S Is for Entropy. U Is for Energy. What Was Clausius Thinking?

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In this *Journal*, in an article entitled "A Brief History of Thermodynamics Notation" (*1*), Battino, Strong, and Wood express hope that their documentation of thermodynamic symbolism has been of interest. The article has indeed been of interest to me, because my students, like theirs, declare the same puzzlement—"where does *S* for entropy come from?" In addition, the article triggered my specific interest in probing further the story of "S" and in filling a gap remaining in their Table 1, "Origin of Symbols Used for Thermodynamic Functions". The gap is that space in the "Source" column that the authors left blank for the name of the scientist who proposed the symbol "U". These goals prompted me to examine more closely a series of papers by Rudolf Julius Emmanuel Clausius (1822–1888), papers that reveal fascinating insights into both the concepts of nascent thermodynamics and the thinking of its founders.

The collection of Clausius's nine seminal works in thermodynamics (originally printed between 1850 and 1865 in German and English scientific journals) was published in English Translation, in 1867, as *The Mechanical Theory of Heat, With Its Applications to the Steam-Engine and to the Physical Properties of Bodies* (*2*). (The original German version of 1864 lacked the classic ninth paper of 1865, and a French translation of 1868 was used by Barón for a general treatment of Clausius's ideas [*3*].) The English version contains not only translations of the Mathematical Introduction and of the papers themselves (called "Memoirs") but also of Clausius's later appendices to individual papers. Clearly, this publication is of great historical value in discerning the development of Clausius's thought. One more major source for the present study is the 1879 edition of *The Mechanical Theory of Heat*, which is *not* simply a revision of the 1867 book, despite its identical abbreviated title (*4*). It is the English translation of Clausius's completely reworked ideas of thermodynamics, presented in the form of a textbook (published in German in 1875), a convincing culmination of his efforts to simplify and popularize the topic. In addition, Clausius permitted inclusion in this book of three appendices authored by the English translator, further demonstrating Clausius's desire to extend the implications of his science.

Modern chemistry students, exposed to the current popularity of first-letter abbreviations (<u>A</u>bsorbance), acronyms (laser), and clever literary allusions (quark), might well expect earlier scientists to have followed similar methods of designating their concepts. However, when Clausius, Professor of Physics at the University of Zurich, introduced the letters "U" and "S" into science literature in the mid-19th century, he was not under this influence. Analysis of Clausius's papers reveals that, as he developed thermodynamic concepts, he chose letters as algebraic conveniences *before* deriving significant words with which to characterize the physical meaning of those letters. Thus he did not search for a letter with which to represent energy or one with which to represent entropy. Rather, he had already defined U and S mathematically; he just didn't know by which descriptive names to call them.

U and Energy

Clausius's search for a brief, appropriate word or phrase to call U occupied at least 14 years (1850–1864), but one could argue that it may have taken the better part of 25 years (1850–1875). He first proposed U in the First Memoir of 1850 as part of a differential equation (*5*):

$$dQ = dU + A \cdot R\frac{a+t}{v}dv$$

where A is the conversion factor for "heat equivalent" of work, R is the gas constant, a is 273, t is temperature in centigrade, v is volume, dv is the change in volume, and dQ is "the infinitely small quantity of heat imparted to another body by the one which is undergoing modification" (*6*).[1] In 1850, Clausius's characterization of U was: "U comprises the *sensible* heat and the heat necessary for *interior* work, if such be present" (*5*). (All italics will be those of the original publications.) In 1854, in a section entitled "Theorem of the equivalence of heat and work", Clausius gave the equation $Q = U + A \cdot W$, where W is work, although in that section, he did not define U in a word or phrase (*7*).

In 1864, in the Appendix to his Sixth Memoir, Clausius notes that (*8*)

> The new conceptions which the mechanical theory of heat has introduced into science present themselves so frequently in all investigations on heat, that it has become desirable to possess simple and characteristic names for them.

He recognizes that U "is of great importance, inasmuch as it presents itself in the first fundamental equation of the mechanical theory of heat." At this time Clausius understands that his own description of U is precise but not concise:

> The definition I have given of this magnitude—*the sum of the increment of actually present heat, and of the heat consumed by interior work*—being for general purposes too long to serve as the name of the quantity, several more convenient ones have been proposed.

Clausius then considers the names for U that have been proposed by his contemporaries. He tersely dismisses Gustav Zeuner's "die innere Wärme des Körpers" (interior heat of the body) as misleading. And he rejects Gustav Kirchhoff's "Wirkungsfunction" (activity function) without any explanation other than that the expression of William Thomson (later given the title of Lord Kelvin), "the mechanical energy of a body in a given state," appears preferable to Kirchhoff's word. Then Clausius continues:

> The term *energy* employed by Thomson appears to me to be very appropriate; it has in its favour, too, the circumstance that it corresponds to the proposition of Rankine to include under the common name energy, both heat and everything that heat can replace.

However, Clausius still seems unwilling here to use the word "energy" alone, because he adds a qualifier: "I have no hesitation, therefore, in adopting for the quantity U, the expression *energy of the body*" (*8*).

Further (still in the Appendix to the Sixth Memoir), Clausius wants it clearly understood that U has two components:[2]

> Since the magnitude U consists of two parts which have frequently to be considered individually, it will not suffice to have an appropriate name for U merely, we must also be able to refer conveniently to these its constituent parts.

He calls the first part *the heat of the body*, or the *thermal content*[3] *of the body* (*Wärmeinhalt des Körpers*), and he devises a new word for that work which has been "measured according to the thermal unit" (as opposed to being measured by the mechanical unit). This word is "ergon" from the Greek word for "work", εργον (*8*). T. Archer Hirst, editor of Clausius's 1867 book, explains Clausius's reasoning in the following way (*9*):

> The author has used the German word *Werk*, which is almost synonymous with *Arbeit*, but he proposes the term *Ergon* as more suitable for introduction into other languages. The Greek word *εργον* is so closely allied to the English word work, that both are quite well suited to designate two magnitudes which are essentially the same, but measured according to different units.

At this point Clausius has a new set of terms with which to designate U (*8*):[4]

> Analogous to the expression *thermal content of the body*, we may introduce the expression *ergonal content of the body*. … Now the quantity U is the sum of the thermal content and ergonal content, so that in place of the word *energy*, we may use if we please the somewhat longer expression, *thermal and ergonal content*.

Thus, in 1864, Clausius appears to be torn between the single inclusive word "energy" and wordier but more specific alternatives.

In his well-known 1865 paper (Ninth Memoir in the 1867 book), recognized for introduction of the word *entropy*, Clausius seems to have become more comfortable with the single word *energy*, and in fact coins the word "entropy" specifically to parallel the word "energy", saying (10):

> I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.

One might think, on the basis of the 1865 paper, that the symbol U now had the name energy assured; however, in his 1879 English text (from the German of 1875), Clausius revisits all the previous labels, plus another one proposed by Zeuner in 1866, "Internal Work of the Body". Finally, in 1875, in a text written specifically for teaching students about thermodynamics, Clausius rejects all terms for U except that of (*4*)

> Energy, employed by Thomson … since the quantity under consideration corresponds exactly with that which is denoted by the same word in Mechanics. In what follows the quantity U will therefore be called *Energy* of the body.

No longer is "of the body" italicized. At last, U is Energy.

S and Entropy

In contrast to the long, multitreatise story of U and Energy, the story of S and Entropy is often credited to a single publication, the 1865 paper (*10*). However, Kim, in a paper entitled "Clausius's Endeavor to Generalize the Second Law of Thermodynamics, 1850–1865" (*11*), points out that Clausius was involved with interpreting the second law even as early as 1850. Certainly, an argument can be made that, at least since 1854, Clausius had been considering ways in which to represent in equations, symbols, and words the idea that "*Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time*" (*7*). Thus, in the Fourth Memoir of 1854 he introduces the equation (*7*):

$$N = \int \frac{dQ}{T}$$

where T is absolute temperature. This equation, of course, looks very similar to an equation for entropy given in the 1865 paper (*10*):

$$\int \frac{dQ}{T} = S - S_0$$

where S is entropy of the final condition of a body, and S_0 denotes entropy of the initial condition of the body. In 1862 Clausius had discussed the physical meaning of the above integral, invoking a new word, "which we will call the *disgregation* of the body, and by help of which we can define the effect of heat as simply *tending to increase the disgregation*" (*6*). Kim (*11*) draws attention to the influence of William Thomson upon Clausius. He particularly emphasized the role of Thomson's 1852 note entitled "On a Universal Tendency in Nature to the Dissipation of Mechanical Energy" (*12*) upon Clausius's notion of entropy. (Thomson used S in his brief paper to refer to temperature of steam.) In 1864, in order to explain a derivation of his own equation for the first law, Clausius uses the symbols S and dS to represent an arbitrary function of t and v, related to U—a function that is almost, but not quite, what he finally defines as entropy in his paper of the next year (*13*). (Even earlier, in 1858, in a paper that evolved into the mathematical introduction of his two books, Clausius used *ds* to be "an element of space" and *S* "the component in the direction of *ds* of the force acting on the point *p*"[*4*]. So, before 1865, he had used S for purposes other than entropy.)

In 1865 Clausius ultimately indicates the relationships between N of the 1854 paper (*7*) and S of the 1865 paper (*10*). One should note that in the 1865 paper, Clausius gives N the opposite sign from that which he gave it in the 1854 Fourth Memoir (previously, it was positive; now it is negative), and he calls it the *uncompensated transformation* (*10*), or *uncompensirte Verwandlung* (*14*). First, he presents his sign-reversed equation for N (*10*).

$$N = -\int \frac{dQ}{T}$$

Then, Clausius considers that, in a cyclical process, the initial-to-final passage of a body can be treated separately from the final-to-initial passage, with one integral for each passage. He represents the final-to-initial process (return) with a small r and offers the following equation (*10*):

$$N = -\int \frac{dQ}{T} - \int_r \frac{dQ}{T}$$

He points out that, because this r process is the return (or reverse) process, the "integral here is to be taken backwards", and he expresses the reverse process in terms of S (*10*).

$$\int_r \frac{dQ}{T} = S_0 - S$$

Finally, by substitution, he derives the equation relating N and S:

$$N = S - S_0 - \int \frac{dQ}{T}$$

Clausius calls S the *transformational content* of the body (*10*), or *Verwandlungsinhalt* (*14*). In the 1865 paper (*10*) he also introduces for S the word *entropy*, deriving it from the Greek τροπη (a turning, or a change), for which Clausius uses the German *Verwandlung* (*14*) and for which Clausius's translators generally use the English *transformation*, following the precedent of Thomson (*11*).

In addition, by writing the following equation (*10*),

$$\int \frac{dQ}{T} = \int \frac{dH}{T} + \int \frac{dZ}{T}$$

where H is the quantity of heat contained in a body, dH is the change of this quantity, and Z is "disgregation" (*6*), Clausius develops his idea of entropy as a function composed of two terms. Thus he further promotes the analogy between Energy and Entropy, U and S (10):

> Let us collect together, for the sake of reference, the magnitudes which have been discussed in the course of this Memoir. …They are six in number, and possess in common the property of being defined by the present condition of the body, without the necessity of our knowing the mode in which the body came into this condition: (1) the *thermal content*, (2) the *ergonal content*, (3) the sum of the two foregoing, that is to say the thermal and ergonal content, or the *energy*, (4) the *transformation-value of the thermal content*, (5) the *disgregation*, which is to be considered as the transformation-value of the existing arrangement of particles, (6) the sum of the last two, that is to say, the *transformational content*, or the *entropy*.

Thus, one can argue that it took Clausius 11 years (1854–1865) to symbolize and name an integral, 15 years (1850–1865) to encapsulate into a single word the physical meaning of the second law, and possibly 25 years (1850-1875) to do the same with the first law. But in 1865 he *did* have the words with which to conclude succinctly (10):

1. *The energy of the universe is constant.*
2. *The entropy of the universe tends to a maximum.*

And by 1875 (as translated in the 1879 English edition), he had sufficient confidence in his symbols to summarize "the two main principles of the Mechanical Theory of Heat by two very simple equations…dQ = dU + dW and dQ = TdS" (*4*).[5]

So, even though criticisms and rivalries[6] and "a long and bitter priority controversy" (*11*) greeted Clausius's work; even though Clausius's math engendered confusion (*15*); even though Max Planck's work was required to explain some of Clausius's statements (*11*); and even though some of Clausius's cleverly coined terms have receded into obscurity; still, more than 150 years after Clausius first published on "The Moving Force of Heat and the Laws Which May Be Deduced Therefrom" (*5*), every general chemistry student is introduced to Clausius's symbols, terms, and concepts. U is for Energy; S is for Entropy. Why? Because—after years of considering the physical significance of his own mathematical constructs of U and S—Clausius said so.

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Notes

1. In his 1864 Appendix B to the First Memoir, Clausius makes clear that the last term in this equation is equal to "Apdv", where p is pressure, "and since pdv denotes the exterior work done during the expansion dv, the last term … obviously represents the heat-equivalent of the exterior work" (*13*). (In current terminology one could say that this term represents "reversible pressure–volume work for an ideal gas".) In considering other characterizations of work, Clausius elsewhere used the term "Vis Viva" as follows: "*The Work done during any time by the forces acting upon a system is equal to the increase of the* Vis Viva *of the system during the same time*" (*4*). Clausius's particular use of this term is explained by a translator's note in the 1879 English edition of his book: "The *vis viva* of a particle is here defined as half the mass multiplied by the square of the velocity, and not the whole mass, as was formerly the custom" (*4*). (In current terminology one recognizes the formula for "kinetic energy.")

2. The "two components" are seen to be dQ and the last term of the differential equation in which Clausius first used U as dU.

3. Curiously, even though Clausius did not subscribe to the caloric theory of heat —in his 1879 book (*4*) he referred to "former times, when heat was considered to be a substance"—he still used the German word *Inhalt*, translated as "content", for heat.

4. The translator of the 1865 paper (*10*) used the term *ergonal content* instead of *work content*—based on Clausius's derived term *ergon* (*8*) even though in the original German paper Clausius had used *Werkinhalt* (*27*). The translator also chose *thermal content* instead of *heat content* for *Wärmeinhalt*.

5. With the first of these equations one should note that Clausius considered dW to have a positive sign, because he defined the term to represent work done *by* the system. Other authors, over the years, have considered dW to have a negative sign when they defined the term to represent work done *on* the system. With the second of these equations one should note that, although Clausius did not designate "reversibility" as it is designated today, he clearly states this condition in his classic 1865 paper (*10*). In that same paper, after defining entropy, he reasons that the entropy of the universe tends to a maximum, stating,

> The second fundamental theorem, in the form which I have given to it, asserts that all transformations occurring in nature may take place in a certain direction, which I have assumed as positive, by themselves, that is, without compensation; but that in the opposite, and consequently negative direction, they can only take place in such a manner as to be compensated by simultaneously occurring positive transformations. The application of this theorem to the Universe leads to a conclusion to which W. Thomson first drew attention.

6. For example, one 19th-century scientist called Clausius's work "nothing more than a rotten nut, which looks well from the outside, but in reality contains nothing whatever." Clausius quoted the above comment and responded to it in his 1879 book (*4*). In both that book and a paper on the history of thermodynamics (*16*), Clausius indicates conflict with others in the field.

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