Thermodynamics – where does it fit?

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Abstract

With the advent of biological engineering and with the changing of emphasis in many agricultural engineering programs around the country, it is time for a fresh look into how some of our engineering science courses are structured. The ongoing shrinkage in the number of hours available in the typical undergraduate curriculum around the US further reinforces this need. Some have proposed alternative treatments of thermodynamics in our discipline. A comprehensive treatment of thermodynamics meeting the needs of all biological and bioresource engineers is not practical at the undergraduate level. The paper will discuss concepts relating to melding relevant thermodynamic concepts with heat transfer for bioresource or agricultural engineers. A similar melding of relevant thermodynamic concepts with a basic physical (bio)chemistry course or basic mass transport course found in biological curriculums could meet the need for these engineers. Similarly, through various modules, thermodynamics instruction may also be linked to 3rd and 4th year courses in the traditional agricultural and bioresource curriculum. The use of modules may facilitate the delivery of the materials to diverse audiences, and several are proposed and some existing ones are discussed. A case is made for a thorough coverage of the topic at the graduate level.

Background

The word *thermodynamics* was coined about 1840 from two Greek roots: *therme*, heat and *dynamis*, power (Haynie, 2001). Based on the strict interpretation of the word, one expects that thermodynamics will have to do with heat and power or its storage, transformation and dissipation. Thermodynamics aims to describe and relate the physical properties of systems of energy and matter. Undergraduate students of engineering often survey the rudiments of thermodynamics in their physics courses, and then move on to one or more courses dealing with aspects of *Thermodynamics.* On completing these courses, the operational definition of thermodynamics typically becomes very specific, relating to work, heat, enthalpy, entropy, equation of state and simple compressible substances. The student pursuing mechanical engineering would add various power cycle applications to their concept. The student who is pursuing chemical or materials engineering will add such concepts as Gibbs functions and chemical potentials to their concept of thermodynamics. Concepts such as Maxwell relationships may be in the deep recesses but mean very little in that they rarely carry over to other courses. Systems beyond the simple compressible substance, if introduced, frequently go unappreciated by students. Textbooks may address topics such as statistical thermodynamics, irreversible thermodynamics and other "far out" topics. Students learn that everything in the universe should be approaching a steady equilibrium state, which seems to be at odds with the development of life processes as we know them. Students frequently have not had or do not appreciate the applications of total differentials and exact differentials that are often presented in thermodynamics courses. Many students do not readily perceive the significance of the course in the grand scheme in their curricula and thus may put it off as long as possible. Undergraduate engineering students have a somewhat disjoint view of thermodynamics and tend to vaguely appreciate those aspects of thermodynamics that relate directly to their other engineering science courses.

Thermodynamics in the sciences and engineering
Thermodynamics is often perceived as an engineering science wherein all controversies have been long since settled and that, like the matter it usually represents, is in or approaching an intellectually uninteresting steady state. Since *thermodynamics* was coined, the body of knowledge has grown beyond the realm of simple compressible substances. For example, Zemansky and Dittman (1997), in a text used for upper class undergraduate physics classes discuss the thermodynamic systems shown in Table 1.

Table 1. Selected thermodynamic systems (from Zemansky and Dittman, 1996).

System	**Intensive coordinate**	**Extensive coordinate**
Simple compressible substance (hydrostatic)	Pressure	Volume
Hydrostatic system	Pressure P	
Stretched wire	Force F	Length L
Surface film	Surface tension Y	Area A
Electrochemical cell	Electromotive force Emf	Charge Z
Dielectric slab	Electric field E	Polarization p
Paramagnetic rod	Magnetic field, μH	Magnetization B

Thermodynamics rapidly grew in the 19th century and now extends far beyond the simple compressible substance as is readily apparent from Table 1. Terms analogous to specific heat at constant volume and constant pressure are definable for other systems. One can begin to grasp the greatly enlarged scope of classical thermodynamics by reviewing Table 1. Generalized equations of state exist for each of the above systems. Thermodynamics is typically delivered in this more generalized context in senior-beginning graduate level courses in many physics curricula.

Chemistry (and related) and related majors typically receive extensive training in thermodynamics through Physical Chemistry. An introductory text in the subject by Lesk (1982) grounds the subject matter of physical chemistry in thermodynamics, statistical mechanics and quantum mechanics. After introducing various states of matter, extensive treatments of energy and the first law, the authors then discuss entropy and the second law and implications for equilibrium. Following further treatments of kinetic theory, statistical mechanics at the molecular level, electric and magnetic properties, quantum theory, spectroscopy and electronic structure of matter, electrochemistry and the dynamics of chemical change is then discussed. Physical chemistry is typically an upper division undergraduate course in chemistry departments.

The delivery of thermodynamics has changed over the years. For example, here is the syllabus summary for ME 220, Thermodynamics I, University of Kentucky in the late 60s:

- Introduction – Concepts, models, laws.
- Energy and the first law
  - Systems
  - Energy
  - Conservation and transfer as work
  - Work modes for simple compressible substances and for simple magnetic substances.
  - Energy transfer as heat
  - First law for a control mass
  - Energy equivalents
- Properties and state
  - Equilibrium and thermodynamic state
  - Temperature
  - Intensive and extensive state
  - Independent variations of the thermodynamic state
  - The state postulate
- States of simple substances
  - Equations of state
  - Using tabular and graphical equations of state
  - Perfect gas
  - Simple magnetic substance
- Energy analyses
  - Control mass
  - Control volume
- Entropy and the second law
  - Entropy as a function of state
  - Thermodynamic definition of temperature and pressure
  - Macroscopic evaluation of entropy
  - Second law analyses
  - Statistical thermodynamics
- Thermodynamics of State
  - Thermodynamic properties of a simple compressible substance
  - Evaluating entropy of simple compressible substance
  - Other differential equations of state
  - Enthalpy
  - Maxwell relations
  - Dense gases
  - Equation of state for the Curie substance
- Wrap-up

This course, based on the first half of a text by Reynolds (1965), stressed the importance of the simple compressible substance, although it attempted to preserve the general nature of thermodynamics by including the simple magnetic substance. The second course in this sequence, taken mainly by mechanical engineers, applied the above concepts to various power cycles and refrigeration, with some treatment of reactive equilibrium thermodynamics in a discussion of combustion processes. Chemical and materials engineers typically either take physical chemistry and/or take a discipline specific course emphasizing equations of state for non-ideal gasses and non-reactive/ reactive equilibrium thermodynamics. More advanced topics were provided in graduate level courses. The syllabus above represents the typical introductory thermodynamics course in many engineering schools (based on an analyses of several common texts).

Contemporary introductory thermodynamics courses focus more on the simple compressible substance and less on other systems (e.g., the simple magnetic substance). Topics such as statistical thermodynamics and the kinetic theory of gases are given less emphasis. There continue to be perceived relevance questions in the minds of the students regarding the significance of this body of knowledge to the practice of engineering, even with the tighter focus (compared to the treatment of the discipline in the sciences).

Combinations of thermodynamics subjects and other courses

The continuing pressure to reduce hours at the BS level provides continuing motivation to reevaluate the structure of the core of courses used to deliver the engineering sciences. One or more ASAE workshops wherein alternative approaches for thermodynamics were surfaced have occurred in the recent past. Cengel (1997) authored a text which attempts to address thermodynamics and heat transfer for those curricula having room for one course in the thermal sciences, although the material given could only be completely covered in two semesters. Seven chapters cover typical thermodynamic subjects (including a chapter on power and refrigeration cycles). The coverage resembles the outline given above but is much less in depth. The remaining six chapters introduce heat transfer (conduction including transient, forced and natural convection, radiation, heat exchangers, applications to cooling electronic equipment). The thermodynamics coverage in effect provides only the basic prerequisite material for limited heat transfer coverage. The heat transfer coverage approaches what classical agricultural engineering accomplished with the coverage of heat transfer in a physical unit operations course (Henderson et al., 1997). The Cengel (1997) text does not cover psychometrics, a critical component for most BAE curricula. It is interesting to note that the Cengel (1997) text does introduce (macro) biological topics at frequent places.

The following four-semester hour course, organized in two-hour modules, is proposed for BAE emphasis areas that are not heavily microbiological.

Module I, Physical Thermodynamics (2 hours)
Introduction – Concepts, models, laws.
- Energy and the first law
  - Systems
  - Energy

Conservation and transfer as work
Work modes for simple compressible substances and for simple magnetic substances.
Energy transfer as heat
First law for a control mass
Energy equivalents

Properties and state
Equilibrium and thermodynamic state
Temperature
Intensive and extensive state
Independent variations of the thermodynamic state
Equations of state
Using tabular and graphical equations of state
Perfect gas
Energy analyses
Control mass
Control volume

Entropy and the second law
Entropy as a function of state
Thermodynamic definition of temperature and pressure
Macroscopic evaluation of entropy
Second law analyses
Thermodynamics of state and enthalpy
Thermodynamic properties of a simple compressible substance

Psychometrics
Important relationships
Simple applications

Module II Introduction to Heat Transfer

Conduction Heat Transfer
Fourier's law – steady state
Thermal conductivity
Cylindrical and spherical geometries
Computing composite conductivity
Transient heat transfer in plates, slabs, cylinders and spheres.

Convection heat transfer
Forced vs. natural convection
Review of fluid mechanics
Convection heat transfer relationships with forced convection
Natural convection
Selecting the convection coefficient

Radiation heat transfer
Electromagnetic spectrum and heat transfer
Wein's displacement law
Stefan-Boltzman relationship
View factor estimation

Fundamentals of Heat Exchangers
- Parallel flow
- Counter flow
- Cross flow
- Heat exchanger effectiveness

These topics are important to the biochemical process engineer as well. However, other pressing topics need to be added to the biochemical engineering curriculum. I propose an additional thermodynamics module for environmental, biomedical engineers and biochemical engineers. This module was inspired by the recent appearance of a text by Price et al. (2001) but could also precede an introductory course supported by texts such as (Bailey and Ollis, 1986).

Module IA, Chemical Thermodynamics (2 hours)
Introduction – Concepts, models, laws.

- Energy and the first law
  - Systems
  - Energy
  - Conservation and transfer as work
  - Work modes for simple compressible substances and for simple magnetic substances.
  - Energy transfer as heat
  - First law for a control mass
  - Energy equivalents
- Properties and state
  - Equilibrium and thermodynamic state
  - Equations of state
  - Using tabular and graphical equations of state
  - Perfect gas
  - Energy analyses
  - Control mass
  - Control volume
- Entropy and the second law
  - Entropy as a function of state
  - Second law analyses
  - Thermodynamics of state, entropy and enthalpy
- Chemical potential
  - Gibbs potential
  - Equilibrium constants
- Redox reactions and electrochemistry
  - Nernst equation
  - Effects of nonideality
  - Using the electromotive series tables
- Chemical potentials and solutions
  - Osmosis
  - Chemical kinetics and single/multistep reactions

Enzyme kinetics

This thermodynamics module could precede a 2-hour transport module taken from a text such as Bird et al. (2002). The transport module would emphasize mass transport as momentum and energy transport is covered in fluid mechanics and heat transfer courses (modules).

Module III. Mass transport (2 hours)
- Diffusivity and mass flux
  - Similarities between viscosity and thermal conductivity
  - Estimating diffusivity
- Shell balances
  - Concentration distributions
  - Application of rectangular, cylindrical and spherical coordinates to common problems
  - Shell balances with reaction
- Concentration distribution in laminar flow
  - Time dependent diffusion
  - Steady state transport in binary boundary layers
  - Gas absorption
  - Boundary layer transport with complex interfacial motions
- Concentration distribution in turbulent flow
  - Concentration fluctuations with time smoothed concentration
  - Semi empirical expressions for turbulent mass flux
  - Turbulent mixing
  - First and second order reactions and turbulent flow.
- Inter-phase transport
  - Correlation of binary transfer coefficients in one phase
  - Definition of transfer coefficients in two phases
  - Mass transfer and chemical reactions
  - Transfer coefficients at high rates.
- Mass transport applications
  - Porous media flow
  - Selectively permeable membranes

Thermodynamics can likewise be combined with other courses commonly found in the Agricultural or Bioresource curriculum at the junior and senior levels. Cundiff and Mankin (2003) have developed a modularized approach that integrates thermodynamic principles into processing and structures and environments for plants and animals. They begin at the microbial level and construct (needed) links to customary mass and energy balances. They organize their course into the following modules:

Module I. Introduction to the dynamics of biological systems
Module II. Development of a general environmental control model
Module III. Dynamics of plant systems
Module IV. Dynamics of animal systems

The text is designed to be available as individual modules, which enables instructors of advanced courses to use only those modules directly relevant to the 3^{rd} and 4^{th} year courses.

There is considerable effort towards more closely linking thermodynamics instruction with other courses in the engineering curriculum. Heat transfer is a link as is mass transport. Other more advanced courses in the traditional agricultural or bioresource curriculum are also likely links for more fundamental thermodynamics instruction. The range of material becoming available in the undergraduate curriculum regarding thermodynamics makes a compelling case that the traditional engineering approach for packaging this subject leaves much to be desired. The downside of all these approaches is a rather fragmented presentation of thermodynamics.

Graduate level thermodynamics course – a place for a comprehensive thermodynamics course

It is apparent that thermodynamics now has grown beyond the (statics) and dynamics of heat. Thermodynamics now encompasses relationships between energy forms that may have little to do with heat per se, except that some heat is lost due to irreversible processes associated with energy conversions. Perhaps a more comprehensive view of the scope of thermodynamics can be appreciated by considering energy interrelationships apparent in Figure 1.

Johnson (1999) provides an extensive treatment of analogies between heat, mass and momentum transfer. He develops generalized effort variables for momentum, mass, heat and electrical transfer and further develops transfer coefficients relating flux and effort. Grabiel (1967) and Decher (1994) provide rigorous treatments of many of the inter-conversions depicted in Figure 2. Grabiel (1967) focuses on implied assumptions usually made in analyzing energy conversions and raises thought provoking questions. The modular approach by Cunduff and Mankin (2003) may be relevant to a graduate discussion in that an overview of all four of the modules does give a synoptic view of the subject, including coverage of the microbial level to the ecological level.

Microbiologists and ecologists are attempting to remold aspects of thermodynamics to increase understanding of biological systems. The enlarged scope of the science calls for terminology of an enlarged scope. Thus, we selected the term *Energetics*, as this term became common following the energy crises of the 1970s (e.g., see Fluck and Baird, 1980).

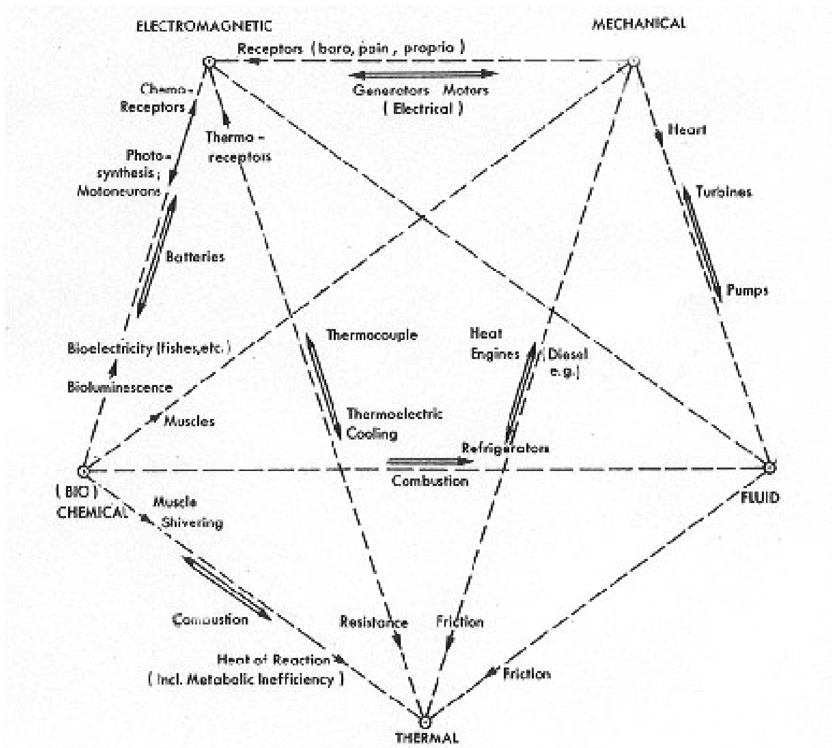

Figure 1. Relations between the various energy forms (from Milsum, 1966).

Grabiel (1967) and Decher (1994) provide examples of rigorous attempts to describe many of the inter-conversions depicted in Figure 1. Grabiel (1967) focuses on implied assumptions usually made in analyzing energy conversions and raises thought provoking questions. Microbiologists and ecologists are attempting to remold aspects of thermodynamics to increase understanding of biological systems. The enlarged scope of the science calls for terminology of an enlarged scope. Thus, the term *Energetics* was selected as this term began to be used following the energy crises of the 1970s (e.g., see Fluck and Baird, 1980). Tollner (2002) provides details on a graduate thermodynamics, or energetics course. The graduate course would provide opportunities for graduate students of diverse interests to explore the panorama of thermodynamics and inquire into questions such as what does it mean to "understand" a system.

Discussion

A case was made for redefining thermodynamics as energetics and emphasizing the course on the graduate level. Likewise, a case was made to merge one semester of the undergraduate thermodynamics course with other courses such as introductory heat transfer, mass transfer or course addressing chemical reaction issues. Thermodynamics as an important "mother lode" becomes extremely relevant at the graduate level in that modern thermodynamics, or, energetics, may explain the development of generalized gradients that lead to transport of mass, heat and charge on the microscopic and macroscopic levels. Some are proposing additional "laws" of thermodynamics in efforts to explain observations at far-from-equilibrium conditions commonly found in many life processes, and these can best be addressed at the graduate level. The author welcomes dialogue on all the topics in the proposed course and on the proper placement and composition of the proposed course and on the proposed effected undergraduate courses.

Far from being a body of knowledge well on the way to a static equilibrium, thermodynamics is embracing the reality that larger scale processes are at work to create and grow disequilibrium, best pursued at the graduate level.

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