A Course in

MODERN THERMODYNAMICS

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IN THE FALL Semester of both 1973 and 1974, a somewhat non-traditional course in Thermodynamics was given within the graduate program at the Chemical Engineering Department of the University of Delaware. The philosophy, scope and possible future evolution of this course are discussed in this report.

The teaching of Thermodynamics, at both the graduate and undergraduate level, in ChE departments is traditionally rather separated from the mainstream of the research and teaching activity of the department as a whole. Thermodynamics is often viewed as a self-contained subject, knowledge of which allows solving such important but rather traditional problems as energy balances, power cycles, and physical and chemical equilibria. This subject matter is what will be referred to in the following as classical thermodynamics.

An analysis of the scope of classical thermodynamics immediately shows that, as far as energy balances are concerned, only the first law is involved; for power cycles, the only materials considered are one-component ideal fluids suffering at the most complex a phase change; and for physical and chemical equilibria, no transformation at all is involved, but only equilibrium states. With these limitations, the powerfulness of the second law as a starting point for a theory of irreversibility of processes undergone by possibly very complex materials is left entirely unexplored; and consequently the core of ChE, say the theory of transport phenomena, chemical kinetics, process dynamics, and so on is developed almost without regard to its relationship with thermodynamics.

The course given at Delaware has been based on the idea that there is no reason why thermodynamics could not, and indeed should not, have a central role in ChE methodology. An effort has thus been made towards the application of thermodynamic thinking to non-traditional areas, and particularly to those where strong research interests exist in the department. This seems a logical requirement for a graduate course in thermodynamics if it wants to have an educational value over and above its purely tutorial content. This also poses the question of the role of thermodynamics in ChE, which will be discussed in some detail in the "future evolution" section below.

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PHILOSOPHY

The syllabus of the course given at Delaware in 1973 and 1974 is summarized in Table I. Particular emphasis was placed on the logical analysis

of the fundamental structure of thermodynamic methodology (see sections B, C1, and D), and applications were restricted to a subject of prevailing interest in the research program of the department, namely, polymer deformation and flow (section C2), and to the traditional subject of equilibria (section E).

The philosophy of the course is non traditional in three aspects. First of all, since frictional heating and dissipation in flowing polymers wants to be analyzed, a thermodynamic theory of **irreversible** phenomena, with no Onsager-type restriction to linearity, has to be considered explicitly. Second, since the phenomena considered involve systems the state of which is in general different at different points in space (suffice it to consider that temperature may be non-uniform, see section B2), a **field** theory of thermodynamics is required. Finally, since the peculiar thermodynamic behavior of polymers is related to their complex response to mechanical and thermal stimuli, and following a trend which has become progressively stronger in the theory of transport phenomena, particular emphasis has been placed on the role of **constitutive assumptions** in a thermodynamic theory.

TABLE I
Syllabus of the Course

Section A.	Mathematical preliminaries. 5 hours
Section B.	Classical continuum thermodynamics. 13 hours
	B1. Isothermal systems. 4 hours
	B2. Non-isothermal systems. 5 hours
	B3. Classical theories (Ideal fluids, Viscous fluids, Elastic solids). 4 hours
Section C.	Materials with memory. 7 hours
	C1. Thermodynamics and memory. 4 hours
	C2. Thermomechanics of polymers. 3 hours
Section D.	Axiomatic foundation for classical equilibria. 7 hours
	D1. Internal state variables, Affinity, Equilibrium. 3 hours
	D2. Axiomatic stoichiometry. 3 hours
Section E.	Classical equilibria. 8 hours
	E1. Phase equilibria. 4 hours
	E2. Chemical equilibria. 4 hours

RATIONAL THERMODYNAMICS

A FIELD THEORY of thermodynamics applicable to irreversible phenomena in materials with complex constitutive equations has been developed in the last ten years mainly by Coleman, Day, Gurtin, Mueller, Owen, Truesdell and Williams; it is usually referred to as Rational Thermodynamics (RT). A critical review of the relevance of RT in chemical engineering is available [1]. The material summarized in Table I has been taught following the methodology of RT.

Teaching RT in an engineering department poses a major challenge. The technical literature on the subject, as well as the two books available up to 1974 [2, 3] are written for an audience of mathematicians and mathematical physicists, and are therefore largely unsuitable for direct classroom use. Some moderately sophisticated mathematical concepts are indeed essential to an understanding of the subject, but certainly much less than presupposed for the reader of the specialized literature. Furthermore, one needs to put into sharp relief the relevance of the subject to the engineering analysis of concrete problems, as well as the physical counterpart of what may at first sight appear unnecessary mathematical wizardry. In view of these difficulties, a set of classroom notes was prepared for the course at Delaware, three fourths of which (covering sections A-C of Table I) have now been published as a short book, *"An Introduction to Non-linear Continuum Thermodynamics"* [4].

RT is a wide and diversified field, so that teaching it implies deciding which grounds to cover, and even more crucially where to start. Every axiomatic science must start **somewhere,** and a few primitive undefined concepts are required, whose only specifications are the requirements laid down in the fundamental axioms. In RT, an abstract mathematical structure may be developed, based on such primitive concepts as state and process [5, 6], and entropy is then obtained as a derived concept (see also Day [3]). One may also start from the notion of entropy, regarded directly as a primitive concept, as has been done in this course. This allows one to proceed much more quickly to results of direct engineering interest, though this choice invariably causes some

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concern among professional scientists, who are not willing to accept entropy, particularly under non-equilibrium conditions, as a primitive undefined concept.

Indeed, among professional scientists an "acceptable" primitive concept is a physical quantity of which one is entitled to speak to colleagues without being asked to define it; or perhaps one which can be introduced in a paper without worrying that a referee may confute its meaningfulness in that context. Entropy of a system outside of equilibrium certainly does not meet these qualifications.

The most common reaction of the students after the course was to ask why they hadn't been taught thermo that way the first time they were exposed to the subject—apparently the most difficult part of the learning process was the unlearning of previously acquired biases.

It turns out that in classroom use primitive concepts are, or are not accepted by students independently of their meeting these qualifications, and in spite of a long training aimed at avoiding their asking embarassing questions, students are still open-minded enough to be about as likely to ask what a force is outside of equilibrium as they are to ask the same question about entropy —and the second question is not any more embarassing than the first one. Indeed, at the end of the seventeenth century most scientists would have nothing to do with forces outside of equilibrium, and Newton felt the need to write: *"In Mathesi investigandae sunt virium quantitates et rationes illae, quae ex conditionibus quibuscumque positis consequentur; deinde ubi in physicam descenditur, conferendae sunt hae rationes cum phaenomenis ut innotescat quaenam virium conditiones singulis corporum attractivorum generibus competant. Et tum demum de virium speciebus, causis et rationibus physicis tutius disputare licebit"* [7]. Newton's statement, with "entropy" substituted for "force," could well be used today as a valid argument in favour of a theory of irreversibility which uses entropy as a primitive concept.

Comparison with the mechanical example of the concept of force is not the only illuminating one; within the same body of thermodynamics the case of energy is an equally strong one. Energy is invariably presented as a primitive concept, the only specification for it being the requirements laid down in the first law; entropy and the second law are the exact counterpart. And indeed some rudimentary example of the validity of the second law is much easier to discuss and much more intuitive than any example of validity of the first law.

Furthermore, students may accept with some reservations the notion of entropy as a primitive concept, but they'll still allow the teacher to go on, and after a couple of classes they'll realize that scores of ideas which had been floating on shaky grounds in their previous thermodynamic training are now deduced with simple but rigorous logic from one unequivocal mathematical statement of the second law; they'll appreciate that by being asked to accept entropy as a primitive concept they are now offered **definitions** of reversibility, irreversibility, dissipation, and so on. They'll find out one can discuss mathematically and precisely mixtures and their properties without ever having to postulate the existence of semipermeable membranes; and what is invariably the stumbling block of any discussion about modern continuum thermodynamics among professional scientists is passed over smoothly and painlessly in the classroom. Indeed, the most common reaction of the students after the course in 1973 was to ask why they hadn't been taught thermodynamics in that way the first time they were exposed to the subject—apparently, the most difficult part of the learning process was the unlearning of previously acquired biases. (In fact, some satisfactory results have been obtained at the University of Naples, where some of the methodology of RT has been introduced in the teaching of thermodynamics at the undergraduate level.)

SCOPE OF THE COURSE

THE CONTENTS OF the course, summarized in Table I, are illustrated in some detail in the following.

In Section A, 3 hours are dedicated to the introduction of tensors as linear transformations of Euclidean vector space into itself, and to the basic algorithm of space and time differentiation of vectors and tensors. Although the classroom notes and reference [4] include the algorithm for

components of vectors and tensors, this is really not required in the balance of the course and was not discussed in the classroom. The remaining two hours were dedicated to a few basic concepts of functional analysis, including topology of function spaces and Fréchet differentiation of functionals.

Section B was dedicated to traditional continuum thermodynamics, following the methodology of RT. Thus two results are obtained: the actual learning of classical thermomechanical theories of ideal fluids, viscous fluids and elastic solids, and the appreciation of the logical rigor, simplicity and mathematical compactness with which RT can yield the classical results. In particular, in section B1 the second law is written in the simple form requiring the rate of heat supply divided by temperature not to exceed the rate of increase of entropy; the classical elementary results of the thermodynamics of ideal fluids are then obtained as a direct consequence of the assumption that the state is identified by the instantaneous values of density and temperature. In section B2, the second law is written in the form of Clausius-Duhem's inequality, and shown to imply such classical results as the maximum possible efficiency of a heat pump without ever introducing a Carnot cycle. The general method of obtaining consequences of Clausius-Duhem's inequality in continuum thermomechanics constitutes the balance of Section B2. Throughout Section B, the only concrete examples of irreversibility which arise are heat transfer and viscous dissipation.

The traditional areas of transport phenomena and process dynamics; the new trends in molecular engineering, rheology and biochemical engineering may be compacted into some unifying central viewpoint: modern non-equilibrium thermo is a likely candidate for such a role.

Section C is dedicated to the thermomechanics of polymers. In section C1, the method of RT is applied to the analysis of materials with memory, so that irreversibility of relaxation phenomena is discussed in general terms; Section C2 applies the results obtained to the specific case of polymeric materials. Heat transfer, flow and relaxation in polymers are discussed. The first three sections exhaust the contents of the textbook [4].

Section D covers the mathematical formalism of the methodology of RT as applied to both reacting and non-reacting mixtures. Since the aim is only to derive the classical equilibrium theory, diffusion is not discussed. In section D1, the general theory of internal state variables (such as the degree of conversion of a reaction and the degree of splitting into phases of mixtures) and their change in time, of affinity, and of both strong and weak equilibrium states is discussed; the irreversible nature of chemical reactions is put into sharp relief. In section D2, the axiomatic structure of classical chemistry is introduced. This allows to deduce rigorously the theory of physical and chemical equilibria, which are then discussed in detail in section E.

FUTURE EVOLUTION

THE COURSE DESCRIBED above has been given both in 1973 and 1974, and taken by almost all the graduate students of the department during their first semester of work. In the Fall semester of 1974, a seminar was also held, meeting once a week, on the teaching of thermodynamics at both the graduate and undergraduate level. The following future evolution of graduate level teaching of Thermodynamics has been planned.

The students will be offered **two** graduate courses; the first one, to be taken in their first year of work, will be a more traditional course than the one described above, while a course in modern continuum thermodynamics will be offered to second-year graduate students starting in the Fall semester of 1976. With the background of a more traditional course, the material in sections D2 and E could well be left out from the second year course, and the 12 hours so recovered could be used for covering one or more of the following subjects:

- **Thermodynamics of diffusion.** This would complete the landscape of the theory of irreversibility of the four basic classes of phenomena of interest to chemical engineers, namely momentum, heat and mass transfer and chemical kinetics.
- **Thermodynamics and stability.** This would fit in very well with some of the strong research interests of the Department, namely stability of non-equilibrium states (flow patterns, chemical

kinetics) and control theory. The connection between process dynamics, stability theory and thermodynamics has been the subject of some very interesting research [8, 9].

• **Relationship between continuum thermodynamics and statistical thermodynamics.** Although RT is strictly a phenomeno-logical continuum theory, it is by no means at odds with statistical thermodynamics; the aim of the latter is to obtain a priori predictions on the constitutive properties of specific materials, while one of the main aims of the former is to obtain general restrictions on the allowable forms of the constitutive equations imposed by the second law. Particularly in the case of polymeric materials, the two approaches may be complementary, as shown by some recent research [10]. Also, the structural modeling of materials may put some of the basic axioms of RT in a correct physical perspective: witness the case of material objectivity, which has been shown to be valid only if Coriolis forces on structural elements can be neglected [11, 12].

It is perhaps interesting, before concluding, to examine the role of thermodynamics teaching in ChE in a historical perspective. ChE has undergone, at twenty years intervals, two major reorganizations of its patterns of thought, research and teaching. In the late 1930's, ChE evolved from the early stage where the emphasis was on Industrial Chemistry of Processes, to the stage where Unit Operations were seen as the core. In the late 1950's, the new change was the switch from Unit Operations to Transport phenomena. Both changes, when looked upon from a distance in time, have the same character: unification of a variety of parallel elements which had grown too large for detailed analysis (the chemical processes up to 1930, the unit operations up to 1950) into a more compact form which allows the traditional material to be seen from some central viewpoint.

A somewhat similar evolution may be in the making, and the late 1970's appear as just about the right time. The traditional areas of transport phenomena and process dynamics; the new trends in molecular engineering, in rheology and in biochemical engineering may be compacted into some unifying central viewpoint; and modern nonequilibrium thermodynamics is a likely candidate for such a role. The trend is already showing up concretely in the area of transport phenomena: two recent books on the subject [13, 14] dedicate a substantially larger fraction of their contents than traditional to the role of thermodynamics in the theory of transport phenomena.

The course given at Delaware in 1973 and 1974 is a first effort in this direction; inclusion of sections F, G and H would extend the area of thermodynamic influence to the whole of transport phenomena, to process dynamics, molecular engineering and rheology, with only biochemical engineering left out. Of course, this would still be only an initial effort, which should and could extend to the methodology of teaching and thinking at the undergraduate level. Equally of course, the traditional areas of physical and chemical equilibria, energy balances and ideal fluids should not be excluded from thermodynamics, but neither should they be regarded as exhausting the subject. □

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