

“Order-to-Disorder” for Entropy Change? Consider the Numbers!

Evguenii I. Kozliak*[†] and Frank L. Lambert[‡]

[†]Department of Chemistry, University of North Dakota, Grand Forks, ND 58202-9024, ekozliak@chem.und.edu
and [‡]Professor Emeritus, Occidental College, Department of Chemistry, Los Angeles, CA 90041,
flambert@att.net

Received June 8, 2004. Accepted November 16, 2004.

Abstract: Defining entropy increase as a change from order to disorder is misleading at best and incorrect at worst. Although Boltzmann described it this way in 1898, he did so innocently in the sense that he had never calculated the numerical values of W using $\Delta S = k_B \ln(W/W_0)$ (because this equation was not stated, k_B was not known, and W_0 was indeterminable before 1900–1912). Prior publications have demonstrated that the word “disorder” is misleading in describing entropy change. In this paper, convincing evidence is provided that no starting system above ca. 1 K can be said to be orderly so far as the distribution of its energy (the fundamental determinant of entropy) is concerned. This is supported by a simple calculation showing that any system with “a practical state of zero entropy” has an incomprehensibly large number of microstates.

Recently, Lambert showed examples of how beginning students can be seriously misled by the long-accepted definition of entropy as disorder [1a] and urged that entropy change be measured by the change in dispersal of motional molecular energy involving temperature [1b, 2]. This approach has been adopted by many authors for the new editions of their general chemistry texts [3]. Even students of moderate ability can visualize that violently energetic, speeding gas molecules will spontaneously move into an evacuated chamber or mix with another gas. Such processes, as well as heating a gas—whereby many more molecular speeds become possible at higher temperatures—can all be summarized as increases in entropy, examples of greater energy dispersal at constant or at changed temperature.

More able students can be led further to molecular thermodynamics—to the distribution of molecular energies on many discrete energy levels, to such distributions that are most probable on multiple energy levels, and to any one of those distributions of indistinguishable molecules being called a microstate. Finally, the fundamental nature of the dispersal of energy in a system is described by the system's total energy being in any one of a very large number of accessible microstates at any one instant; the larger the number, the greater is the dispersal of energy.

Many older texts, however, still use the historic but inadequate description of “entropy is disorder” referring this to Boltzmann who laid the foundation for the statistical approach to thermodynamics (for instance, the number of microstates can be calculated using the Boltzmann distribution of the number of particles among discrete energy levels). An intriguing question can, therefore, be posed: How could an original thinker like Boltzmann make such an egregious error? Addressing this issue is important in today's teaching because our students in general chemistry, if learning that entropy change is the transition from order to disorder, are returned to the science of Boltzmann in 1898.

Several articles have shown that the second part of this statement is incorrect, that is, that *disorder* is a needless and misleading insertion between entropy change and its

explanation via change in the number of accessible microstates for the energy of the system [1a, 2b, 3]. In this paper, we shall show that the first part of this old definition of entropy change is also misleading. According to modern calculations, there is no evident *order* in the almost unimaginable numbers of microstates in any system above ca. 1 K.

Although “entropy as the measure of the disorder (Unordnung)” had been stated occasionally before 1898 [4], in his influential *Lectures on Gas Theory, Part II*, published that year, Boltzmann was the first to strongly emphasize entropy change as “order to disorder” [5]; however, Sommerfeld, his successor as a professor of theoretical physics in Munich, stated that this was not based on calculations [6]. Boltzmann in 1898 could not do any calculations using his famous equation (eq 1) because its final form was given only in 1906 by Planck [6]:

$$S = k_B \ln W/W_0 = k_B \ln W \quad (1)$$

where W is the number of microstates available for the system at its temperature and $k_B = R/N_A$ is Boltzmann's constant, which was first stated and calculated by Planck in 1900 [7b].

In addition, Boltzmann could not have had a valid quantitative way to evaluate his “complexions” (equivalent to modern microstates) because the distribution of energy among discrete levels via quantum mechanics was not developed until long after his death. Finally, Boltzmann's “probabilities” (W) had no reference value, no W_0 , prior to the third law, whose basis ($W_0 = 1$) was established between 1906 and 1912 [7a]; therefore, Boltzmann's error in stating “entropy is disorder” was innocent. It is from his quasi-quantitative treatment, still far advanced for his time, that he concluded that a nonequilibrium system left to itself “rapidly proceeds to the disordered most probable state” and, therefore, was “initially in a very ordered—and therefore very improbable—state” [5a]. Note that some simple definition of entropy was essential at that time for opposing the Newtonian deterministic views on the nature of molecular motion. Thus, Boltzmann should be

given considerable credit for this metaphor in his time that is qualitatively correct in illustrating low-temperature, second-order phase transitions, which are rightfully called order-disorder transitions [8]. Also, in many special fields, experts use order and disorder informally as a rough estimate of entropy changes or differences in systems. Our principal concern here is the instruction of students in beginning and elementary physical chemistry courses.

Why can we not continue using this metaphor today in a fully general sense? Numbers make the difference. By multiplying both parts of eq 1 by Avogadro's number ($k_B N_A = R$), Pitzer indicated that for one mole of a substance at "a practical zero of entropy" ($S = 0.0001R = 0.00083 \text{ J mol}^{-1} \text{ K}^{-1}$), W is of the order of $10^{26,000,000,000,000,000,000}$, its number of microstates [9]. Obviously, this measure of the possible microstates, in any one of which the energy of the system might be at any instant (the basic determinant of entropy), at this temperature cannot be called order in human terms! Using the Debye formula $C_p = aT^3$, where $a = 233.78R/\Theta_0^3$ (Θ is the critical Debye temperature) [10] and integrating $dS = C_p dT$, one can calculate that this "practical zero" of entropy corresponds to 1 to 4 K. This means that any system above ca. 1 K has an unimaginable number of microstates; thus, order is a poor metaphor to describe the distribution of energy in any system prior to its change to disorder [11]. The only proper description of entropy change in molecular thermodynamics involves change in the dispersion of energy for a system as a function of temperature, and that is measured by the change in the number of accessible microstates.

Even though analogies and metaphors are indispensable in teaching chemistry and physics, the 100 years of persistence of wrongly defining entropy as disorder shows that both scientists and educators should be extremely careful in setting the limits of their applications.

Acknowledgment. The authors thank the Bush Foundation for partial funding within the Bush Scholarship program, and R. Baierlein for providing valuable references [4, 6]. The incisive critiques of the reviewers led to essential improvement of the manuscript.

References and Notes

- (a) Lambert, F. L. *J. Chem. Educ.* **2002**, *79*, 187–192; Disorder—A Cracked Crutch For Supporting Entropy Discussions. http://www.entropysite.com/cracked_crutch.html (accessed Jan 2005); (b) Lambert, F. L. *J. Chem. Educ.* **2002**, *79*, 1241–1246 and references therein.; Entropy is Simple, Qualitatively. http://www.entropysite.com/entropy_is_simple/index.html (accessed Jan 2005)
- Leff, H. S. *Am. J. Phys.* **1996**, *64*, 1261–1271; Laird, B. B. *J. Chem. Educ.* **1999**, *76*, 1388–1390; Styer, D. F. *Am. J. Phys.* **2000**, *68*, 1090–1096.
- News for April 2004. <http://www.entropysite.com/#news> (accessed Jan 2005).
- Baierlein, R.; Gearhart, C. A. *Am. J. Phys.* **2003**, *71*, 103.
- Boltzmann, L. *Lectures on Gas Theory*; Brush, S. G., Translator; University of California Press: Berkeley, CA, 1964; pp 442–443; Brush, S. G. *The Kind of Motion We Call Heat, A History of the Kinetic Theory of Gases in the 19th Century*; North-Holland Publishing Company: Amsterdam, 1976; p 625.
- Sommerfeld, A. *Thermodynamics and Statistical Mechanics. Lectures in Theoretical Physics*, Vol. 5.; Academic Press: New York, 1956; p 213.
- (a) Laidler, K. J. *The World of Physical Chemistry*; Oxford University Press: Oxford, 1995, pp 127–128; (b) Laidler, K. J. *The World of Physical Chemistry*; Oxford University Press: Oxford, 1995; pp 318–319.
- Mortimer, R. G. *Physical Chemistry*; Benjamin/Cummings: San Francisco, CA, 1993; p 185.
- Pitzer, K. S. *Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1995; p 67.
- Cetas, T. C.; Holste, J. C.; Swenson, C. A. *Phys. Rev.* **1969**, *182*, 679–685.
- The molar entropy change in solid ice to liquid water at 273.15 K is a change in the number of microstates from $10^{1,299,000,000,000,000,000,000}$ for ice to $10^{1,991,000,000,000,000,000,000}$ for water. (This result comes from eq 1 and S° entropies of 41.34 J K⁻¹ for ice and 63.34 J K⁻¹ for water at 273.15 K.)