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The Curious Incident of the Dog in the Night-Time or What Lessons Lurk in Old Textbooks

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The term entropy and its associated concept have been with us for 130 years and the Second Law for 15 years longer.

This article examines the early presentation of the Second Law of Thermodynamics in physical chemistry textbooks published between 1900 and 1926. It explains how the concept of entropy emerged from obscurity to become a familiar idea and describes how analyzing the history of the development of scientific concepts can uncover hidden “lessons” about how ideas are formulated, digested, and finally accepted.

> [Colonel Ross]: “Is there any other point to which you would wish to draw my attention?”
>
> [Holmes]: “To the curious incident of the dog in the night-time.”

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> [Colonel Ross]: “The dog did nothing in the night-time.”
>
> “That was the curious incident,” remarked Sherlock Holmes.
>
> Sir Arthur Conan Doyle, *The Adventure of Silver Blaze* [1]

Any current general chemistry textbook worthy of the name at least introduces students to the concept of entropy, and it usually provides them with some examples of its use [2]. One thermodynamics text intended for first-year students even organizes its discussion principally around entropy [3]. Furthermore, the inclusion of entropy in the first-year chemistry curriculum is hardly a new development, dating back at least to Pauling’s seminal general chemistry book [4]. Discussions of entropy have even emerged in the high school curriculum [5]. Moreover, entropy took its place in the physical chemistry curriculum long before it was a subject for first-year or high school chemistry students. The meaning of entropy and of the Second Law of Thermodynamics now constitute part of the basic conceptual foundation for any student learning about science.

None of this would seem to qualify as news. The term entropy and its associated concept have been with us for 130 years and the Second Law for 15 years longer (Table 1). Historians also generally agree that one reason why physical chemistry developed as an autonomous discipline was its founders’ desire to apply thermodynamics to chemical problems [6], yet the prominence of entropy in the chemical curriculum was achieved only after decades of doubt about its utility in chemistry.

In April, 1994 the Dibner Institute for the History of Science and Technology at MIT held a two-day workshop constructed around “The Meaning and Use of Entropy.” I was a commentator in a session devoted to chemistry, in which papers were presented by Helge Kragh (a well known historian of the physical sciences) and Laszlo Tisza (a distinguished thermodynamicist who has been studying the history of thermodynamics).

Because my career has involved principally teaching and writing textbooks about chemistry, which covered neither thermodynamics nor history of science, it seemed as if I could make a useful contribution by investigating how entropy had been taught to chemistry students. To this end I gathered together and examined those physical chemistry textbooks published during the period 1900–1926. The results of my explorations were puzzling. In many texts entropy and the Second Law were treated

TABLE 1. Major events in the early history of the entropy concept.

1824	CARNOT PUBLISHES REFLECTIONS ON THE MOTIVE POWER OF HEAT: it contains the Second Law of thermodynamics avant la lettre.
1850	CLAUSIUS AND THOMSON (LORD KELVIN) STATE THE SECOND LAW OF THERMODYNAMICS.
1865	CLAUSIUS ENUNCIATES THE ENTROPY CONCEPT: "THE ENTROPY OF THE UNIVERSE TENDS TOWARD A MAXIMUM." (NB: the entropy "law" is the major scientific law that is **not** a conservation law.)
1875	GIBBS DEFINES FREE ENERGY AND ITS RELATION TO K_{eq}.
1877	BOLTZMANN'S STATISTICAL DEFINITION OF ENTROPY: $S = k \ln w$.
1906	NERNST STATES THE THIRD LAW OF THERMODYNAMICS: $\lim_{T \to 0}\left(\frac{du}{dt}\right) = \lim_{T \to 0}\left(\frac{dA}{dt}\right) = 0$

only perfunctorily, and in some the word “entropy” was not to be found at all. Independently, Kragh had also concluded that entropy did not play much of a role in early theoretical and physical chemistry [7].

Why, for early 20th century chemists, did entropy seemed to resemble nothing so much as “the dog in the night-time,” notable mainly for its silence? Our curiosity led Kragh and me to undertake a review of the development of chemical thermodynamics and its treatment in textbooks during the period 1900–1925 [8]. The “story” we uncovered was richer and more nuanced than our initial sketch, without contradicting the latter’s essential message—entropy was a topic that many of our chemical forebears shied away from, even to the point of ignoring it altogether. I concentrated on analyzing the two dozen or so textbooks, from which I drew the “lessons” that are the subject of this article.

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In current texts the Second Law of Thermodynamics is routinely equated with the law of increasing entropy. That conflation is not only conceptually wrong but also historically misleading [9]. When the Second Law was first propounded by Rudolf Clausius and William Thomson around 1850, entropy was unknown, both as a concept and as a name. Clausius' formulation of 1850 stressed the natural tendency of heat to equalize temperature or the impossibility for a self-acting cyclic machine to transfer heat from a body at a certain temperature to a body at a higher temperature. According to Thomson's equivalent formulation of 1852, it is impossible to gain work by cooling matter below the temperature of the coldest of its surroundings. What Clausius and Thomson enshrined as scientific law was, of course, "common sense"—everyone *knew* that warm bodies naturally transfer heat to colder ones and not vice versa. My first "lesson" is that many scientific laws are based upon commonplace observations. What distinguishes scientists from lay people is less our observational abilities than our creativity at extracting the long range and not so obvious consequences of those observations.

Furthermore, it requires a major intellectual effort to connect commonplace observations with the more abstract, albeit very powerful "scientific" theories such as Boltzmann's statistical conception of entropy. In the classroom we do not customarily discuss the difficulties entailed in that effort—it takes time away from "problem solving." As a result, many students believe that their failure to grasp the fundamental premises of the Second Law is due to their incompetence. The problem may rather lie with the complexity of the reasoning that ties those premises to everyday experience.

Kragh and I were struck early on by the variety of expositions that the Second Law received. This was true both in the research literature and in textbooks where one might have expected a more uniform treatment. While the First Law was presented in a manner that varied little from one text to the next, diverse versions of the Second Law were commonplace over a span of decades (Table 2). The "lesson" to be learned here is that such inconsistent presentation frequently indicates that the concept itself is difficult and a likely source of confusion for the student. This certainly seemed to be the view of a number of the authors who referred to the Second Law as "far from simple," "a difficult subject," "difficult to grasp," and so on.

TABLE 2. A potpourri of expressions of the Second Law of Thermodynamics.

Heat passes of itself from a warm body to a cold one and not in an inverse direction.

Clausius, 1850

It is impossible, by means of inanimate agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

W. Thomson (Lord Kelvin), 1854

Heat can never pass from a colder to a warmer body without some change, connected with it, occurring at the same time.

Clausius, 1854

The energy of the universe is constant; the entropy tends toward a maximum.

Clausius, 1865

S (entropy) = $k \ln W$ (probability).

Boltzmann, 1877

The transformation value of a modification is equal to the diminution that a certain magnitude, connected with all the properties that fix the system but independent of its motion, undergoes through this modification.

Duhem, 1902

An isolated system never passes twice through the same state.

Perrin, 1903

The total energy of the universe is a constant, but... the available energy of the world is constantly decreasing.

Washburn, 1915

We sought some clues to this lack of conceptual uniformity in the historical development of thermodynamics. Chemical thermodynamics developed along two rather divergent lines in the late 19th century. One “axis” was represented by the work of Gibbs, Helmholtz, Duhem, and Planck, in which general and sometimes abstract thermodynamic derivations were couched in mathematically complex expressions. We

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might label this approach the physicalist tradition. The alternative approach, the chemical tradition, is exemplified by the writings of van’t Hoff and Nernst. Their approach was less rigorous, less mathematical, and more closely tied to specific empirical data. Van’t Hoff had little to say about entropy, but Nernst was pretty overt in his disdain for it:

> This conception [entropy decrease] is not, however, more general than that of decrease of free energy.... All results so far known in thermodynamics can be deduced by means of cyclic process…many authors take results which already have been firmly established by means of cyclic processes, and reestablish them by application of the entropy principle.... From a pedagogic point of view a certain value may be attached to such “stricter proofs,” but usually the only thing that is proved is that the author has studied the work of his predecessors with intelligence [10].

Nernst’s scant regard for entropy must seem puzzling if not bizarre to a contemporary audience that identifies him as the creator of the Third Law of Thermodynamics. Here again, what passes for convenient pedagogy is in fact bad history, and it may not be all that good even as pedagogy. The version of the Third Law that says that the entropy of perfect crystals is zero at absolute zero is Planck’s reworking of Nernst’s original statement [11]. The original dealt with free energy and heat capacity and didn’t mention entropy (Table 1)! Nernst neither liked nor accepted Planck’s restatement [12], which to Nernst was an example of the kind of bold speculation by a physicist that went against what he saw as the proper treatment of chemical phenomena.

Uncovering this discrepancy between myth and history prompted another “lesson.” Disciplines such as chemistry and physics are distinguished less by their content than by the analytic tools and styles of reasoning they employ. In particular, chemists often shy away from concepts that cannot be readily translated into an operational form, and this bias was one major reason for their reluctance to embrace entropy. Devotion to a characteristic style of reasoning has certainly provided chemistry with enormous strengths and some distinct limitations as well. On the credit side, the molecular viewpoint enables us to tie together a tremendous range of phenomena. As a chemist I am aware of and grateful for the power inherent in the molecular approach to matter. It was, therefore, initially puzzling to me to find that Boltzmann’s probabilistic formulation of the entropy law met with particularly strong resistance among most authors of physical chemistry and chemical thermodynamics textbooks. Boltzmann’s approach is after all a molecular one, and one might reasonably have expected chemists to embrace it. The problem, however, arises from its dependence on probabilistic thinking and statistical calculation [13].

Chemists have a long explanatory tradition that relies on discussions of individual molecules. Although we know *intellectually* that our domain almost always comprises very large aggregates of molecules, we still rely on deterministic explanations of chemical behavior that invoke the individual molecule as the unit of explanation. (This "lesson" is still *very* relevant today.) Fixated as they were on the properties of individual molecules, our predecessors found it difficult to reconcile their molecular explanations of chemical phenomena with Boltzmann's statistical approach, making them very hesitant toward his treatment of entropy.

It became clear to Kragh and me that chemists' pre–World War I wariness toward the entropy concept arose from a multitude of concerns. Some were very specific — for instance, entropy changes could be determined for only a very few processes, and, once measured, they could not be meaningfully interpreted because of the undifferentiated nature of the entropy concept prior to quantum mechanics. There were, however, other less specific, but no less important, sources of disquiet. For instance, Jean Perrin thought it "risky to speak of the entropy of a living system or of an exploding system," and saw in the Carnot cycle "a principle of life and of evolution" [14]. Even J. R. Partington, a physical chemist (and later preeminent historian of chemistry) who was in a minority in the attention he paid to entropy in his prewar textbook, wondered "whether the second law is applicable to living systems" and "whether it can be enunciated in such a way that the subjective content is eliminated..." [15].

K. G. Denbigh and J. S. Denbigh have shown how the notion of randomness associated with Boltzmann's formulation of entropy became transmuted into "lack of knowledge" and eventually into "subjectivity" [16]. There was uncertainty as to whether entropy is a property of the physical or of the psychological world, and leading scientists as well as lay people doubted that living systems were subject to the law of entropy increase.

The global, even "cosmic," aspects of the Second Law and the entropy principle grabbed the attention of the lay public as well as scientists, and this led to an enormous rash of speculation regarding its meaning and significance [17]. Probably the most famous example of this is Kelvin's notion of the "heat death" of the universe. These speculations ranged from the insightful to the provocative to the near preposterous [18].

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What impressed me is near total lack of allusion to them in the textbooks I reviewed, from which I concluded that these speculations were not welcomed by most chemists. Chemists then (and perhaps also now?) were very concerned about the status of chemistry as a “real science” and extremely nervous about its being in any way associated with lack of knowledge, subjectivity, or vitalism. To them the entropy concept must have seemed not only confusing but dangerous.

As we know entropy was finally incorporated into chemical practice and pedagogy. Several developments coalesced in the post–World War I period to bring about a dramatic rise in its visibility. The attainment of very low temperatures allowed the accurate calculation of absolute entropies [19], which could provide some very subtle insights into molecular energetics [20]. Differentiation of molecular entropies into entropies of rotation, vibration, and so on made the relevance of entropy to chemists’ principal concerns much more apparent. (For example, since the formulation of the theory of absolute reaction rates [21] the entropy of activation has become a standard conceptual tool for explaining reaction mechanisms.) Perhaps most significantly, a new generation of physical chemists consciously allied with the physicalist tradition came to prominence [22].

To contemporary chemists it must seem as if entropy has been domesticated (although by no means rendered transparent), but some older fears still linger. We are still wary when it comes to discussing the social dimensions of chemistry. While we’re fairly ready to expound about the impact of chemistry on society (especially if that impact is unquestionably beneficial), we have collectively shown relatively little interest in the proposition that there is a two-way interchange between science and society [23]. To acknowledge that possibility would be to call into question the “splendid isolation” from mere human affairs that in the eyes of some gives science its exalted status. Not only do I have deep personal reservations about that view but I believe that it turns many students away from science. They rebel against a vision of knowledge that is completely disconnected from the patterns of thought and feeling that inform the rest of their lives. What we conceive of as *ahuman* many students understand as *inhuman* and react accordingly. Yet thermodynamics itself, one of the supreme achievements of modern science, provides ample testimony to the intercourse between the scientific and the social [24]. It is in fact in one of the classic textbooks of thermodynamics that one can find a wonderfully compact and incisive summary of the social and scientific vicissitudes of the Second Law and the entropy concept.

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> The first law of thermodynamics, or the law of the conservation of energy, was universally accepted almost as soon as it was stated; not because the experimental evidence in its favor was at that time overwhelming, but rather because it appeared reasonable, and in accord with human intuition. The concept of the permanence of things is one which is possessed by all. It has even been extended from the material to the spiritual world....
>
> The second law of thermodynamics, which is known also as the law of the dissipation or degradation of energy, or the law of increase of entropy, was developed almost simultaneously with the First Law through the fundamental work of Carnot, Clausius and Kelvin. But it met with a different fate, for it seemed in no recognizable way to accord with existing thought and prejudice. The various laws of conservation had been foreshadowed long before their acceptance into the body of scientific thought. The Second Law came as a new thing, alien to traditional thought, with far-reaching implications in general cosmology.
>
> Because the Second Law seemed alien to the intuition and even abhorrent to the philosophy of the times, many attempts were made to find exceptions to this law and thus to disprove its universal validity, but such attempts have served rather to convince the incredulous and to establish the second law of thermodynamics as one of the foundations of modern science. In this process we have become reconciled to its philosophical implications, or have learned to interpret them to our satisfaction....and especially have we learned its correlation with other familiar concepts, so that now it no longer stands as a thing apart, but rather as a natural consequence of long familiar ideas [25].

Textbooks of Physical Chemistry and Chemical Thermodynamics, 1900–1926

Texts in Which Entropy Is Not Mentioned

1. Bigelow, S. L. *Theoretical and Physical Chemistry*; Century: New York, 1912.
2. Jones, H. C. *The Elements of Physical Chemistry*; MacMillan: New York, 1902; any discussion of entropy is also absent in the 4th edition of 1910.
3. Noyes, A. A. *The General Principles of Physical Science*; Henry Holt: New York, 1902.
4. Senter, G. *Outlines of Physical Chemistry*; Methuen: London, 1909.

Texts in Which Entropy Is Barely Mentioned

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2. Lewis W. C. McC. *A System of Physical Chemistry; Vol. I., Kinetic Theory; Vol. II, Thermodynamics and Statistical Mechanics*; Longmans, Green: New York, 1916.

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Texts in Which Entropy Receives a Limited Treatment

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2. Perkins, H. A. *An Introduction to General Thermodynamics: An Elementary Treatise on the Fundamental Principles and Their Simpler Applications*; Wiley: New York, 1912.

3. Washburn, E. W. *An Introduction to the Principles of Physical Chemistry from the Standpoint of Modern Atomistics and Thermodynamics: A Course of Instruction for Students Intending to Enter Physics or Chemistry as a Profession*; McGraw-Hill: New York, 1915.

Textbooks in Which Entropy Receives a Full Classical Treatment

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Textbooks in Which Entropy Receives a Full Classical and Statistical Treatment

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3. Lewis, G. N.; Randall, M. *Thermodynamics and the Free Energy of Substances*; McGraw-Hill: New York, 1923.

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