Removing the Mystery of Entropy and Thermodynamics – Part II

Harvey S. Leff, Reed College, Portland, OR[a,b]

Part II of this five-part series is focused on further clarification of entropy and thermodynamics. We emphasize that entropy is a state function with a numerical value for any substance in thermodynamic equilibrium with its surroundings. The interpretation of entropy as a "spreading function" is suggested by the Clausius algorithm. The Mayer-Joule principle is shown to be helpful in understanding entropy changes for pure work processes. Furthermore, the entropy change when a gas expands or is compressed, and when two gases are mixed, can be understood qualitatively in terms of spatial energy spreading. The question-answer format of Part I[1] is continued, enumerating main results in Key Points 2.1-2.6.

• What is the significance of entropy being a state function?

In Part I, we showed that the entropy of a room temperature solid can be calculated at standard temperature and pressure using heat capacity data from near absolute zero, denoted by $T = 0+$, to room temperature, $T_f = 298.15$ K. Specifically,

$$S(T_f) \equiv S^0 = \int_{0+}^{T_f} C_p(T)/T\, dT. \qquad (1)$$

One can also evaluate the corresponding enthalpy change $\Delta H = \Delta(U+PV) = \Delta U + P\Delta V$ because the first law of thermodynamics applied to an infinitesimal constant-pressure process leads to $đQ = dU + PdV \equiv dH \equiv C_P(T)\, dT$. Thus

$$\Delta H^0 = \int_{0+}^{T_f} C_p dT. \qquad (2)$$

Note that ΔH^0 is simply the energy needed to heat the material from $T = 0+$ to $T = 298.15$ K. In the following, we take advantage of the fact that for many elements and compounds, S^0 and ΔH^0 are tabulated, or can be calculated from specific heat capacity data. A plot of S^0 versus ΔH^0 is shown in Fig. 1 for dozens of room temperature solids.[2] These systems do not undergo phase changes, enabling direct use of Eqs. (1) and (2). Because $P\Delta V \ll \Delta U$ for solids, ΔH^0 is an excellent approximation for the stored internal energy ΔU at 298.15 K.

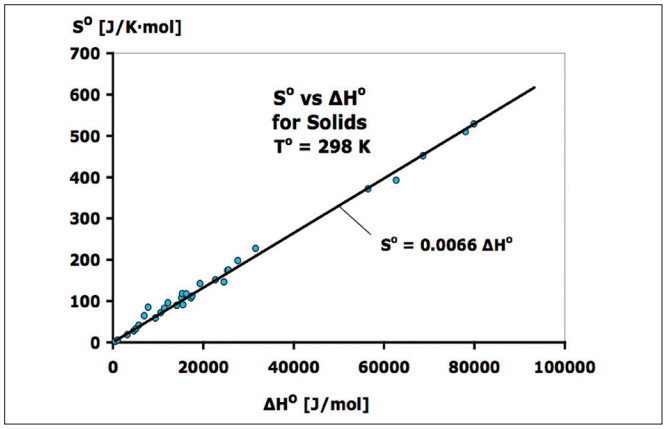


Fig. 1. Entropy of room temperature solids vs energy input from $T \approx 0$ to 298.15 K. Each circle represents a datum for a particular solid.

Although the linear correlation in Fig. 1 is quite striking, the two points to be emphasized here are: (i) the entropy value of each solid is dependent on the energy added to and stored by it, and (ii) the amount of energy needed for the heating process from $T = 0 + K$ to $T = 298.15$ K differs from solid to solid. This strong energy-entropy connection follows from the Clausius algorithm, $dS = đQ_{rev}/T$.

Key Point 2.1: *Entropy at temperature T can be determined numerically by heating from near absolute zero to T, using* $S = \int_{0+}^{T} đQ/T$. *S(T) is strongly correlated with the heating energy,* $\Delta H = \int_{0+}^{T} đQ$. *Most of this heating energy is stored as internal energy in room temperature solids, and the amount stored varies among materials. Notably, entropy is intimately related to both the amount of stored internal energy and how it is stored. Entropy and energy are inextricably linked.*

• How can the energy-spreading concept help us interpret entropy?

A heat process is driven by a temperature gradient. Energy moves from higher- to lower-temperature spatial regions, reducing that gradient. For example, if the two regions contain equal amounts of the *same* material, the final thermodynamic state will have half the energy in each region; i.e., energy spreads until it is distributed *equitably* over space, as illustrated in Fig. 2.

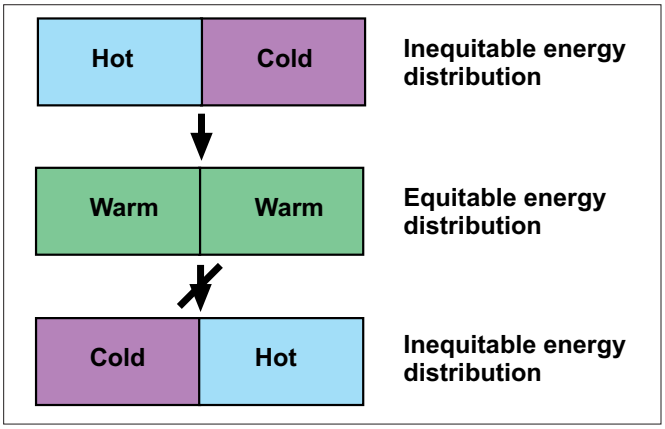


Fig. 2. When hot and cold objects interact thermally, the result is the middle pane, with both objects warm. The process does *not* continue further. For example, the temperatures of the initially hot and cold objects do not become reversed.

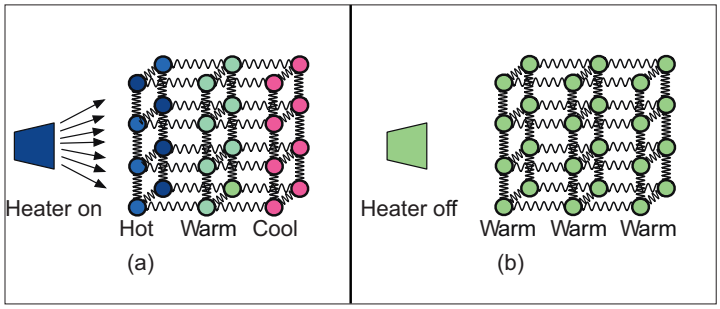


Fig. 3. As a homogeneous solid is heated from the left, energy moves rightward through it. If the heater is turned off shortly after heating began, the entire solid becomes uniformly warm. This assumes negligible energy exchange with the surroundings.

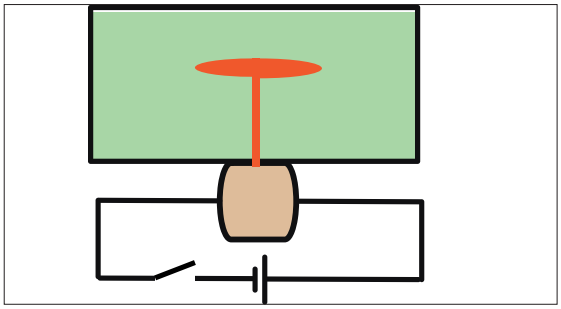


Fig. 4. When the switch is closed, an electrically powered rotating blade energizes water, raising its temperature and entropy via a pure-work process.

The figure indicates that the energy redistribution stops when the energy distribution is equitable (middle pane). Were it to go further (bottom pane), there would be *unspreading* of energy from an equitable to an inequitable distribution. We know from experience that nature does *not* behave this way. If the two objects are not identical—say, one is twice the size of the other—an equitable distribution is one where the larger system has double the energy of the smaller system. If the systems are made of different materials, the condition for an *equitable* distribution is more subtle, and that is discussed in Part V. [3]

To better understand the concept of spatial spreading for a heat process, Fig. 3(a) shows a heater just beginning to radiate increased energy toward a solid (only a small part of the solid is shown). The left-most atoms begin to jiggle and energy is transmitted subsequently to nearby atoms; i.e., energy spreads rightward. Once the heater is turned off, equilibration leads to a uniform energy distribution and temperature, as shown in Fig. 3(b).

Key Point 2.2: *In macroscopic systems, energy tends to spread spatially from less equitable to more equitable distributions. The spreading becomes maximal in the sense that if it proceeded further, the initially warmer and cooler regions would become reversed, which does not happen empirically. Spatial energy spreading parallels entropy increase and can be used to help "understand" when and why entropy increases. For an isolated system, maximal energy spreading corresponds to an equitable energy distribution and maximum total entropy.*

• How can the Mayer-Joule principle and Clausius algorithm help us understand entropy increase for pure-work processes?

Consider a pure-work process, where a stirrer whirls within a container of water, "working" the liquid, as depicted in Fig. 4. The stirrer's blades continually do work on small amounts of the water, increasing molecular kinetic energies near the spinning blades. The energized molecules subsequently move through the liquid, sharing energy with other molecules, ultimately spreading the added energy throughout the liquid's volume, leading to a uniform higher temperature.

Historically, Mayer and Joule showed (independently) that such a work process increases a system's internal energy by $\Delta U = W$, just as a pure constant-volume heat process with $Q = W$ does.[4] This increase occurs despite the fact that no external heat process is involved. Such a system does not "know" how its equilibrium state was reached; i.e., it has no memory. The Mayer-Joule principle is also known as the mechanical equivalent of heat.

To calculate the corresponding entropy increase, the Clausius algorithm, $dS = đQ_{rev}/T$, cannot be used directly for the *irreversible* process because the algorithm requires a *reversible* process. A vain attempt to apply it *incorrectly* gives $\Delta S = 0$ because $đQ = 0$ for the pure-work process. However, a fictitious reversible heat process connecting the given initial and final equilibrium thermodynamic states can be used to calculate the entropy change.

Key Point 2.3: *For both pure-work and pure-heat processes, spatial energy spreading occurs to reduce energy inequities. This spreading parallels entropy increase for the isolated system-plus-environment. If the initial and final states for the two processes are identical, the system's entropy change is also the same because entropy is a state function. This change can be calculated using a fictitious reversible process.*

• What does entropy have to do with heat engines?

The fact that entropy is often introduced in connection with heat engine cycles is an artifact of history. Rudolf Clausius introduced entropy using the concept of a cyclic process, and the reversible Carnot cycle was a useful tool of convenience. More generally, entropy is a property of any macroscopic matter with variable internal energy. Entropy can be introduced and understood without ever mentioning heat engines. Indeed, heat engines make up only a small subset of the physical systems for which entropy considerations are useful.

Prior to his introduction of entropy, Clausius introduced a concept he called *disgregation*, namely the tendency of particles to spread out in space. Although the term disgregation ultimately dropped off the physics radar screen, it is in fact

closely connected to thermodynamic entropy and provides a clue that entropy is a spreading function.

Key point 2.4: *Entropy is ubiquitous and is relevant to diverse physical processes, ranging from heating water to supernova explosions. Its relation to heat engines is purely historical. After Clausius discarded the disgregation concept, the spreading nature of entropy has been largely ignored. Yet an appreciation of spatial energy spreading can shed light on entropy and its changes.*

• Does energy spread when a gas expands?

Yes, it does. Each molecule of a gas possesses kinetic energy and that energy spreads into new spatial regions as a gas expands. Further, the molecules of gas can interact with one another when the gas density is sufficiently high, thereby bringing intermolecular potential energies into new spatial regions. In Fig. 5, this is illustrated with shading connoting regions containing kinetic and potential energies. ΔS can be calculated using a reversible path that connects the initial and final equilibrium thermodynamic states.

Key Point 2.4: *Expansion of a gas spreads energy from one spatial region to another, larger region. The concomitant entropy increase can be understood in terms of this energy spreading.*

• Does energy spread when two gases mix?

Yes, it does. The useful interpretation is that when two species of dilute gas mix, each species carries its energy to new spatial regions. It is well known that what has come to be called "entropy of mixing" is really an entropy of expansion,[5] and this meshes well with the spatial energy spreading interpretation. Typically, ΔS is calculated using a reversible process with two semipermeable membranes, each permeable exclusively to one of the species.

Figure 6(a) shows the mixing of two species and Fig. 6(b) shows the expansion of each species separately. For each species, the entropy change and extent of energy spreading in Figs. 6(a) and 6(b) is the same. The entropy change for Fig. 6(a) and the sum of entropy changes for 6(b) are equal as long as the interactions between the two gas species in Fig. 6(a) are negligible. If the two gas species interact significantly, such equality is not expected.[6] However, the important point is that spatial energy spreading of each species in Fig. 6(a) still correlates with entropy increase.

Key Point 2.5: *When two dilute (ideal) gases mix, each species spreads its energy spatially. The link between energy spreading and entropy change for each species is consistent with the observation that conventional "entropy of mixing" is really "entropy of expansion."*

• How do we know energy spreading occurs?

We've seen that spatial energy spreading can be associated with heat and work processes, free expansions, and the

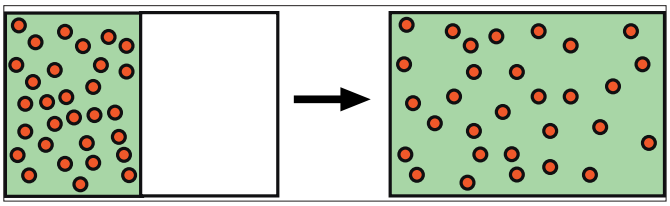


Fig. 5. Kinetic and potential energies, denoted by shading, spread from the left chamber of the container to the whole container as the gas expands.

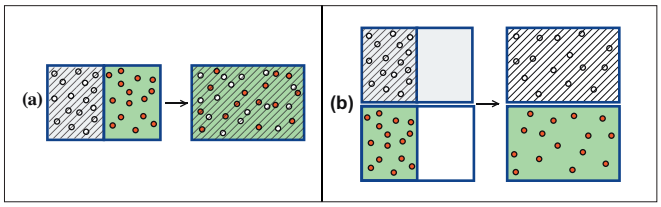


Fig. 6. (a) Mixing of two species of dilute (ideal) gas. The total system can be isolated or at constant temperature. The energy region of one species is crosshatched; that for the other is shaded. After expansion of each, the full volume contains energy from each species. This is an example of energy spreading. (b) Expansion of each species separately. For each species, as long as the gases are ideal, the total system's entropy change is the same for (a) and (b). The same is true for energy spreading.

mixing of gases. Notably for a quick, irreversible adiabatic expansion, spatial energy spreading through the larger volume dominates over the effect of internal energy decrease as work is done, and the entropy increases. Similarly for a quick irreversible, adiabatic compression, the spreading of energy *added* to the system by the external work dominates over the effect of reduced spreading because of the volume reduction and, again, the entropy increases. In the case of a hypothetical slow, reversible, adiabatic expansion, the added energy spreading from expansion is offset exactly by *decreased* internal energy as the expanding gas does work on a piston. This results in zero entropy change.

Key Point 2.6: *Increased energy spreading occurs when a system or a subsystem (a) gains internal energy at fixed volume and/or (b) expands, bringing its energy into a new spatial region. Both (a) and (b) lead to more accessible states and higher entropy. Competing effects, as in a reversible adiabatic volume change, can offset one another.*

Other aspects of entropy for thermodynamic processes and for thermodynamic equilibrium are discussed in Parts III-V.[3]

References

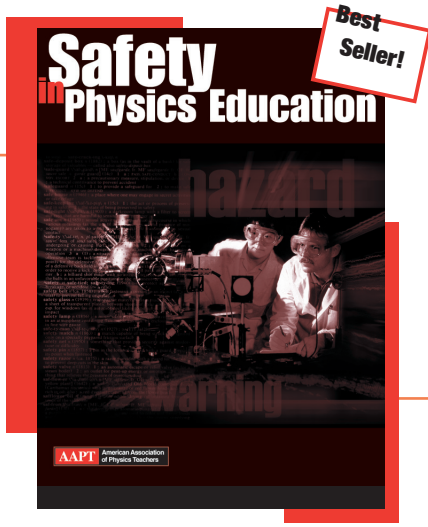
a. hsleff@csupomona.edu

b. Visiting Scholar, Reed College. Emeritus Professor, California State Polytechnic University, Pomona. Mailing address: 12705 SE River Rd, Apt 501S, Portland, OR 97222.

1. H. S. Leff, "Removing the mystery of entropy and thermodynamics–Part I," *Phys. Teach.* **50**, 28–31 (Jan. 2012).
2. F. L. Lambert and H. S. Leff, "The correlation of standard entropy with enthalpy supplied from 0 to 298.15 K," *J. Chem. Educ.* **86**, 94–98 (2009).

3. H.S. Leff, "Removing the mystery of entropy and thermodynamics – Parts III–V," to be published in *Phys. Teach.* **50** (2012).
4. R. Newburgh and H. S. Leff, "The Mayer-Joule principle: The foundation of the first law of thermodynamics," *Phys. Teach.* **49**, 484–487 (Nov. 2011).
5. A. Ben-Naim, "Is mixing a thermodynamic process?" *Am. J. Phys.* **55**, 725–733 (1987).
6. If two gas species, labeled 1 and 2 with separate entropies S_1 and S_2 are ideal, the molecules of the different species do not interact. Then the species are statistically independent, and the entropy of the mixed species $S_{1+2} = S_1+S_2$. If the two gases are not ideal, the species interact with one another, and are not statistically independent. In this case, the entropy change in Fig. 6(a) generally does not equal the sum of entropy changes in Fig. 6(b). Put differently, intermolecular forces can affect energy spreading and entropy change during expansion. See H.S. Leff, "Entropy changes in real gases and liquids," *Am. J. Phys.* **43** (12) 1098–1100 (1975).

Concerned about
the safety of your students?

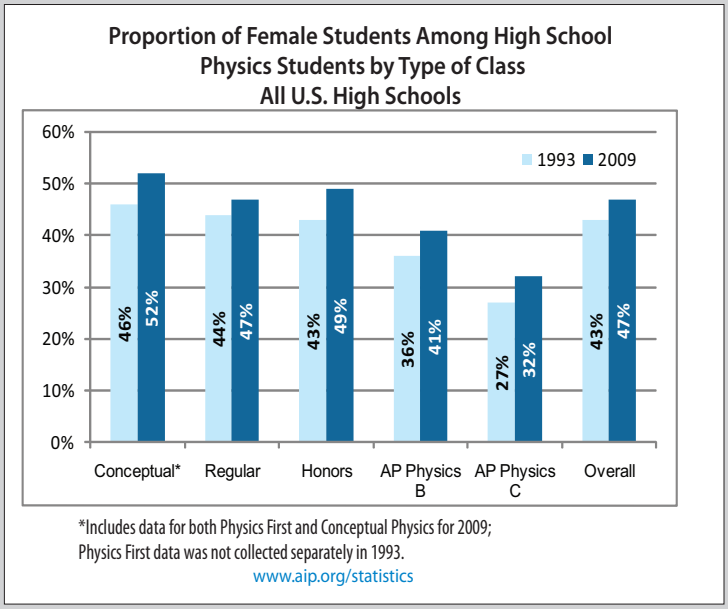


Promote safety awareness and encourage safe habits with this essential manual. Appropriate for elementary to advanced undergraduate laboratories.

Members: $21.95 • Nonmembers: $27.50
order online: www.aapt.org/store or **call:** 301-209-3333

Female representation by type of class

Last month we saw that females make up about 47% of all high school physics students in the United States. This number has changed little since 1997. This month, we take a closer look at female representation by type of class. We last collected class-specific data in 1993; that year, 43% of all high school physics students were female. However, female representation varies by type of class. In both 1993 and 2009, conceptual physics courses had the highest proportion of female students, and AP Physics C had the lowest. The good news is that female representation exhibits growth in all types of classes. In fact, the jump from 27% of the AP Physics C students being female in 1993 to 32% in 2009 represents an almost 20% growth in female representation; this compares favorably to the 9.3% growth overall.



In the March issue, we will begin our examination of teacher retention and turnover. If you have any questions or comments, please contact Susan White at swhite@aip.org. Susan is Research Manager in the Statistical Research Center at the American Institute of Physics and directs the high school survey.

DOI: 10.1119/1.3677282