Letters

Entropy and Constraint of Motion

I would like to make several observations supplementing and supporting the article by Frank Lambert on entropy as energy dissipation, since this is an approach that I have also used for many years when teaching a qualitative version of the entropy concept to students of general and introductory inorganic chemistry *(1)*.

I begin with the everyday interconversion of potential and kinetic energy as exemplified by either a bouncing ball or an oscillating pendulum:

$$\text{Potential Energy} \leftrightarrow \text{Kinetic Energy} \qquad (1)$$

According to classical mechanics, this interconversion is totally reversible and the ball should go on bouncing and the pendulum should oscillate forever. The reason this does not happen, of course, is because once the potential energy is converted into kinetic energy, the kinetic energy is increasingly dispersed, and it is the lower probability of this dispersed kinetic energy reconcentrating into the coordinated motion of the ball or pendulum as a whole that ultimately introduces a directionality into the process:

$$\text{Potential Energy} \rightarrow \text{Kinetic Energy} \rightarrow \text{Dispersed Kinetic Energy} \qquad (2)$$

The point here being that it is not just energy in general that is dissipated, but rather kinetic energy or energy of motion (whether translational, rotational, or vibrational).

This dissipation, dispersion, dilution, or spreading of the kinetic energy need not, however, necessarily correspond to a spreading in space or to a division among a greater number of moving particles, though these are possible mechanisms. A more general concept of dilution is required based on the fact that all kinetic energy is quantized, even in the case of macroscopic bodies in which the quantum spacings are small enough to approximate a continuum. It is the number of available quantum levels, or storage modes, to use Leff's terminology *(2)*, used to store a given amount of kinetic energy that determines its degree of dilution or dissipation, and this, in turn, depends on the masses of the moving particles (whether colloids, micelles, molecules, atoms, or even, on occasion, electrons and nucleons) and on the number of constraints on their motion. These constraints may correspond to:

1. Constraints on the number of independently moving particles; i.e., on whether the particles must move as an aggregate or can move separately.
2. Constraints on the direction of motion.
3. Constraints on the volume in which the motion is executed.

The relevance of the above factors in determining the spacing and degeneracy of the quantum levels is most easily demonstrated using the simple "particle in a box" model found in most introductory treatments of quantum mechanics. The fewer the number of constraints on a system's motion, the smaller the energy spacing between quantum levels and the greater the dilution or dissipation of the kinetic energy. In short, the fewer the constraints on how and where the component particles can move, the greater the entropy. The extent to which the mixing or disorder views of entropy, criticized by Lambert in earlier articles *(3, 4)*, are or are not misleading depends on the extent to which they do or do not parallel changes in these constraints *(5)*. This simple correlation between entropy and constraint of motion also allows one to rationalize the qualitative rules for predicting the net sign of the entropy change in simple chemical reactions given by Sanderson for use in introductory chemistry courses *(6)*.

The above approach is based on a fusion of the energy dissipation approach to the second law first pioneered by Lord Kelvin in 1852 *(7)* and widely used in late 19th-century British and American textbooks *(8)*, with the insights since provided by quantum mechanics and elementary statistical mechanics, as so aptly summarized in the introductory texts by Nash and Bent *(9, 10)*. Indeed, it is interesting to note that the first of these three ingredients formed the basis of the first English-language monograph to deal specifically with chemical thermodynamics, as distinct from the more limited field of thermochemistry. The book in question was published in 1885 by George Downing Liveing (1827–1924) of Cambridge University and bore the title, *Chemical Equilibrium the Result of the Dissipation of Energy (11)*.

Literature Cited

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The author replies:

William Jensen's presentation of entropy increase as solely due to kinetic energy dispersion is stimulating.

Searching for examples of kinetic energy dispersal causing increase in potential energy, I considered phase change. In fusion, for example, the enthalpy of fusion (KE) breaks or alters bonds in the solid to form liquid and thus the KE has become dispersed as potential energy (PE). However, this does not necessarily controvert Jensen's general point because this is a reversible surroundings–system equilibrium process.

Jensen's development of specific constraints that lead to more or less dispersion may indeed be more useful than my generality of "energy spontaneously disperses, if it is not hindered". I trust that in his use of them (and their application to Sanderson *(1)* is impressive), he does not allow them generally to support "disorder" as an explanation for entropy increase!

Literature Cited

1. Sanderson, R. T. *J. Chem. Educ.* **1964**, *41*, 13-22.

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