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# The Conceptual Meaning of Thermodynamic Entropy in the 21<sup>st</sup> Century<sup>1</sup>

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**Invited Article**

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## ABSTRACT

Although entropy change – the process described by Clausius and characterized as the second law of thermodynamics – involves only two terms, energy change and temperature, neither he nor distinguished scientists of the past century focused on that fact. The novel word “entropy” apparently drew them to concentrate on its ‘meaning’ rather than on  $dq$ , the energy becoming spread out or dispersed in phase space in any spontaneous process. Today, beginners and experts can readily see that process as fundamental in thermodynamic change.

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In 1865 Clausius obtained the calculation algorithm  $dS = dq(\text{rev})/T$  as the fundamental quantitative measure of entropy change in a thermodynamic process. He proposed what we now call the second law of thermodynamics. It was a brilliant and profound development. However, his grandiloquent statement was “the entropy [of the world] tends toward a maximum”. But what does that mean? Why is it so? Unfortunately, his principal later publications were attempts to explain mechanical bases for the second law of thermodynamics, but they were failures. Although Clausius had earlier introduced a *disgregation* function to connote a tendency of particles to spread out – now known to be a part of the entropy function -- he never fully clarified the major discovery of his life.

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Just as surprising is the fact that, for more than a century, eminent physicists, mathematicians, and chemists who were intellectually well-capable of explaining entropy failed to do so. In fact, the following comments from a number of them are more revealing about their inability to aid their readers than enlightening:

“...the notion of entropy, ...may repel beginners as obscure and difficult of comprehension.” (Gibbs, 1873).

“...entropy...it is to be feared that we shall have to be taught thermodynamics for several generations before we can expect beginners to receive as axiomatic the theory of entropy.” (Maxwell, 1878).

“Entropy is a shadowy kind of concept, difficult to grasp.” James Johnstone, biology text author, 1914 (Johnstone, 1914).

“You should call it entropy, because nobody knows what entropy really is ...John von Neumann to Claude Shannon.” (ca. 1948) (Tribus and McIrvine, 1971).

“There is no concept in the whole field of physics which is more difficult to understand than is the concept of entropy”. Francis Sears, dominant physics text author, 1950-2000 (Sears, 1950).

A most distressing pronouncement by Boltzmann in 1898 added confusion for a century about the meaning of entropy. Near the end of his “Lectures on Gas Theory” (Boltzmann, 1898) is this paragraph on p. 443. (Italics have been inserted.)

“In order to explain the fact that the calculations based on this assumption [“...that by far the largest number of possible states have the characteristic properties of the Maxwell distribution...”] an enormously complicated mechanical system represents a good picture of the world, *and that all or at least most of the parts of it surrounding us are initially in a very ordered — and therefore very improbable — state.* When this is the case, *then whenever two or more small parts of it come into interaction with each other, the system formed by these parts is also initially in an ordered state and when left to itself it rapidly proceeds to the disordered most probable state.*”

The parts of the world *surrounding us* are initially in an ordered state? This is a sincere statement from Boltzmann, a genius or nearly so, but it is an indication of gross errors that can be made even by superb scientists.

Boltzmann died before the third law was accepted. (This law established that any substance at zero K would have one microstate, one arrangement of its particles on specific energy levels). Further, he never calculated the order or disorder in a system “surrounding us” – in numerical terms, i.e., as the number of microstates for that system. Planck made this possible by writing the original Boltzmann equation of  $\Delta S = k \ln W_{\text{final}}/W_{\text{initial}}$  to be  $\Delta S = R/N_A \ln W_{\text{final}}/W_{\text{initial}}$ .

Thus, anyone believing in Boltzmann’s claim of order in *any* real molecular system might well believe that perhaps a mole of molecules could have not just hundreds of different arrangements – but billions or even  $10^{23}$  different arrangements. But from simple calculations we now know that no system of molecules above 0 K has any “order” in any

conventional use of that term. The comparison of orderly crystalline ice to disorderly liquid water in most 20th century chemistry texts was totally deceptive thermodynamically -- a visual "1898 Boltzmann error" not a proper thermodynamic evaluation. If liquid water at 273 K, with its  $10^{1,991,000,000,000,000,000,000,000}$  accessible microstates is considered "disorderly", how can ice at 273 K that has  $10^{1,299,000,000,000,000,000,000,000}$  accessible microstates be considered "orderly"? The calculations from Boltzmann's equation show only that totally incomprehensible numbers of microstates are possible in each. Clearly, the common words of order and disorder are inappropriate in discussing entropy change.

But why did the scholars quoted above or thousands of other very competent scientists not clearly decipher the meaning of entropy change,  $dS = dq(\text{rev})/T$  fifty or a hundred years ago? Could any serious equation be simpler -- only two terms to define that unknown entropy change (with the function of T being an obvious 'equalizer' so that a small dq/small T would be as important as a large dq/large T)? What are some examples?

A hot piece of iron, placed in a liter-sized chamber of air spreads out some of its energy to any molecules of nitrogen or oxygen in the air that strike it -- and they move more rapidly, dispersing their energy content throughout the volume of the chamber. If a piece of cooler iron touches the hot iron, the cooler piece becomes warmer as the hot iron becomes cooler and ultimately they reach the same intermediate temperature.

Molecules of any gas, whether hydrogen, xenon, or butane are moving energetically at room temperature when they are in a small or a large container or chamber. If they are not constrained by the walls of that chamber to stay in that volume, i.e., if they are given access to an attached, evacuated chamber, we know that they will move to occupy it, as well as their original volume. There is no change in the molecules' temperature, or energy content -- *but it has become spread out in space and in phase space, i.e., its energy-states, microstates are greatly increased.*

Energy of all types tends to disperse -- spread out in space/in phase space to the limits of its constraints. That is the 'secret' of the second law, of why "the entropy of the world tends toward a maximum". The savants of the 20<sup>th</sup> century (who were totally familiar with the obvious phenomena just mentioned) appear to have been seeking some mysterious quality in the word "entropy" itself. But the nature of entropy, its 'tending toward a maximum' of Clausius, is simply the nature of all types of energy, kinetic, light, sound, potential, -- when constraints are decreased or removed.

A conventional response of professors in the 20<sup>th</sup> century who were asked by students, "What is entropy, really?" was "Do enough problems and you will find out." The truth was that students indeed could become totally competent in dealing with the many relationships between S, G, H, A, etc. but never acquired a sense of entropy's meaning. Beginners or experts in thermodynamics in the 21<sup>st</sup> century no longer need be uncertain of the relationship of entropy to a measure of the spontaneous spread/dispersal of energy when it becomes less-constrained.

## **<sup>1</sup>SPECIAL NOTE FOR THE READERS**

*This article is concerned only with the clarification of the meaning of entropy in conventional 'earthly thermodynamics'. It does not consider theories of astrophysicists.*

*A bio of Frank L. Lambert is in Wikipedia and in entropysite.oxy.edu.*

*The simple concept described in this article was independently developed for physicists by H. S. Leff (Am. J. Physics. 64 (10) 1996, 1261-1271). It has been extended by Lambert and others to residual entropy (E. I. Kozliak) and to 'configurational entropy' as detailed in entropysite.oxy.edu. (Also listed therein are the 27 US chemistry texts that have adopted the approach over the past six years – approximately 450,000 students were taught about entropy from them.)*

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