

The Laws of Thermodynamics

Gabriel A. Lozada
Department of Economics, University of Utah,
Salt Lake City, UT 84112, USA
lozada@economics.utah.edu
801-581-7650
<https://orcid.org/0000-0001-7906-5138>

Nov. 21, 2021

Abstract. The Zeroth Law of Thermodynamics defines thermal equilibrium and temperature. The First Law defines heat, work, and internal energy so that energy is conserved. The Second and Third Laws involve entropy, whose interpretation is contested. The entropies of all chemically important substances have been experimentally determined. The Second Law indicates the direction time flows, which is the direction of entropy increase of isolated systems. In Statistical Mechanics, entropy is defined by a combinatorial formula which can but need not be interpreted probabilistically. This formula agrees with the entropy of Classical Thermodynamics. Thermodynamic entropy has nothing to do with disorder (defined intuitively): for example, copper is purified using entropy-increasing chemical processes. Thermodynamic entropy is completely unrelated to information theory despite the same mathematical functional form being used in both. The Third Law asserts that the entropy of all substances at absolute zero is identical (conventionally, zero) for all systems.

Keywords: First Law of Thermodynamics; Second Law of Thermodynamics; Statistical Mechanics; entropy; disorder; information

There are four Laws of Thermodynamics, called the Zeroth, First, Second, and Third Laws because the Zeroth Law was developed last but is now seen to be a fundamental underpinning of the other laws. The Second Law has three equivalent statements and the Third Law has two equivalent statements; proof of these equivalences can be found in Zemansky (1968). The term “entropy” is explained below.

Zeroth Law: Two systems which are in thermal equilibrium with a third are in thermal equilibrium with each other [Dugdale, 1996, p. 13].

First Law: During a process in which no heat is exchanged with the environment, the work done is only a function of the initial and final states of the system, not of the path. Furthermore, during *any* process, the change in the initial energy of the system, $U_f - U_i$, is equal to the heat flow into the system, Q , minus the net work done by the system, W : $U_f - U_i = Q - W$. [Ibid., p. 20; Zemansky, pp. 78–79].

Second Law, Kelvin-Planck statement: No process is possible whose *sole* result is the absorption of heat from a reservoir and the conversion of this heat into work [Zemansky, 1968 p. 178].

Second Law, Clausius statement: No process is possible whose *sole* result is the transfer of heat from a cooler to a hotter body [ibid., p. 184].

Second Law, entropy statement: In an isolated system, entropy is nondecreasing [ibid., p. 234].

Third Law, Unattainability statement: It is impossible to reach absolute zero by any finite number of processes [ibid., p. 498; Dugdale, 1996 p. 177].

Third Law, Nerst-Simon statement: In the limit as temperature goes to zero degrees Kelvin, the entropy change of any reaction is zero [Zemansky, p. 498; Rao, 1985, p. 257; Dugdale, pp. 160–161].

In the Zeroth Law, systems are in “thermal equilibrium” with each other if heat could flow between them but it does not, as evidenced by the observation that no characteristics of the systems change over time. The Zeroth Law is needed to be able to conceive of the idea of temperature, which is the thing that systems in thermal equilibrium with each other have in common. The First Law reflects conservation of energy, and clarifies that heat and work are measured in the same units as each other—the Joule, denoted ‘J’, the metric unit of energy (the English units being calories or BTUs)—and absorption of one unit of heat by a system increases its internal energy in the same way as when one unit of work is done on the system. “Work”

is force times distance, and since it involves distance, it is a macroscopic phenomenon; heat is a microscopic phenomenon. Internal energy changes are defined but the internal energy level has an arbitrary origin (just like gravitational or magnetic potential energy). Heat is often referred to as a “flow” even though its unit is Joules not Joules per second (a “Watt”), because both heat and work happen over time to cause changes in the stock of U . The Third Law concerns behavior near absolute zero, which has little importance for Ecological Economics except for a few points noted below.

Entropy in Classical Thermodynamics. Let T stand for absolute temperature in degrees Kelvin, denoted K. (Kelvin temperature is 273.15 degrees higher than Celsius temperature, and is named after William Thomson, also known as Lord Kelvin.) Let Q stand for the flow of heat into a material (or system, which is a collection of materials). In the “Classical Thermodynamics” developed in the mid-nineteenth century, the change in the entropy “ S ” of the material (or system) is defined to be

$$dS = dQ_{\text{rev}}/T, \quad (1)$$

where the subscript “rev” stands for a reversible process; physicists call a process “reversible” if it involves no dissipative effects such as friction, viscosity, inelasticity, electrical resistance, or magnetic hysteresis [Zemansky, 1968, p. 193, p. 215; Mackowiak, 1965, p. 59]. As Zemansky adds [ibid., p. 225], if a system undergoes an irreversible process between an initial equilibrium state i and a final equilibrium state f , the entropy change of the system is equal to the integral from i to f of dQ/T taken over any *reversible* path from i to f . No integral is taken over the original irreversible path.

Suppose one has an isolated system containing two bodies, one hot and one cold, placed in thermal contact. When a given quantity of heat, Q_0 , flows from the hotter body to the colder one, the change in entropy of the system is

$$\Delta S = \frac{-Q_0}{T_{\text{hot}}} + \frac{+Q_0}{T_{\text{cold}}}.$$

Since $T_{\text{hot}} > T_{\text{cold}}$, $\Delta S > 0$. If heat were to flow in the opposite direction, away from the colder body and toward the warmer body, then the Q_0 terms in the above equation would change sign and ΔS would be negative, violating the Second Law.

Heat can flow from a colder body to a warmer one, and thus entropy can decrease, in a *part* of a system, or in a system which is not isolated, but not in an isolated system.

The statement “in an isolated system, entropy never decreases” implicitly means that “. . . entropy never decreases as time goes forward.” It follows that the Second Law is connected with, manifests, or perhaps even

provides “Time’s Arrow,” that is, the direction in which time flows. Earlier physical laws, such as Newton’s Laws of Motion, are symmetric in time: in their mathematical forms, substituting $-t$ for time t generates true statements, which is called “T-symmetry.” The Second Law is time-asymmetric.

Given two dates t_1 and $t_2 > t_1$, the entropy of an isolated system at t_1 is less than the entropy of the system at t_2 : $S_1 < S_2$. The Second Law means it is then impossible to reverse all of the changes which have happened in this isolated system between t_1 and t_2 —assuming the system remains isolated—because such a reversal would imply a decrease of entropy. This rules out “perpetual motion machines of the second kind.”

Entropy changes can be measured in laboratories. The entropy change undergone by a quantity of copper as its temperature is raised from 300 K to 312 K could be measured if one used a heat source known to deliver “ j ” Joules per minute to the copper. If it took t minutes to heat the copper, ΔS would approximately be the heat flow, $j \cdot t$ Joules, divided by the average temperature, 306 K. A more accurate procedure would be to find the number of minutes t_1 needed to raise the temperature from 300 K to 301 K, multiply it by j , and divide the result by the average temperature, 300.5 K, obtaining the entropy change $\Delta S_1 = jt_1/300.5$; then find the number of minutes t_2 needed to raise the temperature from 301 K to 302 K, multiply it by j , and divide it by the average temperature, 301.5 K, obtaining the entropy change $\Delta S_2 = jt_2/301.5$; and so forth, until 312 K is reached; then sum all the ΔS_i ’s. More precise methods show the entropy change from 0 K to “standard temperature” (298.15 K) under standard pressure (0.987 atmospheric pressure) of 1 mole (approximately 63.5 g) of copper in the solid state is 33.3 J/K. Since such “standard entropies” involve 0 K, which is not attainable, the entropy change near absolute zero cannot be obtained experimentally and instead has to be obtained theoretically by appealing to the Third Law.

The “heat capacity” of a substance (its “specific heat”) is the amount of heat or work needed to raise the temperature of one gram of the substance by one degree Kelvin (or Celsius). As a general rule, near room temperature, metals have low heat capacities (witness aluminum foil cooling quickly when removed from an oven), water has a high heat capacity (witness water on a stove taking a long time to boil), and most other household substances have heat capacities in between them. Letting C_p denote the ‘heat capacity at constant pressure’ of a substance, one can (assuming no phase changes) rewrite (1) as

$$\Delta S = \int_i^f \frac{C_p(T)}{T} dT \quad (2)$$

where ‘*i*’ denotes some initial reference state and ‘*f*’ denotes the state of interest. It follows that near room temperature, metals will tend to have low ΔS values (low entropy changes), water will have a high ΔS , and other common household substances usually have ΔS in between those two.

Using tables of entropy changes for different substances measured in laboratories under standard conditions, the entropy-increasing, and hence spontaneous, direction for chemical reactions can be computed. (This is more commonly done in an alternative but equivalent way using Gibbs Free Energy, as discussed below.) What can be computed is not only the initial direction of the chemical reaction, but also the precise equilibrium proportions of the different chemicals. (While the *equilibrium* direction and extent of any chemical reaction can be determined, not all chemical systems go to equilibrium: some get stuck in a “metastable” state in which an “activation energy” barrier blocks their path to the equilibrium unless the reaction occurs in the presence of a catalyst, which works by supplying the activation energy, which is then returned in full to the catalyst.)

To calculate the total entropy change when an event occurs, the resulting entropy change of the system’s surroundings must be added to the entropy change undergone by the system itself. Under conditions of constant pressure and temperature, the former is “the energy released by the system into its environment” (traditionally represented by $-\Delta H$) times $1/T$, and the latter is ΔS . Adding these two entropy changes together yields a total entropy change of $\Delta H/T - \Delta S = (1/T)(\Delta H - T\Delta S) = (1/T)\Delta G$ where ΔG is known as the “Gibbs Free Energy.” Tables of Gibbs Free Energies of common substances are readily available, and since such a table is all one needs to determine how entropy changes when an event occurs under conditions of a tabulated constant pressure and temperature, Gibbs Free Energy extremely valuable for chemists. This should not obscure the fact that it is overall entropy change, not Gibbs Free Energy, which is the fundamental physical quantity. Similarly, Helmholtz Free Energy $F = U - TS$ (where U is internal energy) is useful in situations where volume and temperature T are constant, but it is not a fundamental quantity either. (See also Beard and Lozada, 1999, Section 5.5 and footnote 10, and Lozada, 1999, Appendix.)

Although there is no such thing as “low-entropy energy,” it is possible to define the entropy of a collection of photons—a “photon gas.”

Another connection between entropy and energy is Lord Kelvin’s “principle of the degradation of energy,” which states that whenever an irreversible process takes place, the effect on the universe is the same as that which would be produced if a certain quantity of energy were converted from a form in which it was completely available for work into a form in which it is completely unavailable for work. This amount of energy is the

temperature of the coldest available heat reservoir times the entropy change of the universe brought about by the irreversible process [Zemansky, 1968, pp. 236, 237, 239]. As a consequence of this Principle, it is never desirable to recycle energy, because accomplishing such recycling requires using up more energy than would be regenerated.

If all the energy in a system has been degraded, the system is in thermodynamic equilibrium, incapable of further entropy increases and therefore incapable of doing further work. Kelvin's concept of the "Heat Death of the Universe" applied this idea to the universe. Lozada (2017) modeled optimal economic growth if economic activity causes acceleration of the heat death of the solar system.

The first application of entropy was to "heat engines"—devices, such as internal combustion engines and steam engines (such as occur in both conventional and in nuclear power plants), which use temperature differences to do their work. The "efficiency" of a heat engine is defined to be its work output divided by its heat input. An important implication of the Second Law is that the maximum efficiency of any heat engine operating between the temperatures T_{low} and T_{high} is $1 - (T_{\text{low}}/T_{\text{high}})$. This is less than 1 because T_{low} is strictly greater than zero due to the unattainability statement of the Third Law. While this establishes a boundary beyond which technological progress will never cross, it only applies to heat engines, and not all engines are heat engines: heat pumps are not (they are heat engines in reverse); fuel cells are not since they do not transfer energy in the form of heat; and living animals are not, even though their muscles resemble engines in that they can do mechanical work, because like fuel cells they do not do work by transferring energy in the form of heat.

Entropy in Statistical Mechanics. While equation (1) gives a precise definition of entropy, it does not explain theoretically why the entropies (or specific heats) of different substances are what they are; it provides no intuitive interpretation of entropy. A theoretical model of entropy, called Statistical Mechanics, was provided by Ludwig Boltzmann (followed by Josiah Willard Gibbs) in the late nineteenth century.

To explain Boltzmann's model, Table 1 illustrates a system composed of $N = 3$ particles (think of them as being electrons), three energy levels, and Total Energy = 6 eV ("eV" stands for "electron volts" and is a unit of energy, approximately $1.6 \cdot 10^{-19}$ J). The electrons can be in any energy level as long as the energy of the entire system is equal to its Total Energy. There are only two ways to arrange the three particles between the three given energy levels that are consistent with the total energy level being 6eV. These two ways, called "Macrostates," are shown in the two columns

	a Macrostate	another Macrostate
Electrons' energy levels	3 eV ————— 2 eV —●●●— 1 eV —————	3 eV —●— 2 eV —●— 1 eV —●—
Macrostate	three in 2 eV	one in 1 eV, one in 2 eV, one in 3 eV
Microstates: in 3 eV		A A B B C C
in 2 eV	ABC	B C C A A B
in 1 eV		C B A C B A
Number of Microstates	$\frac{3!}{0!3!0!} = 1$	$\frac{3!}{1!1!1!} = 6$
Probabilistic Interpretation	1/7 of the time	6/7 of the time
Non-probabilistic Interpretation	0% of the time	100% of the time

Table 1: $N = 3$ particles. Total Energy = 6 eV.

of the Table. The “Microstates” rows pretend that the electrons are distinguishable from each other and give each electron a name: A or B or C. Those rows then illustrate all the microstates which are compatible with the given 6 eV macrostate. Next is the Table’s “Number of Microstates” row, showing the formula which gives the correct number of different microstates corresponding to each of the Tables’ macrostates. With $N = \sum_i N_i$, the expression

$$\frac{N!}{N_1! N_2! \dots N_m!} \quad (3)$$

in combinatorics is called a “multinomial coefficient”; it measures the number of distinguishable permutations of N particles when there are N_i indistinguishable particles of type i . In Table 1, the “Number of Microstates” row is explained by (3), since we consider the electrons to actually be indistinguishable from each other. In the Table’s “Probabilistic Interpretation” row, each macrostate is predicted to occur with the following probability: “the number of microstates compatible with it” divided by “the sum of the number of microstates compatible with each of the system’s macrostates.” (“Compatible” here means “consistent with the system’s total energy and with the macrostate’s first row in the Table.”) In the Tables’ “Non-probabilistic Interpretation” row, the macrostate with the greatest number of compatible macrostates is assumed to occur 100% of the time.

In actual physical systems, there are usually many electrons and energy levels, and therefore very many possible macrostates, and, typically, one of the macrostates would, under the Probabilistic Interpretation, occur with probability much greater than 99.99%. Therefore, it has been experimentally impossible to test whether the Probabilistic or Non-probabilistic Interpretation is correct, because one never observes the system in any macrostate other than the “most probable” (modal) one.

The probabilistic interpretation of the Entropy Law would allow occasional spontaneous decreases in entropy, which the Classical Entropy Law would never allow, and which are never observed. Thus the Probabilistic Interpretation would seem to be wrong. The proponents of the Probabilistic Interpretation reply that it could be right because it predicts the probability of entropy decreases in isolated systems to be so close to zero that they claim this is consistent with no one ever having observed any yet. This debate is important to philosophers of science, but most physicists do not care which interpretation is used because there is no experimentally observable difference between “a probability of zero” and “a probability of x ” for sufficiently small x .

Suppose a system has N particles; E total energy; and m energy levels e_1, e_2, \dots, e_m . The macrostate which the Probabilistic Interpretation says will occur with highest probability, and which the Non-probabilistic Interpretation says will occur with probability 100%, is the state which solves

$$\max_{N_1, N_2, \dots, N_m} \frac{N}{N_1! N_2! \dots N_m!} \quad \text{such that} \quad \sum_{i=1}^m N_i e_i = E \quad \text{and} \quad \sum_{i=1}^m N_i = N. \quad (4)$$

Let $N_1^*, N_2^*, \dots, N_m^*$ denote the maximizing values of N_1, N_2, \dots, N_m . In physics, the objective function of (4), (3), is traditionally given the symbol “ W ” (from the German for probability, *Wahrscheinlichkeit*); denote its maximized value by W^* .

Note that the N_i ’s which maximize W are the same as the N_i ’s which maximize $k \ln W$ if k is any positive constant, since the natural logarithm is an increasing function of its argument. In the Non-probabilistic Interpretation of Statistical Mechanics, if one defines entropy by

$$\text{Entropy} = S = k \ln W^* = k \ln \frac{N!}{N_1^*! N_2^*! \dots N_m^*!} \quad (5)$$

then changes in the entropy so defined, when applied to an ideal monatomic gas, agree with entropy changes derived from the Classical kinetic theory of an ideal gas based on (1) if k is assigned the value 1.38×10^{-16} ergs/K, a

value of k now known as “Boltzmann’s Constant” [Zemansky, 1968, p 265]. In the Probabilistic Interpretation of Statistical Mechanics, if one defines entropy as being a random variable which is the following function of the random variables N_1, N_2, \dots, N_m :

$$\text{Entropy} = S = k \ln W = k \ln \frac{N!}{N_1! N_2! \dots N_m!} \quad (6)$$

where $\sum_{i=1}^m N_i e_i = E$ and $\sum_{i=1}^m N_i = N$, then changes in the mode of this distribution—the mode being the only value ever experimentally observed—agree with entropy changes derived from the Classical kinetic theory of an ideal gas based on (1) if k equals Boltzmann’s Constant.

The equation (1) from Classical Thermodynamics defines only changes in entropy; absolute amounts of entropy are not defined. Equations (5) and (6) can be made consistent with this idea by adding an arbitrary constant S_0 to their right-hand sides. It is sometimes asserted that, instead, in Statistical Mechanics absolute entropy is defined—equivalently, that the constant S_0 *must* be zero. This is not true [Dugdale, 1996, p. 99]; Max Planck’s erroneous treatment of this issue can be replaced by the one in Beard and Lozada [1999, p. 118 fn. 12], which retains Planck’s conclusion that the only functional form which could link W and entropy is the logarithm. This controversy has no bearing on laboratory entropy measurements, and thus on scientific practice, because laboratories only measure entropy differences.

Fallacies: Disorder and Information. One of the most surprising consequences of equation (1) comes from analyzing the mixing of two ideal gases in a container whose walls allow no heat to flow. (An “ideal” gas has molecules which do not interact with their neighbors.) The formula textbooks give for the resulting change of entropy—which is

$$\Delta S = -R \left[n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2} \right] \quad (7)$$

where n_1 and n_2 are the moles of the gases and R is the universal gas constant, 8.31 J/(K · mole)—seems wrong, because since no heat can flow into or out of the container, it seems from (1) that the system’s entropy cannot change. Observers confused by this have even said that (7) represents a new type of entropy, called “configurational entropy” or “the entropy of mixing,” which is different from the equation (1)’s entropy, which they call “thermal entropy.” Actually, however, (7) and configurational entropy are merely other manifestations of thermal entropy, because entropy change is not $\int_i^f dQ/T$ (which is zero in the case of mixing) but rather $\int_i^f dQ/T$ over

a reversible path. The mixing of two ideal gases is not reversible. The only way to calculate the entropy change accompanying the mixing of two ideal gases is to replace the original irreversible path linking the states before and after the mixing with a reversible path linking those same states, then performing the integration. Along the reversible path, heat does flow, and the entropy change (1) turns out to agree with (7). (See Beard and Lozada, 1999, pp. 86–88.)

The result that mixing two gases increases entropy has led observers to mistakenly think that there is more to the idea of entropy than expressed by (1)—that entropy measures increasing mixing, or spatial disorder, or even some general notion of “order,” *per se*. It should be stressed that increasing entropy does *not* in general mean increasing disorder in any intuitive sense. For example, the spontaneous—i.e., entropy-increasing—evolution of an oil/water mixture is towards “oil on the top, water on the bottom,” which is hardly increasing disorder. Treatments which ignore this caveat, such as Erwin Schrödinger’s famous 1944 essay *What is Life* and the enormous literature inspired by it, need to be read with the greatest caution. Moreover, far from being a source of disorder, we learn from Ilya Prigogine that the transformation of entropy from low to high can bring about wonderful “dissipative structures” including, according to Wicken (1987), life on earth.

The industrial purification of common copper ores illustrates entropy-*increasing* processes which result in *increasing* “order,” intuitively defined. Because CuO is thermodynamically stable at room temperatures, breaking it up into copper and oxygen would cause an entropy decrease, so cannot occur spontaneously, but pure copper still can be produced via the introduction of sulfuric acid: a typical reaction is $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{Cu}^{++} + \text{SO}_4^{-} + \text{H}_2\text{O}$ [Biswas and Davenport, 1994 p. 15], which increases entropy and is thus spontaneous. Obtaining pure copper from Cu_2S is done by “burning” the ore: Cu_2S is thermodynamically metastable, and at sufficiently high temperature, entropy-increasing purification reactions such as “ $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2 + \text{energy}$ ” occur, reactions which are so exothermic that the process is autothermal at 1500 K. (See Beard and Lozada, 1999 (5.8); Biswas and Davenport, *ibid.* pp. 194 and 198.)

In typical physical systems the values of the N_i ’s in (5) and (6) are sufficiently large that physicists assume Stirling’s Formula $n! \approx n \ln n - n$ is a good approximation. It can be shown that this implies from (5) that

$$\text{Entropy} = S = k \ln W^* \approx -kN \sum_{i=1}^m \frac{N_i^*}{N} \ln \frac{N_i^*}{N} .$$

The similar expression $\sum_i x_i \ln x_i$ appears in the field of information theory, with of course entirely unrelated meanings for the symbols. This does not imply any connection between thermodynamic entropy and information, any more than the similarity between the formula for the sum of scores on two student examinations ($e_1 + e_2$) and the formula for the sum of the energy of two hotel elevators ($e_1 + e_2$) implies any connection between student examination scores and hotel elevators. The “entropy” that appears in information theory, and that sometimes appears in related fields such as econometrics, has nothing to do with physical entropy, nor with the Second Law of Thermodynamics. (Much has been written on this topic; see the references in Beard and Lozada, 1999, pp. 109–111.)

BIBLIOGRAPHY

- Beard, T. Randolph, and Gabriel A. Lozada (1999), *Economics, Entropy and the Environment: The Extraordinary Economics of Nicholas Georgescu-Roegen*. Cheltenham, UK: Edward Elgar.
- Biswas, A. K., and W. G. Davenport (1994), *Extractive Metallurgy of Copper [Third Edition]*. Oxford: Pergamon Press.
- Dugdale, J. S. (1996), *Entropy and its Physical Meaning*. Bristol, Pennsylvania: Taylor & Francis Inc.
- Lozada, Gabriel A. (1999), “The Role of Entropy and Energy in Natural Resource Economics.” In J. M. Goudy and Kozo Mayumi, eds., *Bioeconomics and Sustainability: Essays in Honor of Nicholas Georgescu-Roegen*. Hants, England: Edward Elgar.
- Lozada, Gabriel A. (2017), “The Hotelling Rule for Entropy-constrained Economic Growth,” *Ecological Economics* **133**: 35–41.
- Mackowiak, J. (1965), *Physical Chemistry for Metallurgists*. New York: American Elsevier.
- Rao, Y. K. (1985), *Stoichiometry and Thermodynamics of Metallurgical Processes*. Cambridge: Cambridge University Press.
- Wicken, Jeffrey S. (1987), *Evolution, Thermodynamics, and Information: Extending the Darwinian Program*. New York: Oxford University Press.
- Zemansky, Mark W. (1968), *Heat and Thermodynamics: An Intermediate Textbook [Fifth Edition]*. New York: McGraw-Hill.