Removing the Mystery of Entropy and Thermodynamics – Part III

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

In Part III of this five-part series of articles,[1,2] simple graphic properties of entropy are illustrated, offering a novel way to understand the principle of entropy increase. The Boltzmann entropy is introduced and shows that in thermal equilibrium, entropy can be related to the spreading of a system over accessible microstates. Finally, constant-temperature reservoirs are shown to be idealizations that are nevertheless useful. A question-answer format is continued here and Key Points 3.1–3.4 are enumerated.

Questions and answers

• *What does thermodynamics imply about the shape of the entropy function?* It is common to consider constant-volume systems and to express entropy S as a function of internal energy U and volume V. A straightforward thermodynamics argument (see appendix) shows that entropy is an increasing function of U for fixed volume V, and in the absence of a phase transition, the slope of S decreases with increasing U [see Fig. 1(a)]. That is, S is a concave downward function and any chord connecting two points on the S versus U curve lies *beneath* the curve (except at the end points).[3] The interpretation is that when added energy spreads spatially through a system, its entropy increases, but more slowly as U grows. A similar property and interpretation holds for entropy as a function of enthalpy H at constant pressure P, as shown in Fig. 1(b).

Recall from Part I that the energy input needed to heat a system infinitesimally from initial temperature T_i to final T_f at constant P is the enthalpy change dH. Notably, from the Clausius algorithm $dS = đQ_{rev}/T$ and the identities $dU = đQ_{rev}$ at constant V and $dH = đQ_{rev}$ at constant P, it follows that $dS = dU/T$ for constant V, and $dS = dH/T$ for constant P. Thus the slope of each curve in Fig. 1 is $1/T$ at each point.
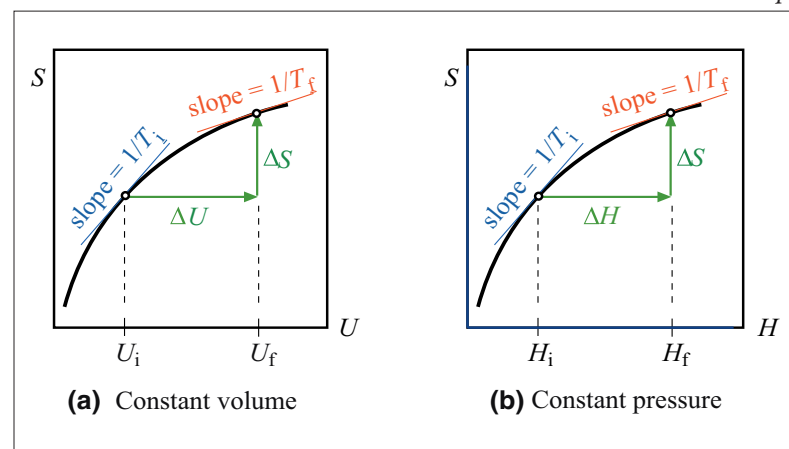
Key Point 3.1: *Entropy is an increasing, concave downward, function of internal energy at fixed volume—and an increasing, concave downward, function of enthalpy at fixed pressure. In either case, the slope of the curve at each point is the reciprocal of the temperature T, which shows graphically that as U or H increases, so does T.*

• *How can the shape of S help us understand the principle of entropy increase?* Figure 2 shows the S versus H curve for each of two *identical* systems (same type and size). When put in thermal contact, the lower-temperature system absorbs energy Q and goes from state $1 \rightarrow f$. Simultaneously the higher-temperature system loses energy Q, going from state $2 \rightarrow f$. This *irreversible* process will not follow the concave curve because it entails nonequilibrium intermediate states, but the initial (1, 2) and final (*f*) equilibrium states *are* on the curve. The graph requires only a single curve because the systems are identical in size and type. Because of the concavity property, the lower-temperature system clearly gains more entropy than the other system loses, and $\Delta S_1 + \Delta S_2 > 0$; i.e., the total entropy increases during temperature equilibration.

Key Point 3.2: *When energy is initially distributed inequitably among the two subsystems that subsequently interact by a heat process, the inequity is rectified by energy-spreading. The concave shape of S assures that the entropy increase of the lower-temperature system exceeds the entropy decrease for the higher-temperature system, so the spreading process is accompanied by an entropy increase of the total system. For two different type and/or size subsystems, two curves are needed, but the graph (not shown) still illustrates that the entropy increase of the initially lower-temperature subsystem dominates and the total entropy still increases. The equality holds only when the subsystems begin with the same temperature—i.e., energy is distributed equitably.*

• *What is the Boltzmann entropy and what can we learn from it?* The so-called Boltzmann entropy[4] for an isolated system with total energy E and volume V is

$$S(E) = k \ln W . \qquad (1)$$

Fig. 1. (a) Entropy S vs internal energy U at constant volume. (b) Entropy S vs enthalpy H at constant pressure. In (a) and (b) initial and final states are shown. The temperature inequality $T_f > T_i$ is evident because $T \equiv 1/slope.$
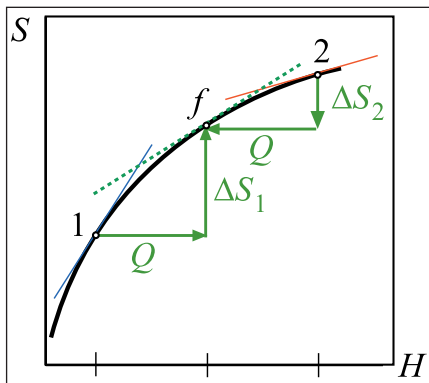
Fig. 2. Two identical systems have the same *S* vs *H* curve. One is initially in state 1 and the other in state 2. When put into thermal contact at constant pressure, equilibrium is ultimately reached, with each system in state *f*. Concavity assures that the second law of thermodynamics is satisfied; i.e., $\Delta S_1 + \Delta S_2 > 0$.

Here W is a function of E and volume V. It is related to the "number of complexions" using a classical description,[5,6] and to the number of accessible microstates for a quantum description. It is typically of order 10^{10^n} (with $n \approx 18 - 21$).[7] For an isolated quantum system, W is the number of quantum states accessible to the system when its total energy is either precisely E or is in an energy interval $\delta E \ll E$ containing E. Because no state is known to be favored over any other state, it is common to *assume* that the W states are equally likely, each being occupied with probability $1/W$. This is called the principle of *equal a priori* probabilities (discussed in Part V, in connection with uncertainty or, equivalently, missing information[8]).

Equation (1) is interesting for at least two reasons. First, its units come solely from the pre-factor, Boltzmann's constant, $k = 1.38 \times 10^{-23} JK^{-1}$.[9] Second, all the physics is contained in the dimensionless quantity W, which is a property of the quantum energy-level spectrum implied by the intermolecular forces, which differ from system to system. Note that this spectrum is for the total system and *not* individual molecules.

Using quantum terminology, if the system is isolated and E is assumed to be known exactly, there are W *degenerate* states—i.e., independent quantum states with the *same* energy. The quantum state of the system is a linear superposition of these degenerate quantum states. Only if a measurement were possible (alas, it is not) could we know that a specific state is occupied. In a sense, the system state is "spread over" all the degenerate states. This suggests that in an equilibrium state, entropy reflects the spread of the system over the possible quantum microstates. Although different from *spatial* spreading in a thermodynamic process, this suggests that entropy is a "spreading function," not only for processes, but also (albeit differently) for equilibrium states.

For actual (nonideal) systems there is never *total* isolation from the surroundings and the energy E is known only to be in a "small" energy interval $\delta E \ll E$. Equation (1) still holds,[10] and energy exchanges with the environment cause the system's occupied state to spread over accessible states from moment to moment. Thus when the system is in thermody-

namic equilibrium with its environment, that equilibrium is dynamic on a microscopic scale and $S(E)$ can be viewed as a *temporal* spreading function.[11,12] The system's time-averaged energy, E, is identified with the internal energy U, so $S = S(U)$. Actually, because the allowed energies typically depend on the system volume, $S = S(U, V)$.

For the system plus an assumed constant temperature reservoir, the number of accessible microstates is the product $W_{tot} = W(E)W_{res}(E_{res})$, where $E_{res} \gg E$ is the reservoir's energy and W_{res} is the number of accessible states of the reservoir. This is because each of the $W(E)$ system states can occur with any of the $W_{res}(E_{res})$ states, and *vice versa*. The equilibrium value of the system energy E is that for which W_{tot} is maximum under the condition that the total energy $E + E_{res}$ = *constant*.

Key Point 3.3: *The Boltzmann entropy, Eq. (1), is a measure of the number of independent microstates accessible to the system. When a system shares energy with its environment, its energy undergoes small fluctuations; i.e., there is temporal spreading over microstates. The maximum possible extent of this spreading in the system plus environment leads to equilibrium. In a process, spatial spreading of energy occurs so as to reach the macrostate with the maximum number of microstates for the system plus surroundings. Subsequently, temporal spreading occurs over these microstates.*

• *What is a constant-temperature "reservoir" and what can we say about its entropy?*

In thermodynamics, we commonly treat a system's surroundings as a constant-temperature reservoir. It is assumed that finite energy exchanges do not alter its temperature. In addition, we assume that the reservoir responds infinitely quickly (zero relaxation time) to energy changes, never going out of thermodynamic equilibrium.

Such a reservoir is especially helpful for a constant-temperature, constant-pressure process. However because $S(H)$ must be a concave function of H, as in Figs. 1 and 2, it is clear that a constant-temperature reservoir is a physical impossibility because a chord on the S versus H curve would not lie beneath the curve, but rather *on* it, violating concavity.[13] Indeed any real system, no matter how large, has a finite heat capacity, and an energy exchange will alter its temperature somewhat. For a sufficiently large system, a segment of the S versus H curve can appear nearly linear and the reservoir's temperature changes little during a thermodynamic process. Figure 3(a) shows the S versus H curves for a normal-sized system, a larger system, and, finally, an ideal reservoir for which S is a linear function of the enthalpy H.

Figure 3(b) shows a finite system with a concave spreading function initially in state A with temperature T_A, the reciprocal of the slope. It then interacts thermally with an ideal reservoir of higher temperature $T_{res} > T_A$, and gains sufficient energy to attain thermodynamic state B with temperature $T_B = T_{res}$. It is clear graphically that $\Delta S_{sys} + \Delta S_{res} > 0$, so the second law of thermodynamics *is* satisfied. Furthermore the
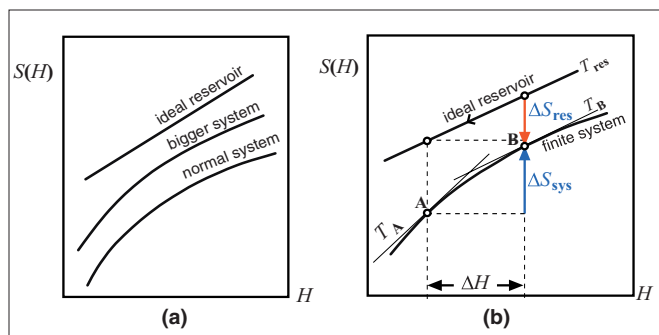
Fig. 3. (a) Curves of entropy vs enthalpy at constant pressure. The enthalpy *H* for successively larger systems, approaches linearity. (b) A linear *S(H)* curve for a so-called *ideal* reservoir, and concave downward *S(H)* for a typical finite system, initially in thermodynamic state *A*. It is then put in contact with the reservoir as described in the text. As before, the slope at each point is 1/*T*. Note that the ideal reservoir does not require infinite enthalpy or entropy values. Also, in (a) and (b), the *H* axis is at *S* > 0.

graph shows that $\Delta S_{res} = slope \times \Delta H = \Delta H / T_{res}$. If the ideal reservoir instead had a lower temperature than the finite system's initial temperature, a similar argument shows that the second law of thermodynamics is again satisfied because of the concave downward property of the finite system's entropy.

Key Point 3.4: *A constant temperature reservoir is an idealized system whose entropy versus energy (at constant volume) or versus enthalpy (at constant pressure) curves are linear. No such system actually exists, but the S versus U (or H) graphs for a very large real system can be well approximated as linear over limited internal energy (or enthalpy) intervals. When a heat process through a finite temperature difference occurs between a system and reservoir, the total entropy of the system plus reservoir increases.*

Reversibility, irreversibility, equity, and interpretations of entropy are discussed in Parts IV-V.[14,8]

Appendix

Apply the first law of thermodynamics to a reversible process, using Eq. (2) of Part I and the work expression $dW = PdV$ to obtain $dU = dQ - dW = TdS - PdV$. Holding *V* constant, this implies $dS = dU/T$ and thus

$$\left(\frac{dS}{dU}\right)_V = \frac{1}{T} > 0 \ \text{ and } \ \left(\frac{d^2S}{dU^2}\right)_V = -\frac{1}{T^2(dU/dT)_V} \leq 0. \quad (2)$$

The derivatives are *partial* derivatives holding the volume fixed.[15] The inequalities follow assuming $T > 0$ and $(dU/dT)_V = C_V > 0$ (positive constant-volume heat capacity) for $T > 0$. The equality holds only for the exceptional case of a first-order phase transition during which "heating" generates a change of state rather than a temperature increase. For example, during a liquid-vapor transition, $S(U) \propto U$, which violates concavity.

Because it is common to make laboratory measurements under (nearly) constant atmospheric pressure, it is convenient to consider entropy as a function of (H, P). If we rewrite the

first law as $dU + PdV = TdS$, add VdP to both sides, and use the denition of enthalpy $H \equiv U + PV$, we obtain $dH = TdS + VdP$. This implies $S = S(H, P)$. An argument similar to that above then shows that

$$\left(\frac{dS}{dH}\right)_P = \frac{1}{T} > 0 \ \text{ and } \ \left(\frac{d^2S}{dH^2}\right)_P = -\frac{1}{T^2(dH/dT)_P} < 0. \quad (3)$$

The second inequality holds if $(dH/dT)_P \equiv C_P > 0$ (positive constant-pressure heat capacity) for $T > 0$.

References

a. hsle@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. H. S. Leff, "Removing the mystery of entropy and thermodynamics – Part II," *Phys. Teach.* **50**, 87–90 (Feb. 2012).

3. Strictly speaking, this is true for typical systems observed on Earth, but fails for systems bound by long-range forces—e.g., stars.

4. This is one of the most famous equations in all of physics and appears on Boltzmann's tombstone at the Central Cemetery in Vienna. Historically the so-called "Boltzmann constant" *k* was actually introduced and first evaluated by Max Planck; it was not used explicitly by Boltzmann.

5. The "number of complexions" is the number of ways energy can be distributed over the discrete molecular energy cells that Boltzmann constructed. This bears an uncanny resemblance to quantized energies despite the fact that Boltzmann's work preceded quantum theory.

6. Boltzmann related *W* to the system's probability distribution; see R. Swendsen, "How physicists disagree on the meaning of entropy," *Am. J. Phys.* **79**, 342–348 (April 2011).

7. H. S. Leff , "What if entropy were dimensionless?," *Am. J. Phys.* **67**, 1114–1122 (Dec. 1999).

8. H.S. Leff, "Removing the mystery of entropy and thermodynamics – Part V," to be published in Phys. Teach. 50 (May 2012).

9. Boltzmann's constant $k = R/N_A$, where *R* is the universal gas constant and N_A is Avogadro's number. For an *N*-particle system with $n = N/N_A$ moles, $Nk = nR$. Typically $\ln W \propto N$, and the total entropy is proportional to *Nk* or, equivalently, *nR*.

10. This follows from the equivalence of the microcanonical and canonical ensembles of statistical mechanics. See W. T. Grandy, Jr., *Entropy and the Time Evolution of Macroscopic Systems*– International Series of Monographs on Physics (Oxford Univ. Press, Oxford, 2008), pp. 55–56.

11. H. S. Leff, "Thermodynamic entropy: The spreading and sharing of energy," *Am. J. Phys.* **64**, 1261–1271 (Oct. 1996).

12. H. S. Leff, "Entropy, its language and interpretation," *Found. Phys.* **37**, 1744–1766 (2007).

13. H. S. Leff, "The Boltzmann reservoir: A model constant-temperature environment," *Am. J. Phys.* **68**, 521–524 (2000).

14. H. S. Leff, "Removing the mystery of entropy and thermodynamics – Part IV," to be published in *Phys. Teach.* **50** (April 2012.)

15. The derivative $(dS/dU)_V$ is commonly written using partial derivative notation, $(\partial S/\partial U)_V$.