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Between Laws of Thermodynamics and Coding of Information

There is nothing wrong with Carnot's cycle, but contemporary thermodynamics may be more useful.

Witold Brostow

"What Is New in Thermodynamics?"

"There exists an additive function of state S, called the entropy, and a set of additive functions of state, called components of content, such that, for any states a and b, $a \rightarrow b$ if, and only if $S(a) \leqslant S(b)$, and $Q(a) = Q(b)$ for every component of content Q." Somehow this does not sound familiar. In fact, this is the fundamental theorem of a thermodynamics of Giles (*1*). Only three primitive concepts are necessary: that of a state, that of addition (+), and that of the relation beween two states a and b such that there exists a natural process leading from a to b ($a \rightarrow b$). By using only these three notions, a coherent structure of classical thermodynamics has been constructed; the results are equivalent to those obtained by other, more complicated approaches.

This was done some years ago. Yet, relatively very little attention has been paid to Giles's construction. This is surprising, as users of thermodynamics are a multitude. Many of these, however, act under a mistaken assumption, that the scope and contents of thermodynamics are time-independent. Thermodynamics is relatively old, compared to other branches of physical sciences, and no longer fashionable. As Landsberg (*2*) said in an article preceding an international conference of the British Physical Society on thermodynamics, it is natural to ask "What is new in pulsars?" while few people ask "What is new in thermodynamics?" Since Landsberg's article and the conference, even further progress has been made. And yet, people still believe that thermodynamics cannot exist without Carnot's cycle. In this article, I would like at least to mention some methods and aspects of the thermodynamics of today.

Information Theory and Statistical Mechanics

Information theory has been successfully applied in many different fields, including molecular biology, linguistics, and now also chemical kinetics (*3*). To comprehend information we might take ignorance as a basic notion, as it is possible to define ignorance by a mathematical formula (*4*, p. 8). We can then define information as the difference between our levels of ignorance before and after receiving a message. While in many fields the informational method is recognized as powerful and versatile, prestige does not necessarily bring popularity (*5*) (except among electronic engineers, who are using it extensively).

To find out what information theory might mean to thermodynamics, let us consider, following Jaynes (*6*), a general, that is informational, partition function Q, written as

$$Q(\lambda_1, \ldots, \lambda_m) = \sum_i \exp[-\lambda_1 f_1(x_i) - \ldots - \lambda_m f_m(x_i)] \quad (1)$$

where the λ's are constants and the f's are functions of some independent variables x_i. At this stage we are not committing ourselves as to the nature of the λ's, f's, and x_i. We can, however, switch from mathematics to physics by specifying, for instance, that we have only one λ, and that

$$Q_T(\lambda, V) = \sum_{i=1}^{\infty} \exp[-\lambda E_i(V)] \quad (2)$$

where V denotes the volume of the system, T is temperature, and the E_i's represent energy levels. We have thus obtained a statistical-mechanical partition function. And we also know, as demonstrated in any textbook of statistical mechanics, that it is possible to obtain statistical-mechanical analogs of the laws and relations of thermodynamics. We have, therefore,

$$\begin{tikzcd}\text{Information theory} \arrow[r] & \text{Statistical mechanics} \\ & \arrow[r] & \text{Thermodynamics}\end{tikzcd} \quad (3)$$

It took some years after Jaynes's paper (*6*) until books of statistical mechanics based on information theory began to appear (*7*). In the meantime, proposals similar to that of Jaynes were made by Ingarden and Urbanik (*8*). The group now working in Torun is highly active in the field: Shannon's information (*9*) was generalized by Kossakowski (*10*); among other things, the Poisson probability distribution was found to be a consequence of the generalization (*11*). Not all the problems have yet been solved. The approach initiated by Jaynes is based on the notion of a reasonable degree of belief;

The author is Boursier de recherche at the Département de chimie, Université de Montréal, Montréal 101, Province of Quebec, Canada.

some conceptual difficulties are involved, and these have been discussed by Friedman and Shimony (*12*). The same authors, however, propose at least three ways of avoiding the difficulties.

A distinct and interesting possibility consists in following the sequence (3) *à rebours*. The idea of implanting methods and techniques of thermodynamics and statistical mechanics into information theory has been advocated in particular by Reiss (*13*). While the relation between the general or informational entropy S and the thermodynamic entropy S_T has been extensively discussed (*14*), Reiss obtained informational counterparts of quantities like temperature, Helmholtz function, or chemical potential. The counterparts have been related to the usual informational notions such as channel capacity or matching of source and channel. The treatment formulated for memoryless sources (*13*) has now been extended so as to deal more successfully with coding of messages in situations involving memory (*15*).

For problems in thermodynamics, the usefulness of the informational approach should probably be judged individually for each case. But let us return for a while to the general role of information theory. One can construct a single and fairly coherent structure of information theory (*16*), but the very existence of this structure has consequences reaching very far, even into philosophy (*17*). The meaning of information theory for our patterns of thought (that is, for intuitive guessing as well as reasoning) forms the subject of a separate volume by Watanabe (*4*).

Approaches to Thermodynamics

Let us at least enumerate the more important ways of building thermodynamics. The most venerable—and still the most widely known—is that of Carnot (*18*). It is rather difficult to comprehend why this approach is still in use. Operating on the level of A.D. 1824 does not only mean disregarding any progress made since. Debating fictitious situations, which cannot be realized in practice, involves serious conceptual difficulties, particularly for the uninitiated, who are trying to understand thermodynamics for the first time. This is probably why, in one of the best textbooks of thermodynamics, the author disposes of the problem with the wry statement (*19*, p. 45), "We shall have no occasion to make any further reference to cycles." To existing admirers (tradition? attractiveness of a model?) of Carnot's story we say that this approach, of course, remains valid even if it is unnecessarily complicated. And there is, as in fact mentioned by Guggenheim (*19*, p. 45), at least one profession for which cycles are very useful indeed: that is, designing refrigerators.

Another venerable approach is that of Carathéodory (*20*). The accessibility or inaccessibility of a point along a line representing a solution of the Pfaff equation is again not always conceptually easy for, say, chemists. Carathéodory's construction possesses a certain mathematical beauty, but so does Giles's theory, with which I started this article. So also does the sequence (*3*), which has the additional advantage of gathering three supposedly distinct scientific disciplines under the same roof.

Five Laws of Thermodynamics—or More?

It is customary to start any discussion of thermodynamics with its laws, so it might be about time that we tackle them too. A striking thing for anybody who has not limited himself to Carnot's approach is the fact that we do not yet know how many laws of thermodynamics are needed and should be in use. Let us count what we have. There is the zeroth principle, which introduces the notion of temperature T. While it is possible to disregard this principle and to introduce temperature later, when talking about the second law (it has been done quite a few times), doing so would mean disregarding the very nature of thermodynamics; in this context, see Guggenheim (*19*, p. 5) for the definition of thermodynamics and its relation to, say, hydrostatics. We then have the first principle, which simply introduces the notion of energy U, while the second introduces entropy S_T. The third principle consists of prescriptions, obtained by statistical methods, for calculating S_T for highly disperse systems (density approaching zero), for very cold systems (temperature approaching zero), and also for mixing of very similar substances, such as isotopes. Incidentally, in many books it is only the second part of the third law (called the Nernst theorem) that is mentioned. All three cases are dealt with, of course (*21*), in Guggenheim (*19*, p. 80).

Real problems begin with the fourth law. The laws mentioned above have been formulated for equilibrium situations. But we also have nonequilibrium situations, and a related field called steady-state thermodynamics, which some years ago used to be called irreversible thermodynamics (*22*). To have some basis for this part, one might take, for example, the Onsager reciprocal relation. Probably a better suggestion is that of Landsberg (*23*): to assume that the usual thermodynamic functions exist, and have intensive or extensive properties, for any closed or open system which in its states of interest is either in equilibrium or resolvable into homogeneous parts. Postulating the existence of both intensive and extensive variables is essential here; earlier laws of thermodynamics do not require this distinction, nor could it be deduced from them. In a book that is already a classic, Prigogine (*24*) stressed the need for a new law as a basis for his irreversible thermodynamics. Landsberg's fourth law has been supported by Wright (*25*), who reconsidered another idea of Landsberg, namely, formulating thermodynamics in terms of set theory (*23*). An end of the discussion of this subject is hardly in sight, but the current answer to the question in the title of this section is: We need no less than five laws of thermodynamics.

To conclude this section, let us consider for a while the thermodynamic potentials, two of which are introduced by the first and second principles, respectively. While the subject of statistical mechanics may well be tackled by discussing the microcanonical partition function first (*26*), it should be remembered that we have no less than eight partition functions Ω. Consequently, we have no less than 16 thermodynamic potentials: eight of the "entropic" type $F_S = k \ln \Omega$ and eight of the "energetic" type $F_U = kT \ln \Omega$. We can also have "mixed" potentials (*27*). Clearly, for a particular problem in thermodynamics, one potential might be more convenient than another. A neat discussion of the 16 basic potentials has been written by Diaz Peña (*28*).

Entropy and Disorder

We mean here, of course, the persistent myth that "entropy is a name given to a quantitative measure of disorder." McGlashan (*29*) has explained that phrases like this are meaningless, except perhaps in the three special cases of mixtures of perfect gases, mixtures of isotopes, and crystals at temperatures near thermodynamic zero. He did not succeed entirely, as some textbooks of thermodynamics published after his article show. The same work of clarifying the confusion has been undertaken again by Wright (*30*). And yet, even today the myth seems to be still alive. The reason for this seems to lie in the fact that one tries to connect an indeed quantitative and exact notion, entropy, with something called disorder, which is loose and subjective and for which no definition exists. Accordingly, three cases are possible, and apparently all three have been taking place.

The first case is when, due to the subjective nature of the notion of disorder, no general consensus exists as to whether disorder increases or decreases in a given process. The second case is when there is some sort of general agreement that the disorder, say, increases in given process, and the entropy happens to increase too—in agreement with the "rule" enunciated at the beginning. In the third case, according to the more or less general consensus, the disorder, say, decreases, while the entropy happens to increase—and the "rule" is violated. Eloquent examples of the last category (crystallization from a supersaturated solution, entropy of rare gases) have been given by both McGlashan (*29*) and Wright (*30*), and I do not intend to repeat them here. A related problem is that of the "heat death" of the universe: The second law of thermodynamics supposedly tells us that our world is approaching a final equilibrium state, in which the temperature and the distribution of matter will be uniform, and, of course, no life will exist. What happens here is that one tries to use terrestrial thermodynamics, which is known to be applicable to bounded and isolated bodies, for the whole universe. When that is being done, one can only repeat the indignant question of McGlashan (*29*) concerning the universe: "Isolated from what?"

There are at least two possible ways to understand the thermodynamic entropy. The first, and in fact quite a convenient one, is to assume that entropy is itself a primary notion. One can then construct thermodynamics in terms of, say, two primordial quantities: entropy (S_T) and temperature. But if one insists on explaining entropy, a very good way is to turn to information theory (*4, 6, 7, 14*).

The disorder story discussed above represents, unfortunately, only one aspect of an otherwise grave problem: bad textbooks of thermodynamics. At first glance, writing a book on thermodynamics is a very easy task. This science has existed for so long, and so many books have already been written, that one can simply extract pieces from several books and sell the compilation as a "new" book. This depressing hypothesis seems to be confirmed by (i) the proliferation of books on thermodynamics; (ii) the obsolescence of many of them—for example, see the discussion above of Giles's and the informational approaches compared to Carnot's cycle; and (iii) the errors and mistakes —there seems to be no other discipline of the physical sciences, quoting McGlashan (*29*) again, so "incredibly badly presented, for the most part by people who do not understand it." The consequences are well known: the frustration of students who, while suspecting some coherent structure and even beauty in thermodynamics, are unable to comprehend it. A characteristic opinion of a student on this subject is quoted by Andrews (*31*):

> To me, thermodynamics is a maze of vague quantities, symbols with superscripes (*sic*), subscripes, bars, stars, circles, etc., getting changed along the way, and a dubious method of beginning with one equation and taking enough partial differentials until you end up with something new and supposedly useful (if that doesn't work you try graphing). I have the impression, however, that to other people, thermodynamics is a logical study of the effects of temperature and pressure on matter and on energy.

Experimental Thermodynamics

Undeservedly, experimental thermodynamics receives even less general attention than theoretical work on the foundations. The indispensability of thermodynamic data in so many fields is obvious, but worth being reminded of once in a while. Enormous recent progress has been made in gathering such data, particularly at low temperatures and high pressures. This has been due mainly to dedication and hard work; even if the principle of a measurement is known, its application under some specific conditions often represents a formidable task. Probably the most important aspect of experimental thermodynamics today consists in utilizing and opening up new possibilities. For example, while the process of extraction is in use in practically every chemical laboratory, the actual mechanism of the formation of two layers in a liquid phase was not seriously studied until recently. Controversial opinions existed. Rinfret and his collaborators (*32*) have found that the demixing process goes through a series of metastable states; the study is being pursued further so as to arrive at the fullest possible understanding of the phenomena taking place. In this case, as well as in others, it is the sophisticated equipment only now available (for example, for the maintenance, measuring, and recording of very small temperature differences) that has made such work possible. A few years ago such a study was not feasible.

As a general feature, one notices that experimental thermodynamics usually represents the first step in the study of properties of matter. With rare exceptions, a description in terms of molecular structure and interactions comes afterwards.

Temperature: Georgian Scale

As far as temperature scales are concerned we seem to have some choice. There is the nice and old-fashioned Réaumur scale. There is the Celsius scale; looking at even the smallest body of water, every continental European will know whether the temperature is "positive" or "negative." We have the Fahrenheit scale, so popular on the North American continent, and of course hopeless on any count. We have the Kelvin scale, distinguished from those named previously by the fact of being thermodynamic.

Is the Kelvin scale the best possible? The answer is no. There is just one temperature scale really convenient in thermodynamics; arguments in its favor have been presented by Georgian (*33*). If this scale is adopted, the equation of state of the perfect gas is

$$PV = T \qquad (4)$$

That is to say, the famous—and completely unnecessary—universal gas constant has been set equal to unity. In this context Jaynes (*6*), in a paper we discussed above for entirely different reasons, proposed that the Boltzmann constant k be set equal to unity. In the Georgian scale, we have $k = N_A{}^{-1}$, where N_A is the Avogadro number, and the temperature is expressed in joules per mole. The freezing point of water is then

$$273.15°\text{K} = 2271.16 \text{ joule/mole}$$

Thermometers with this scale have already been manufactured.

Talking about temperature reminds one of the rather amusing notion of negative temperatures. While the notion is not quite new, it also has not yet found its way into all books of thermodynamics. The quantity to consider is

$$\tau = -T^{-1} \tag{5}$$

varying in the full range from minus infinity to plus infinity. A good discussion is in Landau and Lifshits (*34*).

Some Concluding Remarks

This subtitle is to a certain extent misleading. The main purpose of the present section is to anticipate some criticisms. These might come, roughly, from "conservative" and from "revolutionary" quarters. One conservative criticism might be: "Why should we bother about anything beyond Carnot's cycle if, by your own admission, the cycle remains valid?" The answer is that if somebody needs thermodynamics at all, he might well find that information theory serves his purpose better; this is my current experience, and the reason for my enthusiasm toward information theory. In this context, it cannot be stressed enough that new approaches are not advocated here against the old ones, but only because of their known or potential usefulness. Clearly, the importance of certain approaches only increases with time. A characteristic example is the notion of regular solutions, proposed more than 40 years ago (*35*); the range of applicability of this notion is still growing, as we can judge from the recent book by Hildebrand and his younger colleagues (*36*).

Another possible criticism from the conservative quarters could be: "It is easy for you, a thermodynamicist, to follow the recent developments; but most of us only use thermodynamics once in a while and we just haven't time." The answer is that while I have found following the developments of thermodynamics useful, I am also only one of the users. A shrewd reader (one who approaches every article with the question "Who wrote it?") has certainly noticed by this time that there are no references to my own publications. In fact, I work in the field of the liquid state.

"Revolutionary" criticism might go something like this: "Five laws of thermodynamics? If you yourself had read current research papers instead of ancient textbooks, you would have known that there are now seven laws of thermodynamics." The answer is, I am aware that certain statements made above may be disputed. But this, in turn, proves precisely the main point of this article: that thermodynamics is very much alive and growing.

References and Notes

1. R. Giles, *Mathematical Foundations of Thermodynamics* (Pergamon, New York, 1964), pp. 5, 59.
2. P. T. Landsberg, *Nature* **225**, 1204 (1970).
3. N. I. Kobozev, B. V. Strakhov, A. M. Rubashov, *Zh. Fiz. Khim.* **45**, 86 (1971).
4. S. Watanabe, *Knowing and Guessing—A Quantitative Study of Inference and Information* (Wiley, New York, 1969).
5. The lack of popularity seems, partly at least, related to the "dry mathematics" of the information theory. As this would apply to any discussion of the theory, a particularly nonmathematically minded reader of the present section might like to concentrate only on sequence (3) and comments directly related to it.
6. E. T. Jaynes, *Phys. Rev.* **106**, 620 (1957).
7. A. Katz, *Principles of Statistical Mechanics—The Information Theory Approach* (Freeman, San Francisco, 1967); G. A. P. Wyllie, *Elementary Statistical Mechanics* (Hutchinson, London, 1970); R. Baierlein, *Atoms and Information Theory: An Introduction to Statistical Mechanics* (Freeman, San Francisco, 1970); A. Hobson, *Concepts in Statistical Mechanics* (Gordon & Breach, New York, 1972).
8. R. S. Ingarden and K. Urbanik, *Acta Phys. Pol.* **21**, 281 (1962).
9. C. E. Shannon, *Bell Syst. Tech. J.* **27**, 379, 623 (1948).
10. A. Kossakowski, *Bull. Acad. Pol. Sci. Ser. Sci. Math. Astron. Phys.* **16**, 349 (1968).
11. R. S. Ingarden and A. Kossakowski, *ibid.* **19**, 83 (1971).
12. K. Friedman and A. Shimony, *J. Stat. Phys.* **3**, 381 (1971).
13. H. Reiss, *ibid.* **1**, 107 (1969).
14. J. Rothstein, in *Quantum Theory and Beyond*, T. Bastin, Ed. (Cambridge Univ. Press, London, 1971), p. 291.
15. H. Reiss and C. Huang, *J. Stat. Phys.* **3**, 191 (1971); C. Huang and H. Reiss, *ibid.*, p. 261.
16. J. Peters, *Einführung in die allgemeine Informationstheorie* (Springer, Berlin, 1967).
17. L. Couffignal, Ed., *Le concept d'information dans la science contemporaine, Cahiers de Royaumont* (Gauthier-Villars, Paris, 1965).
18. N. L. S. Carnot, *Réflexions sur la puissance motrice du feu* (Bachelier, Paris, 1824).
19. E. A. Guggenheim, *Thermodynamics—An Advanced Treatment for Chemists and Physicists* (North-Holland, Amsterdam, ed. 5, 1967).
20. C. Carathéodory, *Math. Ann.* **67**, 355 (1909).
21. The few readers who happen to know that I was associated with the Department of Chemistry of the University of Reading when it was headed by Guggenheim might wrongly interpret this "of course." I went to Reading only after finding a book of thermodynamics that I was able to understand.
22. This is not very important, but the word irreversible should be avoided, as it suggests calling the equilibrium part reversible. In view of the fact that reversible processes are impossible, this would indicate that thermodynamics consists of fictitious and real parts.
23. P. T. Landsberg, *Thermodynamics* (Interscience, New York, 1961), p. 136.
24. I. Prigogine, *Thermodynamics of Irreversible Processes* (Thomas, Springfield, Ill., 1955), p. 93.
25. P. G. Wright, *Proc. Roy. Soc. Ser. A* **317**, 477 (1970).
26. R. G. Keil and L. K. Nash, *J. Chem. Educ.* **48**, 601 (1971).
27. R. P. Gordon, *Amer. J. Phys.* **39**, 1295 (1971).
28. M. Diaz Peña, *An. Real Soc. Espan. Fis. Quim. Ser. A* **57**, 95 (1961).
29. M. L. McGlashan, *J. Chem. Educ.* **43**, 226 (1966).
30. P. G. Wright, *Contemp. Phys.* **11**, 581 (1970).
31. F. C. Andrews, *Thermodynamics: Principles and Applications* (Wiley-Interscience, New York, 1971), footnote to p. 3.
32. M. Rinfret and V. T. Lam, *J. Chim. Phys.* **65**, 1457 (1968); *ibid.* **68**, 324 (1971).
33. J. C. Georgian, *Nature* **201**, 695 (1964); *ibid.* **203**, 1158 (1964); *ibid.* **207**, 1285 (1965).
34. L. D. Landau and E. M. Lifshits, *Statisticheskaya fizika* (Nauka, Moscow, 1964), p. 257.
35. J. H. Hildebrand, *J. Amer. Chem. Soc.* **51**, 66 (1929).
36. ———, J. M. Prausnitz, R. L. Scott, *Regular and Related Solutions* (Van Nostrand–Reinhold, New York, 1970).