system (simple, or composite), given enough time, will approach a unique final state for each simple subsystems. This limiting state is called the <u>equilibrium</u> state.

<u>Zeroth Law</u>

If A is in equilibrium with B and B is in equilibrium with C, then A is in equilibrium with C

Establishes transitiveness of equilibrium

Questions to Think about

- Think of an example of a thermodynamics problem (this can be a problem you encountered in research, an everyday life example, a process in industry, etc.)
- How long is “enough” time to reach equilibrium?
- Think of an example of the application of the zeroth law