THERMODYNAMICS: DEATH AND TRANSFIGURATION

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In a recent article[1] I criticized vehemently present approaches to the teaching of thermodynamics. In particular, I argued that thermodynamics at present is based on mysticism and magic when dealing with the fundamental concepts such as temperature, energy, and entropy. I argued that what was needed was a rational approach to the development of concepts and their application to chemical engineering and that, for the non-thermodynamicist, in particular, thermodynamics *should* be viewed as a handmaiden to the major chemical engineering areas such as kinetics, process design and control, and transport mechanics.

In this paper, then, I offer a program which attempts to prepare the graduate engineer for a career in which thermodynamics plays an important, *but not dominant*, role. While this program also has limitation, I should hasten to point out that it has been used successfully at Ohio University on a first-semester graduate level for some time.

Statistical or Mechanical Approach?

As I pointed out in the earlier paper, I consider that the fundamental concepts of thermodynamics are three in number:

1. The concept of temperature
2. The concept of energy
3. The concept of entropy

Traditionally, there are two major ways of introducing these concepts:

1. The intuitive approach, sometimes referred to as a phenomenological approach, in which, for example, the concept of temperature is regarded as a primitive concept, like force and displacement, and therefore, **not** requiring definition, merely illustration.
2. The statistical approach, in which it is necessary to identify a constraint in the system of describing equations with one of the concepts. The describing equations may deal with energy in kinetic form (classical approach), or quantum form, or even level of information form (Tribus).

As I stated earlier, probably the only time the statistical approach is applied in traditional graduate level chemical engineering first courses is in shoring up otherwise weak and faltering developments of the concept of entropy. It is apparent that if the proper approach to the development of the concept of entropy is employed, no shoring up is needed and, hence introduction of statistical concepts into a first course is not needed!

Traditionally, the intuitive approach to chemical engineering thermodynamics has been "moleculeless mechanical thermodynamics," with emphasis on steady-state operations of system containing continua of material. To say that this approach represents a crazy-quilt of sterile applications of sound principles of mathematics and classical physics and empirical rules-of-thumb so typical of chemical engineering in the thirties would undoubtedly insult many so-called chemical engineering thermodynamicists. In this program, I attempt to establish a firm, rational basis for the determination of a working program (no pun intended). I emphasize establishment of rigorous axioms on which we can evaluate the empirical concepts presently in vogue in the literature.[2] Undoubtedly, I cannot hope to prescribe a single remedy that will cure the multiple ills plaguing authors of articles and textbooks in one, introductory course. It is my primary goal to make the average graduate student *aware* of the maladies, so that he can intelligently evaluate work in his chosen field of endeavor.

Our Program: Goals and Gaols*

We begin the course by reviewing the fundamental laws of thermodynamics as primitive concepts, requiring no definition. We then construct concepts total and path differentiation from a mathematical viewpoint. Concepts such as work

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*A biography of Dr. Throne is available in **CEE** 2, 92, 1968.

*The texts we have been using, along with the supporting reference material, are listed in Table 1.

introduced *in metric form* as being the result of relationships between generalized forces and differential displacements.** The close relationship between fluid mechanical systems and thermodynamic systems is then discussed, and the generalized concepts of enthalpy and heat capacities (in terms of generalized forces and displacements) are developed, with specific examples in linear extension, surface extension, and pressure-volume. The theorems of Caratheodory, Pfaff, inaccessible states, and mathematical development of constitutive equations for entropy, reversible heat and temperature are developed. Shaw's method of Jacobian of Transformation[5] and the development of Maxwell's equations are presented, with extension of Shaw's method to multi-component systems. These equations are then applied to the generation of equation such as the Gibbs-Duhem Equation.

Partial molar properties, multicomponent systems, and the natural appearance of the chemical potential are presented. With special emphasis on gases, rules for the development and evaluation of constituitive equations are presented, along with fugacity and perfect mixtures of perfect and nonideal gases. It is emphasized that fugacity *is* the true thermodynamic pressure. The role and limitation of chemical potential, the phase rule, and degrees of freedom are then developed.

We then consider first and higher order phase transitions, developments of Clapeyron and Erhenfest equations from direct integration of Maxwell's equations and from L'Hopital's rule, and their physical implications in single component and multicomponent systems.

We then expend considerable effort in applying the Gibbs-Duhem equation to the selection of constitutive relationships between partial pressure, composition and temperature, emphasizing Raoult's law of ideal systems, Henry's law of equations. It is important to note here that we emphasize the approximate empirical nature of these constitutive equations; we *do not* let these equations live by themselves, as it were.

Application of constitutive equations to engineering systems such as heat of mixing and volume change, depression of freezing point, osmotic pressure, and such, follow. Thermodynamic consistency tests and their relative reliability are stressed.

TABLE I.

Books Used in First Course in Graduate Thermodynamics

Required Texts:

1. Denbigh, K. G. The Principles of Chemical Equilibrium, 2nd Ed., Cambridge 1966.
2. Tribus, M., Thermostatics and Thermodynamics, D. Van Nostrand, Co., 1961.

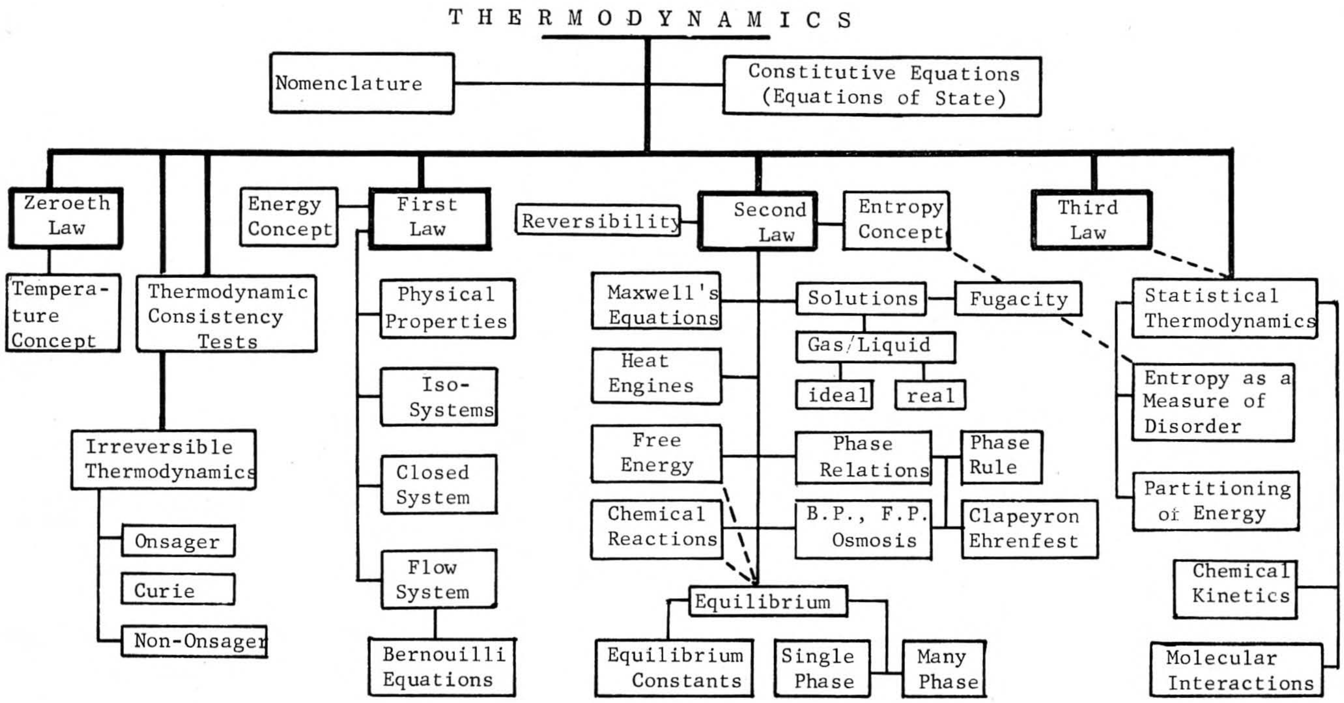
Recommended Reading Reference:

1. Zemansky, M.W., Heat and Thermodynamics, 4th Ed., McGraw-Hill, 1957.
2. Guggenheim, E. A., Thermodynamics, 3rd Ed., North Holland Publishing, 1957.
3. Dodge, B. F., Chemical Engineering Thermodynamics, McGraw-Hill, 1944.
4. Smith, J. M., Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, 1949.
5. Coull, J., and Stuart, E. B., Equilibrium Thermodynamics, Wiley, 1964.
6. Lewis, G. N. and Randall, M., Pitzer, K. S. and Brewer, L., Thermodynamics, 2nd Ed., McGraw-Hill, 1961.
7. Bosnjakovic, F., Technical Thermodynamics, Holt, Rinehart and Winston, 1965.
8. Gibbs, J. W., The Scientific Papers of., Volume 1, Thermodynamics, Dover, 1961.
9. Weber, H. C., and Meissner, H. P., Thermodynamics for Chemical Engineers, 2nd Ed., Wiley, 1957.
10. Van Wylen, G. J., Thermodynamics, Wiley, 1959.
11. Fong, P., Foundations of Thermodynamics, Oxford, 1961.
12. Bridgman, P. W. The Nature of Thermodynamics, Harper, 1961.
13. Fermi, E., Thermodynamics, Dover, 1956.

Finally, we introduce concepts of thermodynamics of the steady state, dealing with the concept of entropy production and the phenomenological coupling tensor between fluxes and forces. We discuss "Curie's theorem" and its logical basis as a fundamental theorem of tensor calculus,[6] and the faults of the present state of irreversible thermodynamics (linear "Onsagerist" approach) and its future role in thermodynamics. We conclude by examining real engineering examples of steady-state thermodynamics in coupled systems such as heat-mass transfer, kinetics-fluid flow, and fuel cell technology.

To implement the development of the course, I present, in flow diagram form, apparent interactions in the major areas of thermodynamics. This diagram is shown below. While I do not pretend to imply that this flow diagram is wholly correct or complete, it does serve graphically to illustrate chemical engineering thermodynamics.

It is important to note that standard approaches to work utilize affine coordinates. While developments of concepts in affine coordinates are satisfactory for explicit problem-solving, development of general concepts, particularly when thermodynamics is used in transport mechanics, **must be made in metric coordinates.[3,4]



Thermodynamics: Who Cares?

First, it is important that the above program makes no mention of cycles, refrigerators, engines, TS diagrams, Mollier Charts, compressibility curves, etc. This is done deliberately. Emphasis is placed on understanding of underlying mathematical, mechanical, chemical, and physical principles. Interrelationships between thermodynamics, kinetics, and mechanics are continually emphasized and illustrated through engineering examples. Why? It is my belief that rational understanding of the role of thermodynamics in the overall concept of chemical engineering comes, *not* from the ability of the student to calculate coefficients in equations of state—given critical properties, *but* from his ability to understand the usefulness and limitations of the present concepts of thermodynamics. It is his ability to intelligently and rationally question existing practices, *not* blindly calculate and manipulate empirical equations, that will make him a valuable member of the chemical engineering community.

Conclusion

Classical thermodynamicists with their minds intently focussed on new P-V-T correlations or n-th degree refinement in the current Mollier diagram for steam or ammonia, are being by-passed and circumvented by people who *need* to answer thermodynamic questions dealing with biological metabolism, kindey or fuel cell operation, kinetic-fluid flow interaction, cyclic operation of non-ideal transport systems, thermomechanical foundations of nonlinear visocelastic media, nonFickian diffusion, sewage disposal and anti-pollution systems. We cannot afford to ignore the challenge of modern chemical engineering by offering material that was designed to support chemical engineering Edisonianism of the 30's.

It is my opinion, then, that Dr. Bates' approach ("First Aid to Ailing Thermodynamics") will eventually lead to the death of thermodynamics as it is traditionally taught. To this, I say, good riddance. For, like the Phoenix of Egyptian mythology, from its ashes shall rise anew a thermodynamics founded on the rational principles of Gibbsian mechanics.

REFERENCES

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4. Brillouin, L., "Tensors in Mechanics and Elasticity," Academic Press, New York, 1964.
5. Tribus, M., "Thermostatics and Thermodynamics," D. Van Nostrand Co., Inc., New York.
6. Fitts, D. D., "Nonequilibrium Thermodynamics: A Phenomenological Theory of Irreversible Processes in Fluid Systems," McGraw-Hill Book Co., New York, 1962.