Fifth LACCEI International Latin American and Caribbean Conference for Engineering and Technology (LACCEI'2007)
"Developing Entrepreneurial Engineers for the Sustainable Growth of Latin America and the Caribbean: Education, Innovation, Technology and Practice"
29 May – 1 June 2007, Tampico, México.

Thermodynamics of Irreversible Processes and the Teaching of Thermodynamics in Chemical Engineering

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ABSTRACT

In this paper the some aspects of the teaching of Irreversible Thermodynamics are discussed, emphasizing relevant concepts needed by the engineering student, and future professional. The irreversible nature of real processes is presented to the student in the introductory level, in place of the more traditional disciplines concentrated on Classical Thermodynamics, which describes systems undergoing reversible processes, and which associates with the tendency of disappearance of structures. Impacts of irreversibility are depletion of natural resources and ecological damage, as we face today. Irreversible, open, non-linear systems are presented as of great interest to the Chemical Engineer. Coherent, purposive, and irreversible biological systems are also considered. Irreversible thermodynamics is presented as an element for the unification of a wide range of disciplines subjected to a fragmentation of a somewhat bureaucratic nature. This integration, resulted from the enormous development of computers and its use in the study of nonlinear dynamics system with wide applications in various fields embracing engineering, biology, ecology, economics, and sociology, leading to familiarity with terms such as chaos, complexity, bifurcations, and attractors.

Keywords: Thermodynamics, irreversibility, nonlinear systems, applications

1. INTRODUCTION

Compared to classical thermodynamics nonequilibrium thermodynamics has been given far less attention than deserved in Chemical Engineering Curricula: *in Carnot's engine the source of energy and* the *sink were* taken *for granted*. Indeed a great deal of science, technology, and money is required to project, construct, and keep the high temperature reservoir hot. Increasing concern has been at last expressed by society with respect to the heat and matter thrown in the lower temperature sink: the environment. Global warming is today an inconvenient reality.

Economic and technological developments have been characterized by open and determined aggression to nature. We inherited the consequences of man's disregarding irreversibility: i.e. a hole in the ozone layer. Global warming, nuclear waste deposited in the oceans.

No attention was given to Wilhelm Ostwald's statement: "Waste not free energy; treasure it and make the best use of it." Meanwhile, in our curricula, emphasis was given to reversible processes in Thermodynamics, as to linearity, and continuity in mathematics. Economy is still dominated by mechanistic, closed models.

Reversibility, and a mechanistic view of the universe remained as *survivals* (to borrow a term from sociology) in the academic world.

As pointed out by Prigogine (Prigogine, 1967), "the majority of the phenomena studied in biology, meteorology, astrophysics, and other subjects are irreversible processes which take place outside the equilibrium state." Classical Thermodynamics is a theory which describes systems undergoing reversible processes and is, however "particularly applicable to *closed systems" (*Katchalsky, and Curran, 1974)

The emphasis given to classical reversible thermodynamics in chemical engineering, a branch of thermodynamics which, as pointed out by Glansdorf and Prigogine (Glansdorf and Prigogine, 1971) "once the second law is formulated, concentrates on the properties of system which have reached thermodynamic equilibrium," limits the application (and teaching) of this science specially when dealing with the *open, irreversible systems*.

Our interest in the this field resulted from a critical view of transport models, at that time frequently applied in the quantitative investigation of hyperfiltration with polymeric membranes, disregarding the formalism of *linear non-equilibrium thermodynamics,* ignoring cross relationships, and thus missing the very nature of membrane selectivity introduced by Onsagers' cross coefficients**.**

2- DISCUSSION

My interest in thermodynamics of irreversible processes is the result of an earlier effort to find an adequate description of semi permeable membrane behavior, without the use of kinetic equations "based on specific models." (Katchalsky and Curran, 1974), where we considered the effective interference, through cross coefficients, between fluxes and forces. Onsagers's cross-coefficients, thus, as pointed out by Katchalsky (Katchalsky and Curran, 1974), introduce "*One of the most interesting aspects of membrane function, the selectivity*" An important concept is <u>*the simultaneous occurrence of two or more of these phenomena*</u> when they interfere, giving rise to very interesting effects.
Well known examples of interference, is thermo-electricity, the Soret effect, Knudsen flow. de Groot (de Groot, 1966) presents the phenomenological equations, consisting of a matrix relating fluxes to thermodynamic forces. We consider a matrix of fluxes, J_i, where

$$J_i \ (i = 1, 2, ...,n) \qquad (1)$$

And, forces X_k, such that

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \qquad (i = 1,2,.....,n) \qquad (2)$$

Onsagers's theory states that if an adequate choice of fluxes and flows is made, the matrix of phenomenological coefficients is symmetric, i. e.,

$$L_{ik} = L_{ki} \qquad (i, k = 1,2,.......,n) \qquad (3)$$

In the case of semi permeable membranes, where fluxes are of volume and species, and forces are pressure and concentrations, a reflection coefficient σ is given by,

$$\sigma = -\frac{L_{pd}}{L_p} \qquad (8)$$

σ will be < 1 if the membrane allows passage of the solute. $\sigma = 1$ if the membrane "reflects" all the solute (ideal semi permeable membrane), and $\sigma = 0$ if the membrane is nonselective (like porous glass in a case of a sodium chloride aqueous solution
Phenomenological coefficients can be "translated" into friction and distribution coefficients which are convenient to physical interpretations, and to the molecular design of membranes, as demonstrated by Kedem and Katchalsky.(Kedem and Katckalsky, 1961) . Pusch (Pusch , 1977) compared the solution diffusion model with the quantitative treatment obtained with the formalism of the of irreversible processes, and concluded that, working with cellulose acetate and commercial ionic membranes, in the latter case representation of data was correct in a wider range of experimental conditions such as salt concentrations and pressures.
Bittencourt (Bittencourt, 1975) and Bittencourt et al (Bittencourt et al, 1981) applied the formalism of thermodynamic of irreversible processes to analyze the reverse osmosis behavior of novel ionic membranes. The quantitative analysis of the results, with basis in the frictional interpretation of the phenomenological coefficients, proved to be coherent, and quite relevant for the molecular engineering of selective membranes

As mentioned by Katchalsky (Katchalsky, 1974) a *coordinated theory of irreversible thermodynamics* was developed based "on the fundamental work of Onsager" consisting in a "new branch of thermodynamics." This coordinated theory has been for some time an established branch of Thermodynamics, with innumerous applications, one of them presented above. With this theory the inequalities of classical thermodynamics are replaced with equalities, resulting in "thermodynamically-fundamentated" transport equations. As pointed out by Prigogine (Prigogine, 1967), *linear nonequilibrium thermodynamics* is today a classical subject, limited however to the vicinity of equilibrium. In the far-from-equilibrium region nonlinear thermodynamics introduces the concept of dissipative structures associated with the "emergence of order both in time and space."

Abrangence of the theory of irreversible thermodynamics includes the phenomena of "creation of structures" extending beyond the "conventional" region of classical engineering problems, and interest to the study of living organisms in biology, to sociology, ecology and economy.

Our interest includes concepts related to the thermodynamics of *open, coherent, purposive, and irreversible systems (OCPIS)* of relevant interest also in the study of biology, economy, sociology, and very relevant to the study of the productive units the chemical engineer will work with.

Furthermore, "the far from equilibrium approach", "... may act as an *element of unification* (Glansdorf and Prigogine, 1971) bringing closer problems belonging to a *wider range of disciplines*." This *element of unification* consists in a powerful instrument for the engineer who is confronted by the increasing demand of interdisciplinary, cooperative study and research work.

In biology, one of the most exciting subjects in the context of the second law, "the idea of evolution is, closely associated with an increase of organization giving rise to the creation of more and more complex structures," (Glansdorf and Prigogine, 1971), whereas in classical thermodynamics, as mentioned above, reigns as the law of *disappearance of structures*.

According to Lotka, in biology, "Evolution is the history of a system undergoing irreversible changes" (Lotka, 1956).

Georgescu-Roegen (Georgescu-Roegen, 1971) claimed "...that the nature of the *economic process* viewed as a whole is purely *entropic*," pointing out " that biology, *not mechanics* is the true Mecca of the economist." However, it should be pointed out that the highest object of the entropic view of the economic process " ...is not through a mathematical system which reduces everything to entropy," but instead, utilize a broader understanding of the process to learn "*what aims are better for the economy of mankind*"

The human being is, according to Spencer, "the terminal problem of Biology and the initial factor in Sociology" (Spencer, 1961) thus establishing a bridge between these two sciences (and establishing the common nature of biology, economy, and sociology).

Georgescu-Roegen points out that economy is still plagued by the *misleading view* of the process as the *mechanistic behavior of* homo *economicus.* causing this science to be "criticized by its own servants ...openly and constantly...". Furthermore, Georgescu-Roegen adds, quoting Jevons, (Jevons, 1906), that "Not even wars nations fought for the control of world natural resources awoke economists from their slumber".

The elementary textbooks in economy still describe the process as "a circular flow between production and consumption with no outlets and no inlets" (Georgescu-Roegen, 1971). By necessity they also are open, purposive systems undergoing irreversible processes.

Referring to the systems found in biology (Glansdorf and Prigogine, 1971), and, quoting Weiss, (Weiss, 1966), that "*Coherent behavior is a characteristic inherent to those systems."* Moreover a production unit behaves in a way analogous to any biological system, when we consider Georgescu-Roegen quote of Erwin Schrödinger's idea that "any *life-bearing structure* maintains itself by sucking low entropy from the environment and transforming it into high entropy."

The theoretical structure of nonequilibrium thermodynamics is absolutely necessary to the quantitative description of living beings: "*Nonequilibrium Thermodynamics in Biophysics"* was written Katchalsky, 1974) "to *introduce* students in biophysics, physical biochemistry, and physiology to this new branch of thermodynamics."

Another important feature inherent to OCPIS is the *self sustaining* capacity which assures the *necessary* degree of stability –this constitutes the principle of *homeostasis* (Brody, 1974) - a measure of the degree of an organism's independence of its environment *due to the ability of maintain its internal environment.*

"Nature has to be considered as a whole if she is to be understood in detail" Bunge

As pointed out, (Glansdorf and Prigogine, 1971) in thermodynamics we are therefore, confronted by two *simultaneous*, and yet apparently conflicting tendencies: *dissipation of order* (as stated by the Carnot-Clausius principle), and the *increase in organization* observed in Biology, Sociology, Science-Technology, and Economy. *[1]

According to Bergson (Bergson, 1963) "The deeper we go into the nature of time the more we understand that duration means invention, creation of forms, continuous elaboration of what is absolutely new."

It was pointed out by Georgescu-Roegen (Georgescu-Roegen, 1971), referring to economists, that the appearance of pollution took by surprise scientists playing with mechanistic models, who should have warned their co-workers in the technological sciences that ""bigger and better" washing machines, automobiles, and super-jets must lead to "bigger and better" pollution."

The dramatic change in the complexity of the world economy, integrating countries of different cultures, sociological status and wealth, demands from technological man a more complex, global, and interdisciplinary education. The chemical engineer will be asked to take decisions involving concepts, which have been traditionally kept outside the world of technical man.

We are now faced by integrated global challenges demanding innovative and more sophisticated strategies, which imply a significant evolution in education.

2-CONCLUSION

The second law, generally introduced following traditional methods with a *dependence*, as pointed out by Denbigh, (Denbigh, 1971) on the use of *heat engines* if based on Clausius or Poincaré approaches, or of *the existence of perfect gases* as demanded by the method of Plank.

According to Margeneau and Murphy (Margeneau and Murphy, 1943), "In most textbooks of thermodynamics the order of presentation parallels the *historical development* of the subject," and as a result "the critical student may feel the need of a more logical and formal approach." The principle of Carathéodory (C. Carathéodory, 1909) based on the properties of Pfaffian differential expressions, seemed to me much more satisfactory and rigorous compared to these "historical" approaches.

It is fundamental for the development of Thermodynamics that dU (U, Internal energy) and dS (S, entropy) are exact differentials.

Physically, the ideal reversible process will correspond to a quasi-static process - "a dense succession of *equilibrium* states, " (Callen, 1985), pages 95-100, observed in a thermodynamic hyper-surface, while a real process is a " temporal succession of *equilibrium and nonequilibrium states."* In quasi-static processes we are dealing with step-by-step removal of constraints and equivalent equilibrium states which depend on the relaxation time of the system. The rate of removal of constraints and the relaxation times determines if any thermodynamic driving force will appear thus making the process irreversible. As stated in a report about the future of Chemical Engineering Education (Groppe, 1985), "Thermodynamics is currently taught in physics, chemistry (general and physical), and chemical engineering (material and energy balances and a separate thermodynamics course). This repetition may involve a wide disparity in nomenclature, conventions and rigor, and hence can often be more confusing than helpful." Consolidation is recommended in the Report to be handled by the chemical engineering faculty. The conclusions and recommendation of this report substantiate the arguments presented in this paper.

We propose to implement the consolidation of thermodynamic teaching in engineering, with simultaneous and substantial incorporation of nonequilibrium thermodynamics to the curriculum. This is necessary to deal with the phenomena associated with the increase in order observed in the "far from equilibrium, nonlinear region." Furthermore, we cannot disregard the creation of order and complexity due to purposive processes observed in biology, sociology, and economy

In Mathematics, as pointed out by Robert M. May (May, 1976), in his excellent article "*Simple Mathematical Models with very complicated dynamics",* "The elegant body of mathematical theory pertaining to linear systems...tends to dominate even moderately advanced University courses in mathematical and theoretical physics which...ill equips the students to confront the bizarre behavior exhibited by the simplest of discrete nonlinear systems..." Furthermore, says May " Not only in research but also in the everyday world of politics and economics, we would all be better off if more people realized simple nonlinear systems do not possess simple dynamical properties."

According to Nicolis and Prigogine the multiplicity of solutions in nonlinear systems "corresponds to a gradual acquisition of *autonomy* from the environment" (Nicolis and Prigogine, 1976), who pointed out that Cultural development, incorporates the duality of deterministic-stochastic elements as demonstrated by the work of Carneiro, (Carneiro, 1965), following Spencer, who differentiates between development (stochastic) and growth (deterministic).

Spencer lists four factors, which can be used to describe social evolution: *invention*, *accumulation, diffusion, and adjustment, (Spencer*, 1961*).* Invention (creation) corresponds to a discontinuity, a stochastic interval, leading to a new "deterministic" phase. Nicolis and Prigogine[] call this event "order through fluctuations."

The thermodynamics of real, irreversible processes has been overshadowed in the traditional teaching of thermodynamics where instead, classical thermodynamics is emphasized. Alternative methods of dealing with the concepts of entropy, and reversibility were briefly discussed: we believe that in these cases the mathematical approach (as opposed to a "historical approach") is absolutely superior for the appropriate grasp of thermodynamic concepts.

In the nonlinear region we are faced with the problem of ordering: to use the title of Nicolis and Prigogine book, [26] "Self Organization in Nonequilibrium Systems- From Dissipative Structures to Order through Fluctuations." Away from the thermodynamic branch the tendency to chaos is substituted by the appearance of ordered (time-space) structures, as predicted by mathematical analysis and verified by experiments.

Although the subjects discussed in this paper send us "venturing into fields we are not qualified to speak" (Glansdorf and Prigogine, 1971)] we should not run away from this challenge.

Acknowledgment

I thank late Professor J. W. Beatty of the Chemical Engineering Department in North Carolina State University for many hours of interesting discussions in the early 70's, related to the problems discussed in this paper

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