

Comments by Milivoje M. Kostic (**MK>**) Regarding “**Removing the Mystery of Entropy and Thermodynamics – Part I through V**” by Harvey S. Leff, *Phys. Teach.* **50** (Jan. p.28-31, Feb. p.87-90, Mar. p.170-172, Apr. p.215-217, May p.274-276) 2012.

[Articles Attached/Follows after the Comments]

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Regarding the Article statement on p. 88: “• 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.”

MK> The above (also related “**Key point 2.4:** Entropy is ubiquitous and is relevant to diverse physical processes ... Its relation to heat engines is purely historical.”) and the latter is oversimplification to say the least and factually inappropriate (Kostic 2008 & 2011).

In fact, the entropy has been deduced (and thus defined and proven) to be a property, i.e., not being a function of a process path, based on Carnot’s reasoning that all reversible cycles, for given temperature reservoirs, must be maximally-possible and equally efficient (that resulted in Kelvin’s definition of absolute temperature $T=T_{ref}*(Q/Q_{ref})_{rev}$, Clausius’ (in)equality and $dS=dQ_{rev}/T$). Furthermore, the reasoning and thus proof, that no cycle could be more efficient than the reversible Carnot cycle, also proves that no heat engine or any other device could “destroy” entropy by converting heat to mechanical (or other) work, thus a proof that entropy could not be destroyed but only irreversibly generated by dissipation of other energy forms to thermal energy. The cycle could not destroy, but only generate heat from work potential and thus generate entropy. Without dissipative heat generation the efficiency would be maximum and entropy conserved, but never destroyed (the latter would imply higher efficiency than Carnot’s)! During reversible heat transfer and conversion to work, entropy is transferred and conserved, and during irreversible dissipation of all energy types (work potential) to heat, entropy is always generated locally, thus at any space and time scale, i.e., increased over-all without any exception. Otherwise, considering reversible equivalency, non-equilibrium would be generated from within equilibrium alone or increased over-all against forced tendency towards equilibrium.

Therefore, the Carnot heat engine cycle concept is not just “a useful tool of convenience,” “purely historical,” nor “artifact of history,” but fundamentally-critical ingenious reasoning, necessary for establishment of the Thermodynamic absolute temperature, Entropy, and the Second Law of Thermodynamics.

Additional Note:

The entropy within interacting systems will always increase due to local irreversibility in closed and/or open systems and accumulate (integrate over space and time), thus contributing to entropy increase of the universe. Without local, irreversible entropy generation (production), the entropy would be conserved in reversible processes, but it could never be destroyed! Entropy can be locally transferred with heat (out or in), thus decreased (but not destroyed!) or increased (due to heat transfer out or in, cooling or heating, respectively), and generated (produced, thus increased) due to irreversibility of any kind, i.e., dissipation of any work potential via heat to thermal energy, including dissipation of the Carnot thermal work potential during heat transfer or mechanical throttling (or unrestricted expansion), or similar. The ideal Carnot cycle provides for the both, evaluation of maximum reversible work extracted from heat at high temperature during reversible heat transfer to lower temperature, while conserving entropy. If that work is irreversibly dissipated (converted) to heat, the entropy will be generated but then heat will be conserved (sum of irreversible and reversible heat) resulting in a process like in heat exchanges, where the “caloric” heat is conserved, since there is no conversion of heat to work (no work interaction), nor conversion of any other energy type to heat (no heat generation). The Carnot cycle resolves the subtle issues due to coupling of thermal and mechanical energy, by decoupling the maximum-possible work and reversible heat transfer, see (Kostic 2004, 2008, 2011)

There are subtle implications of the ingenious Carnot's reasoning of reversible processes and cycles as is described in my publications (Kostic 2008 and 2011): "No wonder that Sadi Carnot's 'Réflexions sur la puissance motrice du feu {Reflections on the Motive Power of Fire [1]},' original version published in 1824, was not noticed at his time, when his ingenious reasoning of ideal heat engine reversible cycles is not fully recognized, and may be truly comprehended by a few, even nowadays.

- Kostic, M. (2011), [Revisiting The Second Law of Energy Degradation and Entropy Generation: From Sadi Carnot's Ingenious Reasoning to Holistic Generalization](#), >[Abstract](#), [THE SECOND LAW OF THERMODYNAMICS: STATUS AND CHALLENGES](#) Symposium; University of San Diego, San Diego, CA, June 12-16, 2011. ISBN: 978-0-7354-0985-9; Citation: AIP Conf. Proc. 1411, 327 (2011); doi: 10.1063/1.3665247. [FULL paper](#), [\(2ndLaw\)](#)
- Kostic, M. (2008), [Sadi Carnot's Ingenious Reasoning of Ideal Heat-Engine Reversible Cycles](#), ([PDF](#) or [PDFw](#)) Proceedings of the [4th IASME/WSEAS International Conference on ENERGY, ENVIRONMENT, ECOSYSTEMS and SUSTAINABLE DEVELOPMENT \(EEESD'08\)](#), Algarve, Portugal, June 11-13, 2008. In NEW ASPECTS OF ENERGY, ENVIRONMENT, ECOSYSTEMS and SUSTAINABLE DEVELOPMENT (Editors: T. Panagopoulos, T. Noronha Vaz , M. D. Carlos Antunes), [ISBN: 978-960-6766-71-8](#); [ISSN: 1790-5095](#), p.159-166, WSEAS Press, 2008.
- Kostic, M. (2004), [Irreversibility and Reversible Heat Transfer: The Quest and Nature of Energy and Entropy](#), IMECE2004, ASME Proceedings, ASME, New York, 2004

MK> There are many puzzling issues surrounding Thermodynamics, including subtle definitions and ambiguous meaning of very fundamental concepts. The theory of classical Thermodynamics was originally based on thermal and mechanical energy transformations, but it has been expended to all other types of work and heat interactions and thus effectively has resulted in Thermo(multi)dynamics, the general energy science, considered by some to be "the Mother of all sciences."

Thermodynamics is characterized by a so-called "phenomenological" approach, formulated on empirical, but logical and universal principles that deny the possibility of various kinds of perpetual motions. The supremacy of phenomenological (classical) Thermodynamics lies in the fact that it avoids speculative assumptions about the microscopic constitution and complex dynamics of the involved material systems. The physical systems are regarded as "black boxes" and all specific Thermodynamic quantities and their general properties are derived by means of these principal laws. This is the approach to the theory taken by the pioneers: Carnot [1], Clausius, Kelvin, and Planck, and with some exceptions by Gibbs.

[1] Sadi Carnot, Reflections on the Motive Power of Heat, English translation by R.H. Thurston (1824) <http://www.thermohistory.com/carnot.pdf> or <http://www.history.rochester.edu/steam/carnot/1943/>

Some other comments:

On p.30 above Eq.(3) "When a system is heated very slowly and reversibly ..." is also true if a system is heated fast and irreversibly ("caloric effect"), except that a source entropy at higher than necessary temperature will reduce less, thus resulting into entropy generation (as you have rightfully stated in "**Key Point 1.2:** State functions in thermodynamics describe equilibrium thermodynamic properties. They do not depend on how equilibrium was reached; i.e., they have no path or history dependence.").

MK> Therefore, the entropy is related to internal thermal energy (U_{th}) and absolute temperature T , but not to other types of internal energies unless and after they are converted into thermal energy. Heat is defined as thermal energy transfer (in time) as is Work defined as transfer of other energy types (in time), or as rightfully stated in "**Key point 1.3:** Heat and work are processes... It is important to understand that Q and W are transient process energies and are not stored."

MK> Furthermore, the "work potential" is dissipated into thermal energy (via heat), known as "heat generation" which results in thermal energy generation and thus in entropy generation, since the entropy is "stored integral thermal energy per absolute temperature" as expressed in Eq.(3) on p.30 for a direct

heating of a solid system (without any other energy interactions: $v \& P = \text{constants}$ for incompressible solid). It is irrelevant how the simple system is heated: reversibly and slowly, at infinitesimal temperature difference by the variable temperature heat source or infinitely many temperature sources, or irreversibly by dissipation of other energy types via generated heat to thermal energy.

Key Point 1.3:

MK> 'Spreading' of energy is too general and ambiguous, sometimes not related to entropy (like isentropic expansion), and is done for many (if not all) other properties, things are redistributed in space (occupied by a material system) over time. It is important to state that it is 'spreading' of thermal energy per absolute temperature as explicitly defined by Clausius correlation based on the Carnot's reasoning. Only if and after other energy types convert (i.e., dissipate via heat) into thermal energy, it will contribute to entropy generation, in addition to reversible heat (and thus entropy) transfer (or redistribution). If other energy types are reversibly stored and "spread" within the system, like electrical charge, elastic deformation, mechanical lifting of weight, etc., it will not affect entropy unless it is involving thermal energy.

Key Point 2.1:

MK> Again, as stated above, the reference to internal energy is in general inaccurate but should be internal thermal energy. Since in addition to mechanical motion bulk energy, many other types of energy, not directly related to entropy, are internally stored in a system (with zero bulk momentum), like nuclear, chemical, electrical, magnetic, elastic, etc.

NOTE: in the follow-up email-correspondence with the Author (Harvey Leff) we further disagreed about the "Thermal energy" as a fundamental concept, namely:

From: Prof. M.Kostic profmkostic@gmail.com Date: Sun, Feb 10, 2013 at 10:06 AM
Subject: Re: Comments regarding Key Points in "Removing the Mystery of Entropy and Thermodynamics"
To: "Harvey S. Leff" hsleff@csupomona.edu

Dear Harvey,

Since we do not agree about **Thermal energy**, we may stop debate with your (HL) statement: "*I (HL) will simply reiterate here that your use of "thermal energy" is inconsistent with the equations of thermodynamics. There is NO defined thermal energy. If it is not defined, why use it? ... There is only internal energy U (a stored quantity) and the energy transfers, heat Q and work W. Of course there are also the Gibbs and Helmholtz functions and enthalpy, but no "thermal energy."*"

MK> However, for my record I (MK) will make this statement: The "Thermal energy" is as real as it could be (the foundation of Thermodynamics and Heat Transfer) and the most "universal and ultimate" form of energy, since all other energy types always and ultimately convert to, YES, the **thermal energy**, whose transfer is known as heat, both related to temperature and entropy:

$T(\text{boundary surface}) * S(\text{rate}) * dt = T(\text{system}) * dS(\text{system}) = dU_{th}$ (when other work-energy interactions are absent).

Google search for < [thermal energy](#) > is showing about 22,800,000 results (more than 22 Million hits! on 9 Feb. 2013 at 18:23). We cannot "close our eyes" just because we are not quite sure about precise definition. For an incompressible substance you used to define entropy, Eq.(3): $S = \int (cdT/T)$, the thermal energy would be $U_{th} = \int (cdT) = \int (TdS)$ since all work interactions are negligible. The "thermodynamic internal energy" data tabulated as function of temperature and pressure (or entropy) in fact represent "thermal energy" since the all other internal energy types (nuclear, chemical, etc.) are fixed (no other than thermo-mechanical interactions), and for convenience taken as zero reference value. The coupling of thermal and mechanical energy is present with compressible gasses ($Pv = f(T,S)$), are "fixed" with enthalpy ($h = u + Pv$) and the thermal energy Carnot work potential. I am trying to further resolve that coupling (and this motivating discussion is helping clarify some issues) to be elaborated in my in-progress manuscripts.

All Best – Milivoje

MK> (on 6Feb2013)> I like to follow-up on Thermal Energy concept (*U_{th}*) as part of (total) Thermodynamic Internal Energy (*U*) even if it may not be strictly defined. It may be ambiguous since it is coupled with internal mechanical (elastic) energy within simple compressible systems and possibly with other energy types in more complex systems, since in different interactions, different energy types could be converted to each other. Yours and others comments may help to differentiate thermal energy and possibly define it better. Below are my thoughts and your feed-back will be appreciated. Thanks always.

As I have stated, the thermal energy is part of internal energy as a system property, and it is not energy transferred through boundary (that would be process heat transfer). However, energy transferred through the boundary will change internal energy and may or may not change the thermal energy. For example, ideal (reversible) charging of a capacitor with electrical work will increase the internal electrical-potential energy but not thermal energy, or winding an ideal elastic spring will increase the spring's internal (mechanical-elastic) energy but not thermal energy. I meant, $dU(\text{thermal})=TdS$ if no any other work interactions, thus isohoric process ($V=\text{constant}$) in simple compressible system with thermo-mechanical interactions only (no chemical, electrical, nuclear, etc. interactions). The thermal energy change (as property change $dU(\text{thermal})$) on the left-side is caused by heat transfer TdS on the right-side if $V=\text{constant}$). In latter case $(TdS)_{\text{boundary}}=(TdS)_{\text{system}}$, regardless if reversible or irreversible boundary heat transfer (please comment if objecting!), but

$$dS(\text{system})=dS(\text{boundary}) * T(\text{boundary})/T(\text{system}).$$

Energy transfer through boundary (imaginary surface) will change internal energy within the material system, but interactions within the system volume may cause the conversion of one energy type to another and change other properties. The boundary heat transfer (rate) is equal $T(\text{boundary}) * S(\text{rate})$ and we cannot state if it is reversible or not, since irreversibility is a dissipative process within a system volume (not boundary A), so it will happen "along" some material thickness dX (thus system volume $dV=A dX$) if there is a corresponding potential gradient $dPot/dX$ etc.

For example, if we transfer 1 kJ of heat to an ideal gas at constant volume (*isohoric* process) its internal energy will change for 1 kJ to certain temperature and pressure with increase of entropy, BUT if we isentropically add 1 kJ of work (instead of heat) the internal energy will increase for the same 1 kJ and to the same temperature (if ideal gas specific heat is constant: $u=C_v T$), but to the higher pressure (thus another state with the same internal energy but different entropy and different values of thermal and elastic mechanical energies (which are coupled) than in the first case. I am trying to distinguish "*Thermal energy*" as part of total "*Internal energy*" and decouple it from mechanical elastic energy and any other type of internal energies, like chemical, nuclear, etc. Transfer of that "Thermal energy" would be "Heat transfer" the way "Work transfer" is transfer of any other than thermal energy type. However, different types of energy may be coupled and convert to each other like during electrical, chemical or nuclear reactions (i.e., interaction).

I have also stated "that during reversible heat transfer from higher to lower temperature there is Carnot work potential W_c to be extracted" and less heat will be reversibly transferred to lower temperature: $(Q_{\text{low}}=Q_{\text{high}}-W_c) < Q_{\text{high}}$. However, if Carnot work potential W_c is not extracted, then it will irreversibly dissipate to heat at lower temperature, $Q_{\text{diss}}=W_c$, so we will have $Q_{\text{low}}+Q_{\text{diss}}=Q_{\text{high}}$, thus thermal energy (some call it heat) will be conserved, like heat during common heat transfer with negligible work interactions of any kind. I want to call such processes "*caloric processes*," where heat is conserved. This is another view to reversible heat transfer concept and its irreversibility if (Carnot) work potential is not utilized, see my paper at > <http://www.kostic.niu.edu/Kostic-Energy-Entropy-Irreversibility.pdf> .

Key Point 2.3, 3.4, and 3.6:

MK> If a system (while expending without external boundary resistance) is internally and reversibly converting thermal energy to work and winding an elastic spring, for example (or charging an internal capacitor, or similar), the internal energy will be the same (but not thermal internal energy), so the stated is only correct if the whole work potential is irreversibly converted (dissipated via heat) to thermal energy, but not in general (for complex systems, for example). If all conversions are reversible, there will be no entropy generation (entropy will be conserved) even though the system volumetrically spread (expend) over larger volume but “shrink” internally within other energy type spaces. The “spreading” or “shrinking” may be in (overlapping) multi-dimensional energy spaces, aside and beyond, 3-D volumetric space of simple compressible thermo-mechanical systems.

The reference to energy should be replaced with thermal energy in most of the other statements and the Key Points.

Key Point 4.1:

“Reversible processes do not exist in nature, but are a useful limiting case for envisaged infinitely slow processes ...” **MK>** The latter is not quite true in general. If a system responds “fast” against an external force with the internal equilibrium resistance, like in elastic processes, then virtually reversible process could be rather fast (as an elastic spring compression and expansion, and similar). “*Quasiequilibrium*” is more appropriate than “*quasistatic*” and the two are not necessarily the same (as in the above example)!

Key Point 4.3:

MK> The irreversible (optimal) heat engine $\eta^*=1-(T/T_+)^{1/2}$ is misleading since it maximize power output instead of efficiency, under its simplified operational conditions. Higher efficiencies could be (and are) achieved in reality by lowering the power output for a given engine capacity (design size), and then engine size could be enlarged to achieve any power output, optimizing the cost, for example. Real optimization is based on multiplicity of constrains and Eq.(3) on p. 217 is an outcome of a very simplistic modeling.

On p. 274: “ • *Is entropy a measure of a system’s disorder? In general the answer is a firm “no.” A common definition of disorder is: a lack of systematic or regular arrangement. This has a spatial or orientational connotation and is appropriate only when there are clear spatial patterns.*”

MK> However, the disorder may be dynamic, related to motion in space. The temperature and thermal energy are fundamentally related to “*disordered motion*” at micro-scale (random in all directions), and *disorder*, as related to entropy, which is directly related to disorder of thermal energy ($E=U_{th}$) contained in a system, i.e., a number of (energy occupied) microstate $W(E)=\Omega(E)$ that represents a given macro (energy) state. All complexity is masked by ‘open’ definition of $\Omega(E)$. After all, the Boltzmann statistical definition of entropy is $S=k_B \ln[\Omega(E)]$. All these concepts, including “*spreading*,” are too general and have to refer somehow to thermal energy, including to part of potential energy content related and equivalent to relevant and integral thermal energy per absolute temperature, i.e., real classical entropy as defined in phenomenological Thermodynamics and measured in laboratory. The related statistical randomness (disorder) and probabilistic concepts are far-fetched and have to represent the randomness of thermal motion of very complex system structure. Only for a very simple structures, like an ideal gas, the statistical modeling could be properly correlated to physical thermal energy, temperature, and entropy. In other realistic systems, the statistical methods are only simplified metaphorical-concepts and could not account for the complex reality, and thus could not quantify the real, phenomenological entropy without an empirical adjustment based on physical measurements of phenomenological concepts. The statement on p. 274, “*This [disorder] is an undesirable oversimplification of a profound physical entity,*” could refer to any representation of physical entropy by any statistical and probabilistic modeling, including the “energy-spreading” metaphor favored in Leff’s article. I do not see any reasoning, let alone facts, to support the statement on p. 274, “*The energy-spreading metaphor can be applied successfully to all of these.*” I am confused about reference to example of 1 m^3 and 2 m^3 of copper, since the entropy is an

extensive property and tabulated as a specific property (per mass or volume or mole, thus specific-intensive), and so could be disorder or spreading if properly defined (a matter of using synonyms, a word choice).

Probably, I am missing the utility of the concept of disorder and its uncertainty, as well as the concept of energy spreading in this article, as related to measurable physical entropy. Equally confusing is the example of "*Fe rusting*" in the article (p.274) since entropy of all involved systems is increased (as expected) confirming conversion of useful (free) energy to heat, thus generating thermal energy (dynamic) disorder and entropy. Again, the entropy has to be related to thermal energy, and 'spreading' of thermal energy is related to increase of dynamic randomness of thermal motion over system mass and space. We are replacing one term with another and claiming that the latter is more appropriate than the former, regardless that they are directly related and both implicitly must represent the same physical quantity. In that regard **Key Point 5.1 and 5.2** statements are confusing and misleading in my opinion. Furthermore, the uncertainty (of randomness) and randomness (itself) are related since the Shannon probabilities (uncertainties) are reduced to the Boltzmann statistical concept of entropy, random number of all possible thermal-energy microstates that represent a given thermal-energy macrostate.

We could model (thermal motion) disorder as *the number of all accessible states over which a composite system energy can randomly spread in all directions (randomly occupy)*. Statistical methods are useful tools to explain physical concepts related to random equipartition of motion energy in all directions as underlying phenomena behind temperature, thermal energy and its transfer or heat, as well as entropy, integral thermal energy per absolute temperature content as defined by Clausius, the latter based on ingenious reasoning of reversible heat engine cycle by Sadi Carnot and his followers. The forced tendency of energy transfer towards equilibrium is the cause-and-effect force-flux phenomena, also resulting in maximum probability, the latter being a mathematical concept of the former physical phenomena. Universality of entropy is due to the fact that all structural energies (thus directional energy in their own right) ultimately dissipate (stray away in all directions) in thermal energy, thus universality of thermal random motion which tends to come to its own dynamic equilibrium with net-zero mass-energy interchange.

Additional Related Comments communicated with Frank Lambert:

From: Prof. M.Kostic kostic@niu.edu Date: Tue, Feb 5, 2013 at 1:06 PM

To: Frank Lambert flambert@att.net >

(Frank Lambert and Harvey Leff are co-authors of papers promoting "*Dispersal/Spreading*" and demoting "*Disorder*," see more at entropysite.oxy.edu)

Dear Frank (Cc: Harvey),

In my humble opinion "*Dispersal/Spreading*" is as useful (or lousy) as "*Disorder*" since it is too general (refer to anything, diffusion of any kind and more) and need to be specifically defined to represent the Thermodynamic "*Entropy*" which is well-defined thermo-physical property and thus measured and tabulated in many data tables with the uncertainty of the measurements. *Clausius* defined/quantified it so well to be measured (based on ingenious *Carnot's* reasoning) but fully comprehended by a few even nowadays. Even *Boltzmann* defined entropy as $S=k*\log(W)$, as inscribed on his tombstone, thus 'transferring' the complexity of dynamic randomness of thermal micro-motion to 'W':

http://en.wikipedia.org/wiki/File:Zentralfriedhof_Vienna_-_Boltzmann.JPG

Could you define specifically (possibly quantify) your "*Spreading*" as related to the Thermodynamic Entropy of Clausius? Then I'll tip my hat to you. Otherwise it is so general to be useless, even meaningless!? *Things are always more simple, but also more complex than what we think they are*, and I agree that many in the past have made a myth out of entropy due to lack of their subtle comprehension of ingenious *Carnot's* reasoning of '*reversible processes*' that led to discovery of (absolute) Thermodynamic Temperature, Entropy, and generalization of the Second Law of Thermodynamics.

Respectfully and Sincerely,
Milivoje Kostic

Removing the Mystery of Entropy and Thermodynamics – Part I

Harvey S. Leff, Reed College, Portland, OR^{a,b}

This is the introductory part of a five-part series. Parts II-V will elaborate considerably on the material presented here.

Energy and entropy are centerpieces of physics. Energy is typically introduced in the study of classical mechanics. Although energy in this context can be challenging, its use in thermodynamics and its connection with entropy seem to take on a special air of mystery. In this five-part series, I pinpoint ways around key areas of difficulty to reduce that mystery. In Part I, the focus is on building an understanding of fundamental ideas of thermodynamics, including its connection with mechanics, and how entropy is defined and calculated. A central thread is that energy tends to spread within and between macroscopic objects, and this spreading is a surrogate for entropy increase. Specific questions are posed and answered, building on foundations laid in prior articles.^{1–8} Parts II-V elaborate considerably on the ideas introduced here. A question-answer format is used throughout, with major results enumerated in Key Points 1.1-1.5.

In 1996 and 2007,^{9–11} I suggested viewing entropy as a “spreading function.” Independently, chemist Frank Lambert^{12–15} proposed a similar idea. Stimulated by Lambert’s work, the energy spreading metaphor has been adopted by the authors of over two dozen general chemistry and physical chemistry textbooks. In contrast, the connection between energy spreading and entropy has not been widely embraced by authors of physics textbooks. This two-part article is an attempt to promote greater appreciation of the fact that entropy is in essence a spreading function.

Questions and answers

•What distinguishes thermodynamics from classical mechanics?

An inability to answer this question can make thermodynamics seem confusing. Classical mechanics deals with point particles and rigid bodies. Both of these are fictitious model systems that do not exist in nature, and are *not* thermodynamic systems. A point particle can neither rotate nor vibrate and thus cannot store energy within it. This differs from a real atom, which stores energy internally—energy that can vary by absorption and/or emission of radiation.

A rigid body’s atoms are assumed to be point-like, with fixed positions relative to one another, so energy cannot be added to or taken from such a model system. The simplicity of a rigid body makes it useful for approximating the behavior of real physical systems in classical mechanics, when changes in internal energy are negligible. In contrast, thermodynamics deals with systems that have internal degrees of freedom. For example, the molecules of a gas have kinetic energies and interact with one another via mutual potential energies. Figure 1

depicts (a) a hypothetical rigid solid with zero internal energy, $U = 0$ and (b) a dilute gas whose internal energy $U > 0$ and is variable.

In a macroscopic system the number of individual kinetic and potential energy terms is enormous and impossible to deal with individually. The many molecules of solids typically vibrate about localized lattice sites and have numerous translational, rotational, and vibrational energy modes. Similarly the prodigious number of molecules in a gas have kinetic and intermolecular potential energies. Recognizing the impossibility of dealing with these systems microscopically, the macroscopic internal energy function U is postulated in thermodynamics.

Key point 1.1: *The existence of internal energy that can be varied makes a system “thermodynamic.”*

• What is a “state function” and why is internal energy a state function?

A state function is what we normally call a *function* in mathematics. The internal energy function U , envisaged as an average total energy, is postulated to be a function of a small number of thermodynamic variables, e.g., temperature T , system volume V , and number N of molecules; i.e., for a given thermodynamic state, (T, V, N) , the internal energy $U = U(T, V, N)$. Typically, for systems with sufficiently short-range intermolecular forces, U is an increasing function of temperature T for fixed V and N .

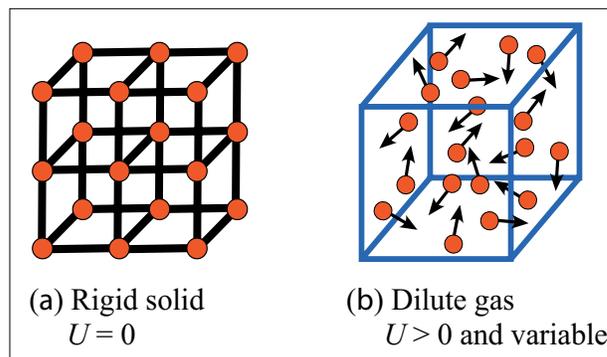


Fig. 1. Depictions of (a) a rigid solid, with zero internal degrees of freedom and zero internal energy, and (b) a dilute gas, whose internal energy consists primarily of the sum of all molecular kinetic energies. The model in (a) is *not* thermodynamic because its atoms are assumed to be point particles that are fixed relative to one another; i.e., there are no internal degrees of freedom and the internal energy is zero and unchangeable. The model in (b) represents a thermodynamic system with nonzero, variable internal energy.

Key point 1.2: State functions in thermodynamics describe equilibrium thermodynamic properties. They do not depend on how equilibrium was reached; i.e., they have no path or history dependence. Internal energy represents the energy stored within an object for a given thermodynamic state specified by a small number of thermodynamic variables such as (T, V, N) .

• **Why are heat and work NOT state functions?**

It is important to understand that neither heat nor work is a function. Heat and work are best viewed as adjectives that indicate process types. Historically, however, the term *heat* was considered as either motion of *small particles*—even before the existence of atoms was established—or a conserved, stored entity referred to as heat or *caloric*.¹⁶ Largely because of remnants from the erroneous and obsolete caloric theory, the history of heat and the language used for it has been a tortuous one.¹⁷

In modern terms, a heat process is an energy transfer induced by a temperature difference, with the transferred energy denoted by Q . For example, heating water on a stove entails a temperature difference between burner and pot. A very different, but important, class of processes called *adiabatic* are *pure work* processes with $Q = 0$.

The simplest *work* process is an expansion or compression of a gas, induced by a pressure difference that results in the gas doing positive or negative work on its surroundings. We define W as the work done by the gas, so $W > 0$ when the gas expands, and $W < 0$ when the gas is compressed. With this convention, in an adiabatic volume change, if the work done is denoted by W_{ad} , then $\Delta U = -W_{ad}$. That is, in a slow adiabatic expansion, the gas does positive work, reducing its internal energy.

Generally, for a combination work plus heat process, we write the first law of thermodynamics as

$$\Delta U = Q - W. \quad (1)$$

Knowing the work W_{ad} for any adiabatic process that connects two equilibrium states determines $\Delta U = W_{ad}$. Then for any nonadiabatic process connecting the same two states, Q can be deduced by measuring W and using Eq. (1), $Q = \Delta U + W = W_{ad} + W$. This gives an operational definition of Q in terms of measurable work values for two different processes that connect two given states.

Suppose a gas is heated from state A to state B at constant pressure. It could instead be heated at constant volume from state A to an intermediate state C, with zero work, and then brought to state B by an adiabatic expansion. Because $\Delta U = U_B - U_A$ for both paths, AB and ACB, $Q_{AB} - W_{AB} = Q_{ACB} - W_{ACB}$, or equivalently, $Q_{AB} - Q_{ACB} = W_{AB} - W_{ACB}$. Path ACB entails higher pressures than AB, and thus $W_{ACB} > W_{AB}$ and $Q_{AB} > Q_{ACB}$.

The latter result is an example of the important point that rather generally, any two equilibrium thermodynamic states A and B can be connected by many different combined work

and heat processes. For example a process might entail segments with T , P , or V constant, each with different Q and W values. For each such combination, Q and W depend not only on A and B but on the specific path connecting them.

Key point 1.3: Heat and work are processes. The values of Q and W in $\Delta U = Q - W$ are dependent on the specific thermodynamic paths that connect equilibrium states, but notably, ΔU is the same for all paths. It is important to understand that Q and W are transient process energies and are not stored. Once a process is over, the system stores internal energy U , and there is no memory of Q or W , or the particular heat and/or work paths.

• **What is entropy and why does it occur in thermodynamics and not in mechanics?**

Entropy can be viewed usefully in terms of its changes during thermodynamic processes, which generally entail spatial redistributions of *internal energy*. As such, entropy has significance only for systems that store *internal energy*. Because neither a point particle nor a rigid body, the two mainstays of classical mechanics, stores internal energy, their entropy values are zero and unchanging. Thus, entropy is normally not even mentioned in classical mechanics. In contrast, macroscopic gases, liquids, and solids have internal degrees of freedom and store internal energies that can be varied by work and/or heat processes. Even an ideal gas, though composed of point particles, has internal energy because those particles have kinetic energy.

In a real thermodynamic process, an internal energy redistribution occurs and entropy is generated in the universe. For example, when a hot cup of soup cools, heating its surroundings slightly, energy spreads from the cup and soup to the surroundings until there is a uniform temperature. Were spreading to continue further, the soup would become cooler than the surroundings, which obviously does not happen! In this sense, energy spreads maximally—i.e., as much as is needed to generate temperature equality between soup, cup, and surroundings. The central idea of energy spreading maximally is the essence of the second law of thermodynamics. This is discussed in detail in Parts II-V of this series.

If two identical solid copper blocks at different temperatures are put in thermal contact, energy spreads as much as possible, becoming distributed equitably, namely uniformly, with each block having half the energy. Because different materials store internal energy differently, when equal masses of two different materials have equal temperatures, their internal energies differ in general, and the meaning of an equitable energy distribution is less evident *a priori*. This is addressed in Part V of this series.

Although it is possible for energy to “unspread” spatially, clumping in finite spatial regions, this happens only in special cases, and is accompanied by compensating redistributions of energy.¹⁸

Key point 1.4: Thermodynamic processes entail spatial redistributions of internal energies, namely, the spatial spreading of energy. Thermal equilibrium is reached when energy has spread maximally; i.e., energy is distributed equitably and entropy is maximized. Thus, entropy can be viewed as a spreading function, with its symbol S standing for spreading. Although not Clausius' motivation for using S , this can serve as a mnemonic device. Energy spreading can entail energy exchanges among molecules, electromagnetic radiation, neutrinos, and the like.

• **How is entropy calculated?**

Though it is often overlooked, every macroscopic material in thermodynamic equilibrium has a numerical entropy value that depends on its temperature, pressure, and possibly other variables, and these are tabulated in handbooks and on the Internet. Clausius' algorithm,

$$dS = \frac{dQ_{\text{rev}}}{T}, \quad (2)$$

enables calculation of entropy changes, namely, for a slow, reversible heating process,¹⁹ where infinitesimal energy dQ_{rev} is transferred to the system. We use the notation dQ_{rev} rather than dQ to remind us that Q_{rev} is not a state function and thus dQ_{rev} is not an "exact" differential; i.e. $\int_a^b dQ \neq Q_b - Q_a$. Indeed there exist no functions Q_a and Q_b .

The term *algorithm* is appropriate because Eq. (2) is a calculation tool that requires a *fictitious, reversible* process rather than the actual irreversible process (in Part IV, we explain that all real processes are irreversible). Given initial and final equilibrium states, any reversible path suffices. If the energy transfer is from the system, then $dQ_{\text{rev}} < 0$. The generalization of Eq. (2) for an irreversible process is $dS > dQ/T$,²⁰ where dQ is for the *actual* process. For example, an infinitesimal adiabatic free expansion, with $dQ = 0$, has $dS > 0$.

When a system is heated *very slowly* and *reversibly* at constant atmospheric pressure P , the added energy for each added tiny increment is $dQ_{\text{rev}} \equiv C_P(T) dT$, which defines $C_P(T)$, the heat capacity at constant pressure. (At constant volume, $dQ_{\text{rev}} \equiv C_V(T) dT$.) If heating is from initial temperature T_i to final temperature T_f , the constant-pressure entropy change is

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P(T)}{T} dT. \quad (3)$$

Available data for C_P for solids at atmospheric pressure as a function of temperature enables numerical evaluation of ΔS . One can also calculate the enthalpy change,²¹ $\Delta H \equiv \int_{T_i}^{T_f} C_P(T) dT$, for many real solids using the lowest achievable minimum temperature $T_i \approx 0$ K and $T_f = 298.15$ K (a common reference temperature). For $T_i \rightarrow 0$, a simplification occurs using the third law of thermodynamics, namely, the zero temperature limit of entropy is zero for all pressures P . Thus $\Delta S = S(298.15) - 0 \equiv S^\circ$, the so-called *standard* entropy. Numerical values obtained using this procedure for solids will be presented in Part II.²²

Key Point 1.5: Heat capacity data for a solid from near absolute zero to 298.15 K at atmospheric pressure enables a numerical evaluation of standard entropy. Because all non-zero entropy values entail adding energy to a substance, it is clear that entropy and energy are intimately related. If the substance is a liquid or gas at 298.15 K and standard pressure, the entropy calculation is slightly more complicated, entailing a knowledge also of the so-called latent heat of melting and (for a gas) vaporization.

In Parts II-V of this series,²² we discuss the Clausius and Boltzmann entropies, numerical entropy, connections with stored internal energy, entropy's spreading nature, and its relationship with uncertainty. We show that entropy can be viewed with simple graphs, and is related to reversibility, irreversibility, constant-temperature reservoirs and the concept of equity.

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18. Clumping can occur in various ways. One example of clumping is the gas-liquid phase transformation for which clumping of particles in the liquid is accompanied by energy spreading to the surroundings, which preserves the second law of thermodynamics. Another example occurs in outer space, where long-range gravitational forces dominate. The formation of galaxies and stars entails clumping, along with continual spatial energy redistribution of kinetic and gravitational energy, electromagnetic radiation and neutrinos, which spread widely. The second law of thermodynamics is believed to be satisfied.
19. Reversible processes are discussed in depth in Part IV.
20. This inequality is useful only if T is well defined, which is not so for some irreversible processes. A more rigorous expression is $dS \geq dQ/T_{res}$, where T_{res} is the temperature of an (assumed) constant-temperature environment supplying the energy dQ . The equality holds only in the limit $T_{res} \rightarrow T$ and $dQ \rightarrow dQ_{rev}$. Constant-temperature reservoirs and reversible and irreversible processes are discussed further in Part III and IV of this article.
21. Enthalpy H is defined by $H = U + PV$, so $dH = dU + PdV + VdP$. From the first law of thermodynamics, $dU = dQ - dW$, and for a sufficiently slow and reversible process $dW = PdV$. Thus, $dH = dQ + VdP$, and for a constant pressure process, $dH = dQ \equiv C_p(T)dT$.
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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 I¹ 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,

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

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 $dQ = dU + PdV \equiv dH \equiv C_p(T) dT$. Thus

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

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.

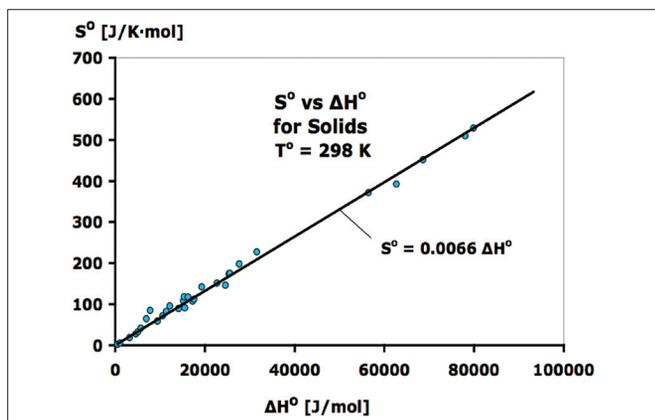


Fig. 1. Entropy of room temperature solids vs energy input from $T \approx 0$ to 298.15 K. Each circle represents a datum for a particular solid.

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, $dS = dQ_{\text{rev}}/T$.

Key Point 2.1: Entropy at temperature T can be determined numerically by heating from near absolute zero to T , using $S = \int_{0+}^T dQ/T$. $S(T)$ is strongly correlated with the heating energy, $\Delta H = \int_{0+}^T dQ$. 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.

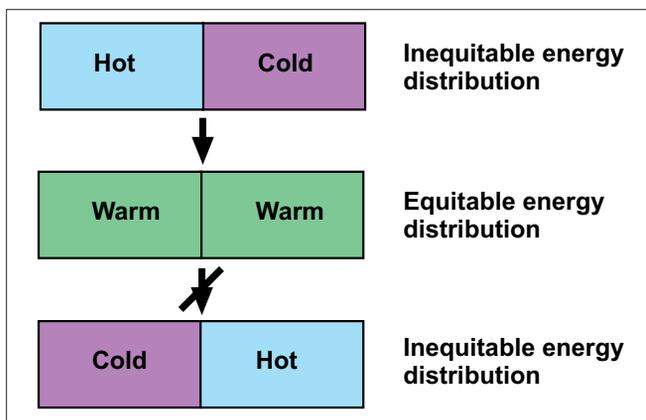


Fig. 2. When hot and cold objects interact thermally, the result is the middle pane, with both objects warm. The process does *not* continue further. For example, the temperatures of the initially hot and cold objects do not become reversed.

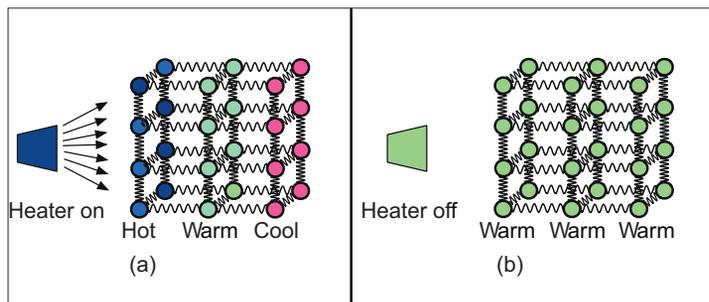


Fig. 3. As a homogeneous solid is heated from the left, energy moves rightward through it. If the heater is turned off shortly after heating began, the entire solid becomes uniformly warm. This assumes negligible energy exchange with the surroundings.

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.

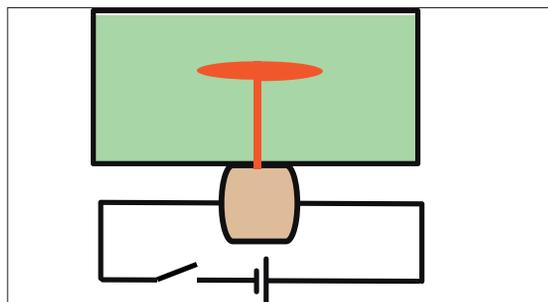


Fig. 4. When the switch is closed, an electrically powered rotating blade energizes water, raising its temperature and entropy via a pure-work process.

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, $dS = dQ_{\text{rev}}/T$, 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 $dQ = 0$ 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

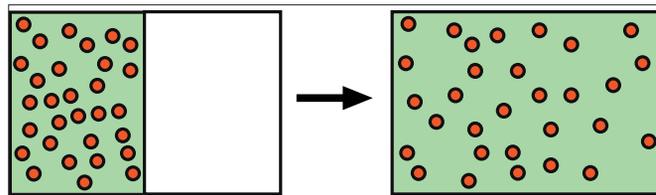


Fig. 5. Kinetic and potential energies, denoted by shading, spread from the left chamber of the container to the whole container as the gas expands.

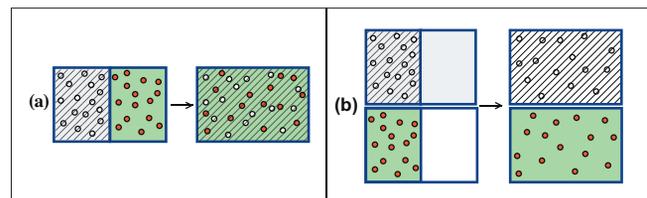


Fig. 6. (a) Mixing of two species of dilute (ideal) gas. The total system can be isolated or at constant temperature. The energy region of one species is crosshatched; that for the other is shaded. After expansion of each, the full volume contains energy from each species. This is an example of energy 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.*

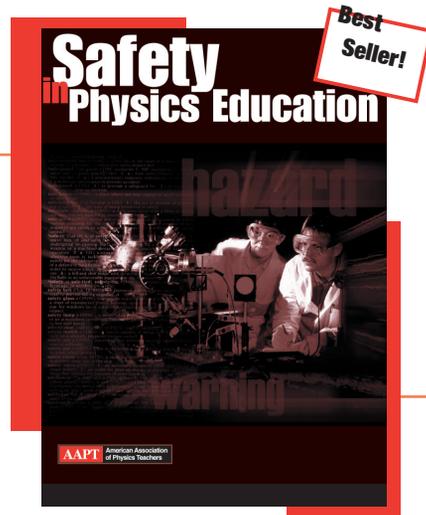
Other aspects of entropy for thermodynamic processes and for thermodynamic equilibrium are discussed in Parts III-V.³

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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).

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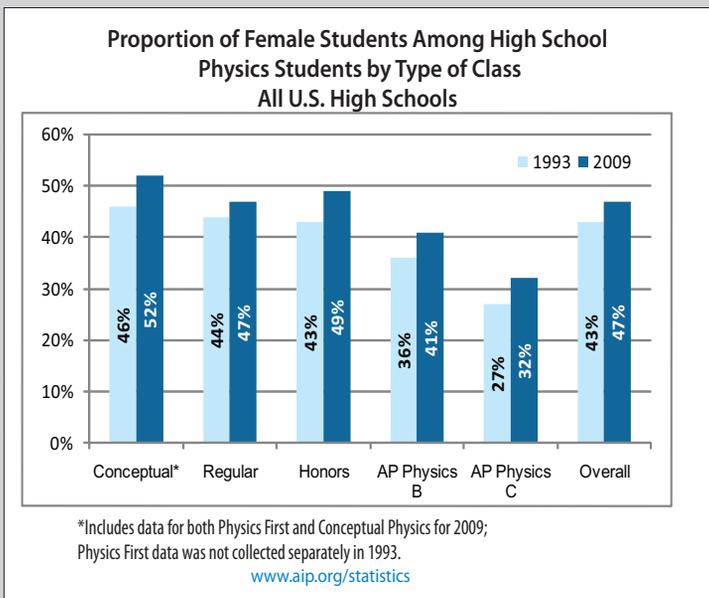
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Female representation by type of class

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

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 $dS = dQ_{\text{rev}}/T$ and the identities $dU = dQ_{\text{rev}}$ at constant V and $dH = dQ_{\text{rev}}$ 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.

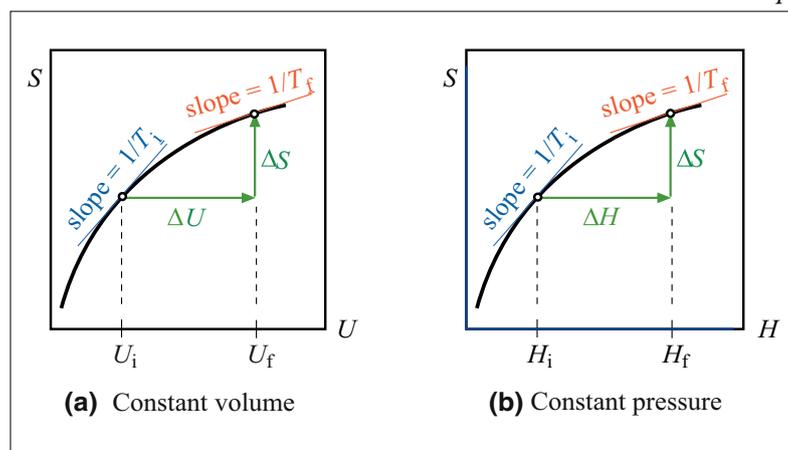


Fig. 1. (a) Entropy S vs internal energy U at constant volume. (b) Entropy S vs enthalpy H at constant pressure. In (a) and (b) initial and final states are shown. The temperature inequality $T_f > T_i$ is evident because $T \equiv 1/\text{slope}$.

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

entropy⁴ for an isolated system with total energy E and volume V is

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

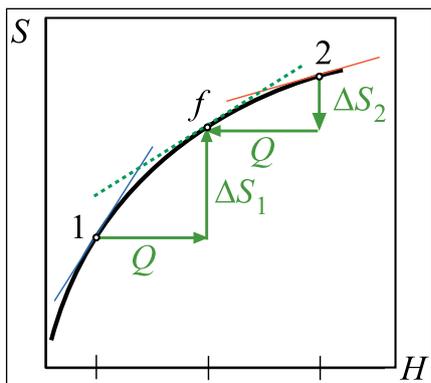


Fig. 2. Two identical systems have the same S vs H curve. One is initially in state 1 and the other in state 2. When put into thermal contact at constant pressure, equilibrium is ultimately reached, with each system in state f . Concavity assures that the second law of thermodynamics is satisfied; i.e., $\Delta S_1 + \Delta S_2 > 0$.

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 information⁸).

Equation (1) is interesting for at least two reasons. First, its units come solely from the pre-factor, Boltzmann’s constant, $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$.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-

amic 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 $W_{\text{tot}} = W(E)W_{\text{res}}(E_{\text{res}})$, where $E_{\text{res}} \gg E$ 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 $W_{\text{res}}(E_{\text{res}})$ 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 $E + E_{\text{res}} = \text{constant}$.

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 $T_{\text{res}} > T_A$, and gains sufficient energy to attain thermodynamic state B with temperature $T_B = T_{\text{res}}$. It is clear graphically that $\Delta S_{\text{sys}} + \Delta S_{\text{res}} > 0$, so the second law of thermodynamics *is* satisfied. Furthermore the

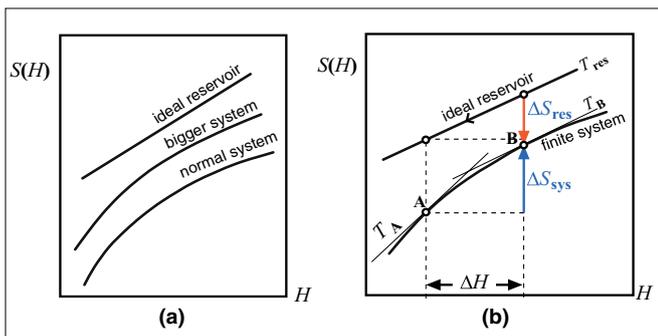


Fig. 3. (a) Curves of entropy vs enthalpy at constant pressure. The enthalpy H for successively larger systems, approaches linearity. (b) A linear $S(H)$ curve for a so-called *ideal* reservoir, and concave downward $S(H)$ for a typical finite system, initially in thermodynamic state A . It is then put 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 $\Delta S_{\text{res}} = \text{slope} \times \Delta H = \Delta H/T_{\text{res}}$. 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

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

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 definition 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

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

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

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- Strictly speaking, this is true for typical systems observed on Earth, but fails for systems bound by long-range forces—e.g., stars.
- 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.
- 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.
- 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).
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- 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 .
- 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.
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- The derivative $(dS/dU)_V$ is commonly written using partial derivative notation, $(\partial S/\partial U)_V$.

Removing the Mystery of Entropy and Thermodynamics – Part IV

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In Part IV of this five-part series,^{1–3} reversibility and irreversibility are discussed. The question-answer format of Part I is continued and Key Points 4.1–4.3 are enumerated.

Questions and Answers

• **What is a reversible process?** Recall that a reversible process is specified in the Clausius algorithm, $dS = \delta Q_{\text{rev}}/T$. To appreciate this subtlety, it is important to understand the significance of reversible processes in thermodynamics. Although they are *idealized* processes that can only be approximated in real life, they are extremely useful. A reversible process is typically infinitely slow and sequential, based on a large number of small steps that can be reversed in principle. In the limit of an infinite number of vanishingly small steps, all thermodynamic states encountered for all subsystems and surroundings are *equilibrium* states, and the process is reversible.

By definition, a process that proceeds solely through equilibrium thermodynamic states is called *quasistatic*, and all reversible processes are quasistatic. Although most quasistatic processes are reversible—namely, can be reversed, with the surroundings also reversing the original path—some are not. Examples that are nearly quasistatic, but clearly irreversible, are air flowing from a slowly leaking tire, and any ultra-slow frictional mechanical process that converts mechanical to internal energy. Reversibility is required in the Clausius algorithm. If nonequilibrium states are encountered and if T is well defined, then $dS \geq \delta Q/T$.¹

Any heat process that transfers energy through a *finite* temperature difference—e.g., heating water on a stove—is irreversible. Suppose energy is transferred from a reservoir with temperature T_A to the system, which is initially at temperature

$T < T_A$. That energy enters through a surface, heats the matter near that surface to a temperature greater than T , and subsequently energy spreads to other parts of the system at lower temperature. The system's temperature is nonuniform during the ensuing energy-spreading process, nonequilibrium thermodynamic states are reached, and the process is irreversible.

To approximate reversible heating, say, at constant pressure, one can put a system in contact with many successively hotter reservoirs. In Fig. 1 this idea is illustrated using only initial, final, and three intermediate reservoirs, each separated by a finite temperature change. Step 1 takes the system from temperature T_A to the next reservoir temperature $T_1 > T_A$. Energy $Q_1 > 0$ is released by the reservoir, whose entropy change is $\Delta S_{\text{res},1} = -Q_1/T_1$, with $Q_1 = \int_{T_A}^{T_1} C_p(T)dT$, where the integrand is the system's heat capacity. The system's entropy change is

$$\Delta S_{\text{sys},1} = \int_{T_A}^{T_1} C_p(T)/T dT.$$

Thus, the total entropy change in step 1 is

$$\Delta S_{\text{sys},1} + \Delta S_{\text{res},1} = \int_{T_A}^{T_1} C_p(T)[1/T - 1/T_1]dT.$$

Because $T \leq T_1$, the integrand and thus $\Delta S_{\text{total},i} \geq 0$. Generalizing to the i^{th} step, we have

$$\begin{aligned} \Delta S_{\text{total},i} &= \Delta S_{\text{sys},i} + \Delta S_{\text{res},i} \\ &= \int_{T_{i-1}}^{T_i} C_p(T)[1/T - 1/T_i]dT \geq 0. \end{aligned} \quad (1)$$

Note that the equality in Eq. (1) holds *only* in the limit as the temperatures T_i and T_{i-1} approach each other. This happens as we increase the number of steps keeping temperatures T_A and T_B fixed. This can be done by doubling the number of intermediate reservoirs from 3 to 6, to 12, . . . , reducing successive temperature differences accordingly. In the limit of an infinite number of steps we have $\sum_{i=1}^{\infty} \Delta S_{\text{total},i} = 0$. In this limit, the system and environment are always in equilibrium states, and the process can, in principle, be reversed.⁴ Some define a reversible process as one for which the entropy of the universe is unchanged.⁵

Extending the discussion to volume changes, the rapid adiabatic expansion or compressions of a gas is *irreversible*.² For a rapid expansion, the gas develops a lower-density region near a receding piston and, subsequently, particles and energy spread spatially, increasing the entropy. For the infinitely slow *reversible* adiabatic expansion, the work done by the gas causes a decrease of internal energy sufficiently large to offset

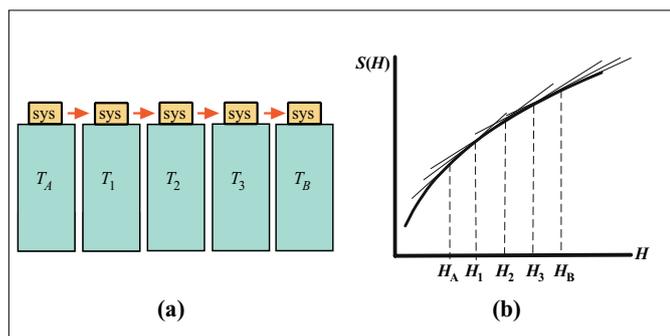


Fig. 1. (a) A system (sys) is heated using five sequential, progressively hotter reservoirs. Each step entails a *finite* temperature difference and is irreversible. (b) Sequentially hotter states (A, 1, 2, 3, B) for a system shown on an S-vs-H plot. Temperatures are the reciprocals of the line slopes. Reversibility is achieved in the limit of an infinite number of reservoirs with successive temperature differences approaching zero.

the effect of energy spreading to a larger volume, and the system's entropy is unchanged.

For a rapid adiabatic compression, a higher-density region is generated near the piston. Subsequently, the “extra” energy in that region spreads spatially, increasing entropy. In the reversible limit, the energy gain from work done on the gas offsets the decrease in spatial spreading because of the volume decrease, leaving the entropy unchanged. A straightforward mathematical treatment linking irreversible compressions and expansions to entropy increase is in Ref. 6.

Key Point 4.1: *Reversible processes do not exist in nature, but are a useful limiting case for envisaged infinitely slow processes that entail only equilibrium states of a system and surroundings. Because $\Delta S_{\text{tot}} = 0$ for a reversible process, the reversed process can be executed without violating the second law of thermodynamics. Irreversible, variable-volume work processes either add internal energy (compression) or spread energy to new spatial regions (expansion), increasing energy spreading and total entropy. When $\Delta S_{\text{total}} > 0$, there is no way to recover the initial entropy values of the system and surroundings because the entropy of an isolated system cannot decrease.*

• **Why are reversible processes important?** Reversible processes are staples of thermodynamics. Because they are quasistatic, they make it possible to draw diagrams of pressure versus volume, temperature versus entropy, and other useful diagrams. And because they can be reversed, they enable the treatment of systems such as refrigerators and heat pumps, simply by running reversible heat engines “backwards.” Reversible processes also give us the ability to establish a limit on the thermal efficiency of heat engines that operate between specified higher and lower constant-temperature reservoirs. Finally, reversible processes are needed in the Clausius entropy calculation algorithm. We may use any reversible path to connect thermodynamic equilibrium states *A* and *B* to calculate $\Delta S = S_B - S_A$. Because entropy is a state function, the latter ΔS is valid even when states *A* and *B* are connected by any irreversible path.

The importance of reversible processes is evident if one examines the well-known reversible Carnot cycle using the temperature-versus-entropy diagram in Fig. 2. Applying the first law of thermodynamics to the heat engine cycle 12341, we know that $\Delta U = 0$ (initial and final states are the same), so $\Delta U = Q - W$ implies $Q = Q_{\text{in}} - Q_{\text{out}} = W$, where each quantity is defined to be positive. Along isothermal segment 12, $dS = dQ/T_h$, which leads to $Q_{\text{in}} = T_h(S_{\text{max}} - S_{\text{min}})$, the area of the combined white+shaded rectangles. Similarly, along 34, $Q_{\text{out}} = T_c(S_{\text{max}} - S_{\text{min}})$, the area of the shaded rectangle, and the thermal efficiency is

$$\eta \equiv \frac{W}{Q_{\text{in}}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_c}{T_h}. \quad (2)$$

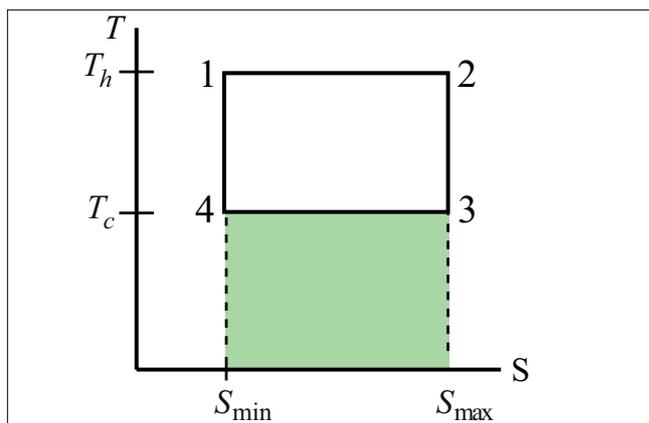


Fig. 2. Reversible Carnot cycle heat engine 12341. Segments 12 and 34 are isothermal, and 23 and 41 are adiabatic processes. The shaded+white area represents the input energy Q_h at the higher temperature T_h , and the shaded area is the output energy Q_c to the colder reservoir at T_c . The work done in one cycle W is the white rectangular area and the thermal efficiency $\eta = W/Q_h$ is (white area)/(white+shaded area).

This is the well-known Carnot efficiency. Note that the temperature-versus-entropy diagram shows clearly that the Carnot engine's efficiency is independent of the minimum and maximum entropy values S_{min} , S_{max} because in calculating η , the ratio of the work (white area) to the input energy (white+shaded areas), the difference $(S_{\text{max}} - S_{\text{min}})$ cancels out. Thus, Carnot cycles producing any amount of work must have the same thermal efficiency for given T_c and T_h . Note that Eq. (2) is independent of the working substance.

If the cycle is run in the reverse order, 43214, it is a refrigerator that removes energy Q_c from the colder region and delivers energy $Q_h = Q_c + W_{\text{ext}}$ to the higher temperature region, where each quantity here is defined to be positive. In particular, $W_{\text{ext}} = -W > 0$, namely the negative of the negative work done by the heat engine's working fluid. There is no violation of the second law of thermodynamics here because external work is needed to move energy “uphill”; it does not occur spontaneously, and the entropy of the universe does not decrease. If the reversed Carnot engine is intended to heat the hotter region, it is called a *heat pump*. If it is intended to cool the colder region, it is called a *refrigerator*.

An important characteristic of reversible heat engines that is not well appreciated is that each cycle must take an infinite amount of time and therefore must generate zero power! In contrast, real heat engines are useful only if they generate sufficient nonzero power levels—e.g., an automobile's internal combustion engine. Similarly a reversible engine run in reverse will have zero heating rate at T_h and zero cooling rate at T_c .

Key Point 4.2: *Reversible processes enable graphs of well-defined thermodynamic paths, consideration of helpful heat engine models, determination of maximum efficiencies for heat engines, and calculations of entropy changes.*

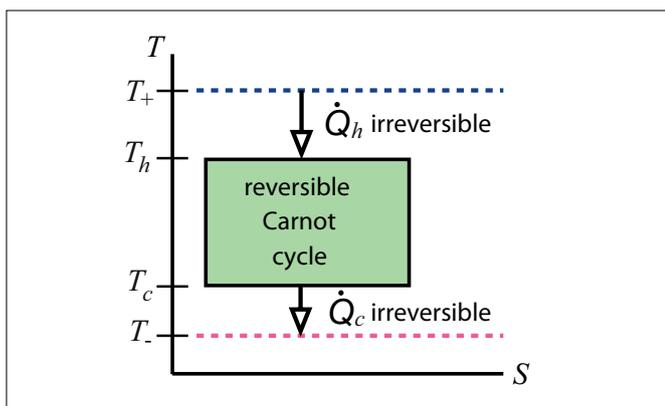


Fig. 3. A reversible Carnot cycle with irreversible heat processes at its hotter and colder temperatures. The temperatures T_c and T_h are assumed to be variable and can be chosen to maximize the output power $\dot{W} = \dot{Q}_h - \dot{Q}_c$.

• **How can irreversibility be taken into account?** To get around the zero power limitation of a reversible heat engine, some have proposed⁷ combining a reversible Carnot cycle with irreversible heat processes at the hotter and colder temperatures, as in Fig. 3. The temperatures T_+ and T_- represent high and low reservoir temperatures. The reversible Carnot cycle runs between hotter and colder temperatures $T_h < T_+$ and $T_c > T_-$. For example, T_+ could be chosen as the temperature of a burning fuel-air mixture in an internal combustion engine; T_- could be the outdoor air temperature.

Each cycle, though treated as reversible, must occur in finite time, with finite rates \dot{Q}_c and \dot{Q}_h (in $J/s = \text{watts}$) that are assumed to be proportional to $(T_c - T_-)$ and $(T_+ - T_h)$, respectively. If T_c approaches T_- and T_h approaches T_+ , the transfer rates \dot{Q}_c and \dot{Q}_h approach zero and the power output vanishes. In this limit the efficiency is maximum, namely, the Carnot efficiency, $\eta_c = 1 - T_-/T_+$. Also, the entropy production rate from the two reservoirs, $\dot{S} = \dot{Q}_c/T_- - \dot{Q}_h/T_+ \rightarrow 0$; i.e., the process becomes reversible.

On the other hand, if T_c approaches T_h , the Carnot cycle's area approaches zero and, again, the power output approaches zero. Here, \dot{Q}_h is finite but $\dot{W} \rightarrow 0$, so the thermal efficiency approaches zero. In this limit, the Carnot cycle "vanishes," there is zero power output, and the heat process takes energy at rate \dot{Q}_h from the reservoir with T_+ and delivers it to the reservoir with T_- , maximizing the entropy production rate, $\dot{S} = \dot{Q}_h(1/T_- - 1/T_+) > 0$.

Between these zero power limits, there is a pair (T_c, T_h) for which the power output is maximum and the thermal efficiency lies between zero and the Carnot efficiency, namely,⁷

$$\eta^* = 1 - (T_-/T_+)^{1/2} \leq 1 - T_-/T_+. \quad (3)$$

The corresponding entropy production rate is between zero and the above maximum entropy production rate.⁸ The efficiency η^* also arises in the context of some reversible heat engine models.⁹

Key Point 4.3: An irreversible heat engine, operating between two reservoirs, has an efficiency less than the corresponding Carnot efficiency. The expression $\eta^* = 1 - (T_-/T_+)^{1/2}$ is a good guide to the efficiencies of electrical generating plants. This seems fortuitous because the model from which it is derived entails a reversible cycle to be operated in finite time. Despite this lack of realism, the irreversible model is valuable because it indicates, albeit roughly, a way that maximum power output can arise.

In Part V, we discuss interpretations of entropy and the concept of "equity" in thermodynamic equilibrium.¹⁰

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Removing the Mystery of Entropy and Thermodynamics – Part V

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Part V ends this five-part paper series.^{1–4} We discuss the interpretation of entropy as uncertainty and connections between spreading and uncertainty. The too commonly used disorder metaphor for entropy is roundly rejected. Finally, a generalization of the equity concept that was introduced in Part III is presented. The question-answer format is continued and Key Points 5.1–5.3 are enumerated.

Questions and Answers

• *Is entropy a measure of a system's disorder?*

In general the answer is a firm “no.” A common definition of disorder is: *a lack of systematic or regular arrangement*. This has a spatial or orientational connotation and is appropriate only when there are clear spatial patterns. For example crystalline solids are typically more ordered spatially than gases. On the other hand, a sufficiently hot solid, or sufficiently large, cold solid, can have a higher entropy than a cool gas; spatial order alone does not guarantee low entropy. A proper metaphor should entail energy, which is a key ingredient in both the Clausius and Boltzmann definitions of entropy.

Introduced by Helmholtz⁵ and Boltzmann,⁶ the disorder metaphor, unfortunately, has been adopted by many textbook authors and researchers. However, dismissing entropy simply as “a measure of disorder” ignores entropy's intimate relationship with energy. This is an undesirable oversimplification of a profound physical entity. Of course, one certainly can envisage ordered motion for molecules all moving in a specified direction and relatively “disordered” motion for typical gas molecules. Yet no single definition of disorder describes molecular jiggling, spatial irregularity, orientational randomness, and the expansion of a gas to a larger volume. The energy-spreading metaphor can be applied successfully to *all* of these.

Disorder can be an unhelpful or misleading metaphor. For example, 2 m³ of copper has twice the entropy of 1 m³ under the same external conditions. But the 2 m³ sample is not more disordered in any obvious sense. There are more particles in the larger sample and more uncertainty about them, but uncertainty and disorder are *very different* concepts. The disorder metaphor is unhelpful here.

An example of a misuse of the term *disorder* is a quotation from the *Encyclopedia of Earth*: “The entropy law describes the tendency for all objects to rust, break, fall apart, wear out, and otherwise move to a less ordered state.” As observed by Styer,⁷ this is misleading because in the reaction for rust, $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_3$, the entropy change is $-549.3 \text{ J} \cdot \text{K}^{-1}$. This entropy decrease does not support a tendency toward disorder of the iron-oxygen system. Because the concomitant enthalpy change is $-1684 \text{ kJ} \cdot \text{mol}^{-1}$, the entropy change of the surroundings is $1684 \text{ kJ} \cdot \text{mol}^{-1} / 298.15 \text{ K} = 5650 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; i.e., energy spreads from the system to the environment. But

there is no evident increase in “disorder,” and the disorder metaphor is misleading. The upshot is that the disorder metaphor is unacceptable as a general interpretive tool, which has given rise to various critiques.^{8–15}

Key Point 5.1: *Disorder is generally an unacceptable metaphor for entropy. It gives the misimpression that entropy is governed by spatial or orientational regularity rather than the distribution of energy over the system's volume and spreading over accessible microstates. The disorder metaphor is not consistent with either the Clausius or Boltzmann entropy forms, each of which entails energy.*

• *Is entropy a measure of uncertainty? Missing information?*

Yes, for both. The Boltzmann entropy $S = k \ln W$ can be interpreted as a measure of uncertainty or, more specifically, missing information. Suppose a set of W possible microstates has probabilities $\{P_1, P_2, \dots\}$, where $0 \leq P_i \leq 1$ is the probability for microstate i , $i = 1, \dots, W$, and the sum of all probabilities equals one. Using methods from information theory, one can obtain a “least-biased” estimate of the individual probabilities.¹⁶

This is done by finding the set of probabilities that maximizes the Shannon missing information function, $MI \equiv -c[P_1 \ln P_1 + P_2 \ln P_2 + \dots + P_W \ln P_W]$ relative to known constraints, where $c = \text{constant}$. If the only constraint is that the sum of the probabilities is unity, the results of this procedure are: $P_i = 1/W$ for all i , and $MI = -cW(1/W) \ln(1/W) = c \ln W$. Further, if the arbitrary constant c is chosen to be k , Boltzmann's constant, the Shannon missing information function MI is identical to the Boltzmann entropy, $S = k \ln W$. Therefore, we interpret S as a measure of missing information—i.e., uncertainty.

Key Point 5.2: *Uncertainty is a good metaphor for entropy. This uncertainty is associated with the missing information about which of the W microstates with energy $E (= U)$ is occupied at any instant. The missing information approach provides a way to justify the principle of equal a priori probabilities, namely, the probability of each state being occupied is the same, $1/W$. This is also related to equity, because no microstate is favored over any other. Energy is central here because the microstates are energy states.*

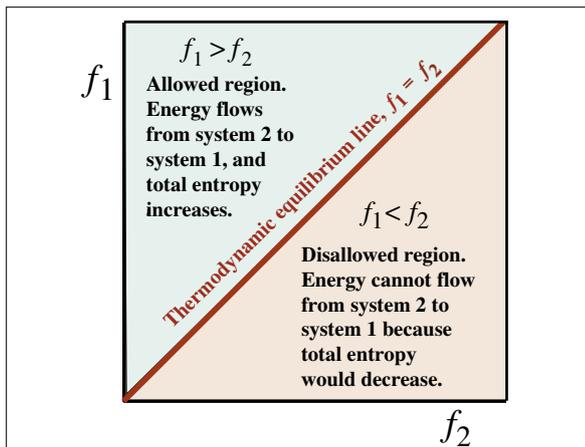


Fig. 1. Graph showing allowed and disallowed regions for an infinitesimal energy transfer from donor system 2 to receiver system 1, as described in the text. Along the 45° line, we say there is “equity,” and thermodynamic equilibrium exists.

• **How can the meaning of equitable energy distribution be understood generally?**

Here, we illustrate definitions of *equity* that are suggested using the Boltzmann entropy form. Suppose two subsystems of an isolated composite system exchange an amount of energy via a heat and/or work process. System 1 gains a small amount of energy and system 2 loses an equal amount of energy. Because entropy increases with increasing energy, the number of accessible microstates for the receiving system increases and that for the donor system 2 decreases. Because the number of accessible states increases with energy, $dW_1 > 0$ and $dW_2 < 0$. And because $S_i = k \ln W_i$ for $i = 1, 2$, and the total number of states for the composite system is $W_{\text{tot}} = W_1 W_2$ and $S_{\text{tot}} = k \ln W_{\text{tot}}$ it follows that $S_{\text{tot}} = S_1 + S_2$. The second law of thermodynamics requires that

$$dS_{\text{tot}} = k \left[\left| \frac{dW_1}{W_1} \right| - \left| \frac{dW_2}{W_2} \right| \right] = k [f_1 - f_2] \geq 0. \quad (1)$$

Here, $f_i \geq 0$ is the fractional change of the number of states in system i , for $i = 1, 2$. Equation (1) shows that to satisfy the second law of thermodynamics, system 1 cannot gain a smaller fraction of states than system 2 loses. This assures that the total number of microstates of the composite system, and thus the total entropy, increase.

Under a small energy exchange that increases the energy of system 1, energy proceeds to flow in that direction provided $f_1 > f_2$, and continues until $f_1 = f_2$, when thermal equilibrium exists. If an energy fluctuation leads to $f_1 < f_2$, the fluctuation corrects itself—i.e., there is no finite energy flow increasing the energy of system 1 because the total number of states over which the composite system can spread would decrease. This would lower the entropy and violate the second law of thermodynamics. If $f_1 = f_2$, thermodynamic equilibrium exists, and the receiving system increases its number of states by the same fraction that the donor system loses.

If a finite energy exchange were to reverse the inequality

in Eq. (1), this would violate the principle of entropy increase. Measurable energy transfers in this “wrong” direction, though possible in principle, have such low probabilities that they are not observed. A graphic view of “equity” is given in Fig. 1.

Key Point 5.3: For an isolated composite system with two subsystems, an equitable energy distribution exists when any infinitesimal energy exchange brings equal and opposite fractional changes in the numbers of accessible states of the subsystems. This signals equity in three ways: (i) the receiving and donor systems are on par with one another, with neither experiencing a greater fractional change in its number of accessible states; (ii) the number of accessible states over which the composite system can spread is maximized; away from thermodynamic equilibrium, there is less equity in that fewer states are accessible—i.e., more are excluded; (iii) the principle of equal a priori probability implies that no accessible microstate is favored over another.

Notice that if the composite system consists of two *identical* systems, the total number of states $W_{\text{tot}} = W(E_1)W(E_2)$. It is straightforward to show that W_{tot} is maximized for $E_1 + E_2 = E = \text{constant}$ for $E_1 = E_2 = E/2$. This agrees with our earlier findings regarding equity.^{2–3}

Discussion

Relating entropy to spreading is not new. Clausius hinted at it with his introduction of *disgregation*, which was mentioned in Part II,² and others have mentioned the relevance of spreading—though typically of particles rather than energy per se. Traditionally entropy has been described qualitatively in ways that do not entail energy explicitly—e.g., using the disorder metaphor, which is rejected here. This is surprising given the Clausius algorithm, $dS = \delta Q_{\text{rev}}/T$, which explicitly relates energy and entropy and the Boltzmann form $S = k \ln W$, in which W is a function of the system energy.

I examined connections between energy and entropy in three prior articles^{17–19} and independently, Lambert^{8–11} proposed a similar idea. He prefers the term “energy dispersal” rather than “spreading,” but the basic idea is the same. Authors of dozens of general and physical chemistry textbooks have adopted this concept and purged their books of references to disorder. Far better than disorder are the metaphors of entropy as spreading (or dispersal) and missing information or, equivalently, uncertainty. Together, these metaphors can help illuminate entropy.

Although no metaphor is perfect and oversimplifications can mislead,¹³ both the spreading and missing information metaphors highlight the fact that entropy is related to *choice*. Spreading a given amount of energy over a larger volume of material or adding more energy to a fixed volume results in more accessible microstates—i.e., higher multiplicity.²⁰ This results in more choice, namely, the system can spread over more states, and there is greater uncertainty—more missing information—about which microstate is occupied. Spreading and missing information provide complementary, useful views of entropy.²¹

A strength of the spreading metaphor is that it explicitly entails energy, which lies at the very heart of physics generally and thermodynamics in particular. This is explicit in both the Clausius and Boltzmann entropy equations. Additionally, spatial energy spreading can be related qualitatively to heat and work processes, which is aesthetically pleasing. This inspires an apt closing poem:

“S stands for spreading; it’s easy as can be. This mnemonic sheds light on entropy.”

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