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Entropy Without Carnot Cycles

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Introduction

In the teaching of chemical thermodynamics, a compromise must often be struck between rigour and haste, and inevitably entropy - the most confusing and foundational concept of all - leaves students lost and dissatisfied. In the author's opinion, the most common approaches taken in textbooks contribute to this situation. On the one hand, axiomatic texts, such as Callen (1960), postulate the existence and properties of entropy up front, but provide little rigorous justification. This is helpful for clearly demonstrating the mathematical structure of the theory, and for moving on to more advanced topics, but does not necessarily ground the students' knowledge. Alternatively, texts such as Denbigh (1981), Kardar (2007) or Dugdale (1996), prove the existence of entropy and temperature via historical arguments built upon the laws of thermodynamics, and in particular the properties of Carnot cycles (in some cases requiring elaborate arrays of infinitely many infinitesimal Carnot cycles to fully work out their points.) These arguments are reasonably rigorous, but may take more time to carefully work through than is practical in an application-oriented course, and even when their logic is understood, they don't necessarily shed much light on the physical significance of entropy. Recently, several authors have suggested introducing entropy as a measure of the 'spread' of energy (Leff, 1996; Lambert 2002). While this definition may provide a helpful qualitative understanding of the concept, it is difficult to explain its connection to the mathematical definition of entropy, $dS = dQ_{\text{rev}}/T$ in a closed system, and such a definition also runs the risk of obscuring the intimate connection between entropy (a concept students know they don't understand) and temperature (a concept students don't know they don't understand.) Yet another approach is to ignore the macroscopic definition of entropy, and instead motivate the subject from a statistical or information theoretical perspective. However, as Callen (1960) observed, 'The fundamental-ity and profundity of statistical mechanics are treacherously seductive,' and 'the amalgamation of thermodynamics and statistical mechanics...tends to eclipse thermodynamics.' More seriously, motivating entropy in a purely statistical way runs the risk of divorcing the students' intuitive understanding of entropy (as $S = k \log W$ or $S = -k \sum p_i \log p_i$) from the practical definition,

$dS = dQ_{\text{rev}}/T$, on which chemical thermodynamics is built. Furthermore, the foundations of statistical mechanics are a particularly subtle and controversial area of active research, and in many respects the internal consistency of macroscopic thermodynamics, founded solely on a few self-evident phenomenological laws, is preferable to deep questions of ergodicity or eigenstate thermalisation.

The purpose of this article is to demonstrate that entropy and temperature can be defined clearly and rigorously, and all their key properties proved (entropy is a state function, it is additive, and it never decreases in an isolated system; temperature is a state function, and heat never flows from low temperature to high temperature) via purely macroscopic arguments, and without recourse to Carnot cycles. Instead, we define entropy directly as heat that must be supplied by a heat bath at unit temperature during a reversible process. We show that this definition is consistent with various intuitions of entropy (entropy as 'disorder', as the 'spread of energy', and as related to the probability of a particular macrostate), while at the same time being transparently connected to the mathematical definition $dS = dQ_{\text{rev}}/T$, as required for practical calculations. In what follows, we follow a slower, didactic route, which we hope will be of use to both teachers and their students.

A Brief Prelude: The Laws of Thermodynamics

The laws of thermodynamics are the axioms upon which the rest of macroscopic thermodynamics is constructed. We will require the first and the second laws for the arguments that follow.

First Law: The total energy of a system which is completely isolated from the rest the universe is constant.

Second Law (Clausius): No process may have the sole effect of converting heat from one body completely into work.

While the first law is now part of our cultural heritage, it is far from obvious. After all, when a rolling car comes to a stop, its kinetic energy seemingly vanishes. Of course, thanks to the careful calorimetric experiments of Joule and others, we now know that

whenever kinetic energy is lost due to friction, an equal amount of heat is produced, and this is stored as internal energy in the slightly warmer bodies heated up by the friction. When such changes in the internal energy are accounted for, energy is indeed conserved.

The second law provides a directionality to the universe. It is possible to convert work completely into heat via friction, but the second law says this process can never be reversed. Heat may be generated as a rolling car gradually comes to a halt, but a car will never spontaneously start moving as it cools its surroundings down. Of course, heat can be converted into work (otherwise a fossil fuel powered car couldn't run at all) but the second law says there will always be some inefficiency, some waste heat. This inherent directionality is closely related to the definition of a reversible process:

Reversible Process: A process which can be completely reversed, so that the entire universe (both the system and its surroundings) can be brought back to its original state.

It is important to emphasise that reversibility requires the restoration of the *entire universe* back to its original state, and not just the system. If a system changes its state from $A \rightarrow B$, it is not enough for us to be able to run a reverse process $B \rightarrow A$; we must restore $B \rightarrow A$ and must *also* restore the surroundings to their original state. The second law implies that frictional processes are inherently irreversible, because once work is fully converted into heat via friction, it cannot be fully converted back, at least not without affecting some other part of the universe. Note also that this definition makes no reference to 'infinitely slow processes' or 'infinitesimal driving forces'; such ideas may (or may not!) follow as a consequence of the above definition, but they are not the definition itself.* We also require the following definition:

Heat Bath: A body of constant volume much larger than the system of interest, so that its intensive properties may be taken as constant.

Entropy and Temperature

The change in the *entropy* of a closed system between any two states A and B is traditionally defined by the following integral, taken over *any* reversible transition between the two states:

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ}{T} \quad (1)$$

where the thermodynamic temperature, T , is defined in terms of Carnot cycles. It is somewhat surprising that this integral is path-independent, especially as $\int_A^B dQ$ is a path function. Mathematically, $1/T$ acts as an integrating factor for dQ , ensuring dQ/T

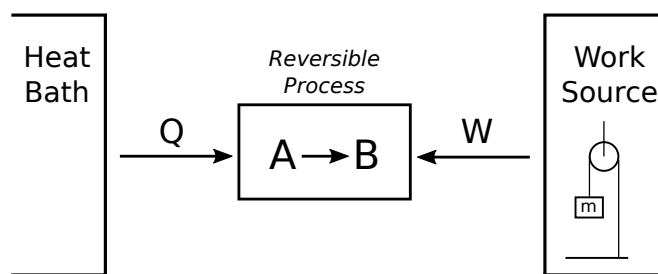


Fig. 1 A system reversibly transforming from $A \rightarrow B$ while absorbing heat and work.

is an exact differential. The various proofs that Eq. (1) defines a state function are quite complicated, and they shed little light on the integral's physical meaning.

Consider, instead, the closed system shown in Figure 1. The system is transitioning from $A \rightarrow B$, and in the process is receiving heat, Q , from a heat bath and work, W , from a suspended weight. In general, while the *total* energy absorbed by the system depends only on its initial and final states ($Q + W = \Delta U = U_B - U_A$) the *individual* heat and work flows are path functions. However, if the process is conducted reversibly, Q and W in Figure 1 become state functions as well. This is easily demonstrated.

Suppose not. Suppose there *were* two different reversible processes in which $A \rightarrow B$, such that the system absorbed more heat (and correspondingly less work) in the first process than in the second. Then run the first process in the forward direction, moving from state A to state B , and then run the second process in reverse, converting the system from state B back to state A . The net effect (see Figure 2) is to remove heat from the heat bath and convert it completely into work, breaking the second law. Therefore, if the process shown in Figure 1 is conducted in a reversible manner, Q depends only on the initial state, A , the final state, B , and the heat bath from which heat is drawn.[†]

This new state function is closely related to the entropy: all that remains is to specify which heat bath the heat is drawn from. Suppose we have some standard heat bath in a reproducible state, and let us specify a temperature scale by arbitrarily stipulating that this bath is at unit temperature. Then we have the following definition:

Definition A. The change in the *entropy* of a closed system between two states A and B is the heat the system must absorb from a unit temperature heat bath during any reversible process $A \rightarrow B$ (Figure 3).

The principle advantages of this definition of entropy are the physical clarity of Figure 3, and the simplicity of the proof that entropy, so defined, is a state function. By the time entropy is

* We can easily imagine an 'infinitely slow process' that is irreversible: heat flowing from a hot body to a cold body through an exceptionally well insulated wall is a straightforward example; no matter how slow the heat flow may be, it can never be reversed, at least not without some other part of the universe being affected. The idea of 'infinitesimal driving forces' is closer to the idea of reversibility (see Denbigh (1981) or Callen (1960)), but the definition above is clearer and more straightforward to apply.

[†] Q does not depend on the source of mechanical work. Because ideal mechanical processes are perfectly reversible, the second law makes no statement about the distribution of energy among purely mechanical energy sources.

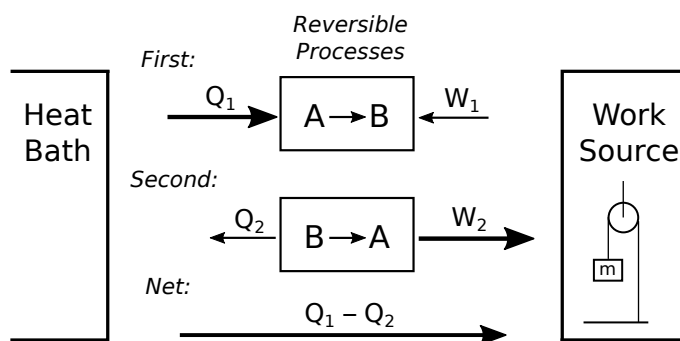


Fig. 2 If the heat absorbed from a heat bath during a reversible transition $A \rightarrow B$ could take two different values, Q_1 and Q_2 , then by running $A \rightarrow B$ followed by $B \rightarrow A$, heat could be converted directly into work, breaking the second law. Larger arrows indicate greater energy flows.

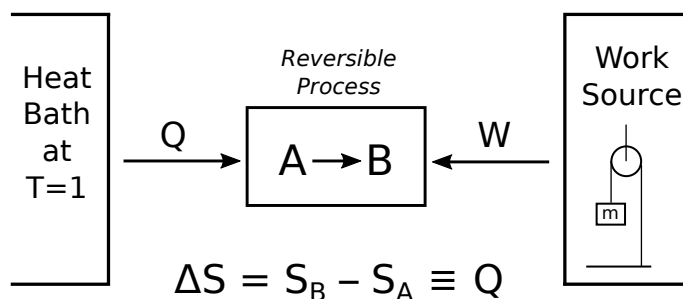


Fig. 3 The definition of the change in *entropy* of a system: the heat it must absorb from a unit-temperature heat bath during any reversible transition.

introduced, students are well aware that, unlike ΔU , Q and W are both path functions. To then show them the one situation in which Q is also a state function, and to relate this directly to the entropy, is intuitively straightforward. We may define the thermodynamic temperature in a similar way:

Definition B. If, during a reversible transition $A \rightarrow B$, a system absorbs T times more heat when connected to some heat bath, H , than it does when absorbing heat from a unit-temperature heat bath, then the *temperature* of this heat bath, H , is equal to T (Figure 4).

The temperature describes the variation in Q for different heat baths; it is *defined* to ensure that, whatever heat bath is used, $Q_{\text{rev}}/T = \Delta S$ will be same for any reversible transition $A \rightarrow B$. The above definition differs slightly from standard scientific practice, in that we define a unit-temperature reference state rather than defining, say, the triple point of water to have a temperature of 273.16. But this is merely a matter of convention, and we find the simplification clarifies rather than obscures the underlying ideas. We now prove that entropy and temperature, as defined above, have all their expected properties.

Properties of Entropy and Temperature

The entropy of an adiabatically isolated system cannot decrease.

Suppose not. Suppose that the entropy of an adiabatically isolated system did decrease in some pro-

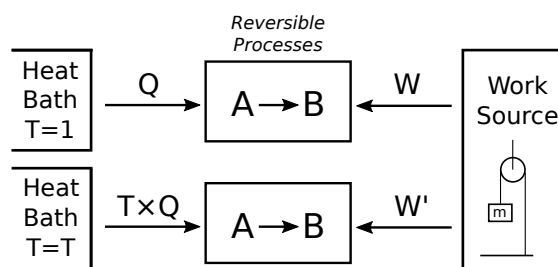


Fig. 4 The definition of the *temperature* of a heat bath: the increase in the heat it must supply during a reversible process, relative to the reference heat bath at unit-temperature.

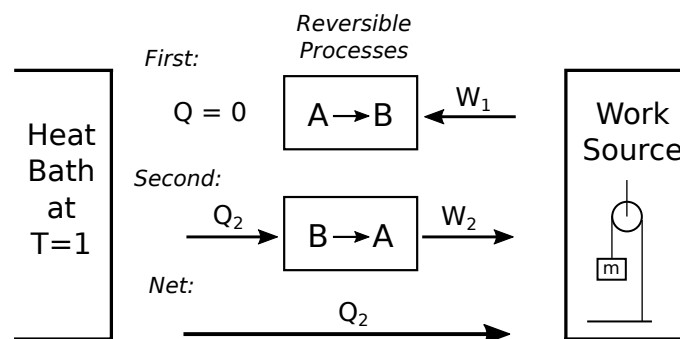


Fig. 5 Proof that the entropy of an adiabatically isolated system cannot decrease. If it did decrease, then by running the backwards process in a reversible way, heat could be converted directly into work, breaking the second law.

cess $A \rightarrow B$. Then imagine first running the process $A \rightarrow B$ under adiabatic conditions, and then running a *reversible* process $B \rightarrow A$ with the system connected to a unit-temperature heat bath (Fig. 5). Because $A \rightarrow B$ involves a decrease in the entropy, $B \rightarrow A$ involves a corresponding increase, and so heat is absorbed from the heat bath. The net effect, then, would be to remove heat from the heat bath and transform it into work, breaking the second law. Therefore, entropy cannot decrease in any adiabatically isolated process.

A corollary to this is that entropy is constant in a reversible, adiabatically isolated process, $A \rightarrow B$, as $S_B - S_A \geq 0$ and $S_A - S_B \geq 0$ imply that $S_B = S_A$.

The entropy is additive.

This is best seen by example. Suppose some process $A \rightarrow B$ has entropy change ΔS_1 , and some other process $C \rightarrow D$ has some other entropy change ΔS_2 . Then a composite system composed of A and C transforming into a composite system composed of B and D will involve entropy change $\Delta S_1 + \Delta S_2$ (see Fig. 6), because the heat that must be reversibly absorbed is additive.

Temperature is a state function.

It is not yet clear that the *temperature* of a heat bath, as defined above, is unique. We have said that if, in some

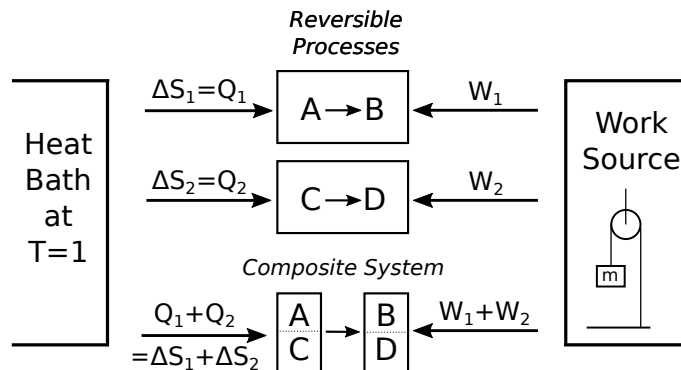


Fig. 6 The entropy is additive. If Q_1 must be supplied during the reversible transition $A \rightarrow B$, and Q_2 must be supplied during the reversible transition $C \rightarrow D$, then to transform a composite system A and C to a new system composed of B and D , then the heat supplied must equal $Q_1 + Q_2$.

reversible process $A \rightarrow B$, a system must absorb T times more heat from some heat bath, H , than it did from a unit-temperature heat bath, then the temperature of H is T . But what if there were another reversible process $C \rightarrow D$, such that the system absorbed T' times more heat from H than it did from a unit-temperature heat bath, with $T' > T$? If that were the case, the temperature of the heat bath H would not be well defined. However, such a situation is not possible. To see this, suppose it were possible, and suppose, without loss of generality, that $S_B - S_A > 0$ and $S_D - S_C > 0$. Then imagine we had many replicates of A and of D , and suppose we first set them up so they all transformed reversibly from $A \rightarrow B$ and $D \rightarrow C$ while connected to a unit-temperature heat bath (Figure 7.) Suppose we then connected the resulting systems to the heat bath H , and allowed the reversible processes, $B \rightarrow A$ and $C \rightarrow D$, to run. Now, if we chose *just* the right number of replicates of A and D so that there was no net flow of heat into or out of the unit-temperature heat bath in the first step, then the net effect of this process would be to remove heat from H and convert it completely into work, breaking the second law. Therefore, we cannot have $T' > T$ (or, similarly, $T > T'$), and so temperature is a well-defined function of state.

Heat cannot flow from low temperature to high temperature.

Suppose not. Suppose that heat *could* spontaneously flow from a low temperature heat bath, H_L , to a high temperature heat bath, H_H . Then consider any process $A \rightarrow B$ such that $S_B - S_A < 0$, and suppose we do the following. First, we run $A \rightarrow B$ reversibly while dumping heat from H_L . Then we run the reverse process $B \rightarrow A$ reversibly while drawing heat from H_L . Finally, we allow heat to flow in the wrong direction, from H_L to H_H , until H_L has lost all the heat that was dumped into it in the reversible process $B \rightarrow A$. Then the net effect will be to draw heat from the heat bath H_H and to convert it completely into work, breaking the second law. There-

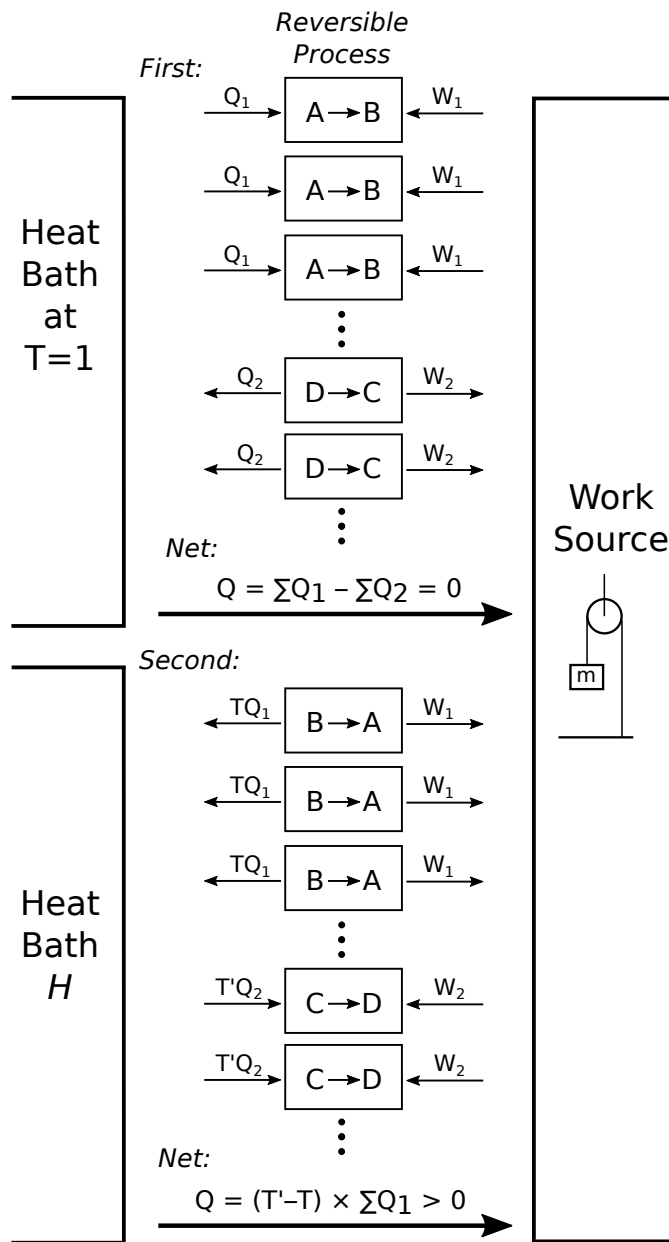


Fig. 7 The temperature of a heat bath is a state function that is independent of the particular process by which it is measured. If this were not the case, a large array of identical systems could be used to convert heat directly into work, breaking the second law.

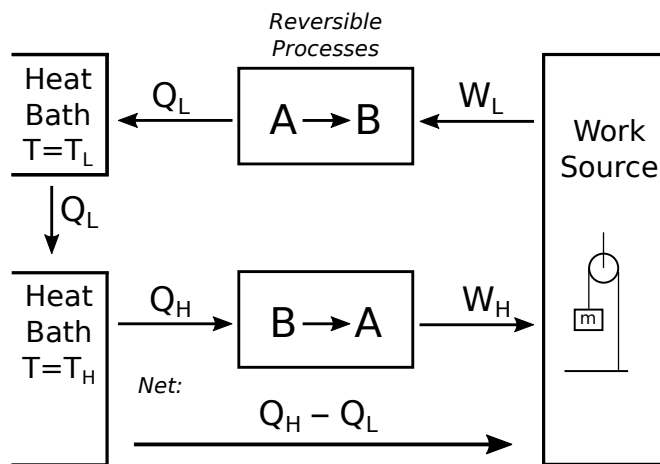


Fig. 8 Heat cannot flow from low temperature to high temperature. If it could, then by first running a reversible process $A \rightarrow B$ connected to a low-temperature heat bath, and then running the backwards process $B \rightarrow A$ reversibly while connected to a high-temperature heat bath, and finally allowing heat to flow from the low- to the high-temperature bath, heat can be directly converted into work, breaking the second law.

fore, heat cannot spontaneously flow from low to high temperature.

Discussion and Conclusion

The goal of this article was to provide an alternative, macroscopic definition of both entropy and temperature, which were equivalent to the traditional definitions but simpler to understand, and for which the basic properties of each function could be proved in a straightforward manner. Such definitions having been presented, this article could (and perhaps should!) be wrapped up here. However, we would like to briefly outline a few ways in which such a direct definition grounds a deeper intuition for these difficult concepts.

As noted above, the *logical* clarity of Definition A and the *visual* clarity of Figure 3 are in many ways preferable to the mathematical difficulties associated with Eq. (1), and these definitions and figures may also assist in the development of *conceptual* clarity. Why is Q^{rev} in Figure 3 a state function? And what has the system *gained* in reversibly absorbing this heat? While the answers are not obvious, at least the questions are clear. And all intuitive notions of entropy - as disorder, or the dispersal of energy, or some measure of probability - must work in this simplest possible case. We now briefly outline, on an informal level, how some of these intuitive ideas may be linked to Definition A above.

Consider entropy as 'disorder' - a term that has been criticised in recent years (Lambert, 2002), but which does have a reasonable pedigree.[‡] If we wanted to quantify 'disorder', we would need a reference by which it may be measured: a system which contains some standard quantity of disorder. It seems reason-

able to suppose that (for any sensible definition of disorder) the addition of heat to a heat bath will increase the bath's disorder (think of the effect of the heat spreading among the random motions of the bath's constituent molecules.) Let's define one unit of 'disorder' as the effect of the addition of one unit of heat on the molecules of a reference heat bath which we will define to be at unit temperature. In a similar way, any sensible definition of 'disorder' should lead to a quantity that can never decrease in time, and this implies disorder must be conserved in any reversible process. Thus, when the disorder of a heat bath decreases in a reversible process, an equal amount of disorder must 'flow' into the heat bath's surroundings, increasing the surrounding's disorder by an equal amount. In this way, the disorder of any system may be measured in reference to the heat it reversibly exchanges with a reference heat bath. The analogy between entropy and 'disorder' should be clear.

Alternatively, we may consider the intuitive notion that energy tends to spread out as evenly as possible among the various macroscopic and microscopic 'degrees of freedom' in which it may be stored. Work may be converted into heat because energy will happily spread out into many microscopic movements, but the reverse is impossible, as energy dispersed over many random molecular motions will not spontaneously order itself into a single macroscopic degree of freedom, such as the height of a weight. Consider a system undergoing a reversible, isoenergetic process (i.e. $\Delta U = 0$) while connected to a unit-temperature heat bath. Then if the system absorbs heat it must do an equal amount of work, and in this manner energy dispersed over perhaps 10^{25} microscopic degrees of freedom (heat) is converted into energy concentrated in a handful of macroscopic degrees of freedom (work). In order to compensate for this concentration of energy from heat into work, the energy inside the system itself must spread out (perhaps as its volume expands or its phase changes), so that, overall, there is no net concentration of energy. In this special case, then, $Q^{\text{rev}} = \Delta S$ represents the degree of energy dispersal that occurs *inside* the system: the spread of energy inside the system is great enough to compensate for the concentration of Q^{rev} worth of unit-temperature heat into work. For an isolated system (for which we also have $\Delta U = 0$) entropy never decreases because the energy in the system will always tend to spread out. This approach may also motivate temperature: the heat in hotter bodies is more concentrated in the available degrees of freedom (the individual molecules are moving and spinning faster), and so its energy will tend to spread out to cooler bodies with less energy per degree of freedom. Q^{rev} in Figure 1 would be greater for a hotter heat bath, because if the heat is initially less dispersed, more heat can be transferred to work for the same degree of energy concentration.

This definition may also be connected to the statistical understanding of entropy. It is intuitively reasonable that adding heat to a heat bath will increase the number of microscopic configurations available to the system. If the heat bath is a unit-temperature ideal gas, it is straightforward to quantify this intuition and show that a heat transfer dQ will increase the bath's

[‡] See, for instance, the use of 'unordnug' (disorder) by Helmholtz (1882), the use of 'mixed-up-ness' by Gibbs (1903) or the use of 'disorder' by Feynmann (1964) and Hawking (1987).

available phase volume, Ω , in such a way that

$$dS = dQ \propto d(\log \Omega) \quad (2)$$

From this we may hypothesise the more general idea that entropy is proportional to the logarithm of the volume of the phase space consistent with the specified thermodynamic variables. States of greater entropy are far more likely than states of lower entropy, as they have exponentially more microscopic configurations, and this is the origin of the irreversibility of an increase in entropy.

These intuitive interpretations of entropy are clearly consistent with the phenomenological Definition A. However, the goal of this article was not to propose a new intuition for entropy, but simply to suggest a more streamlined version of the traditional macroscopic introduction to the topic, which highlights, as clearly as possible, its dependence on the second law, and which avoids messy calculations involving infinite arrays of Carnot cycles that only obscure the basic underlying ideas. The second law of thermodynamics implies that, in a reversible process in which heat is drawn from one source, the heat absorbed is a state function. This mysterious new state function is defined to equal the entropy if the heat were drawn from a reference heat bath defined to be at unit ‘temperature’, and if a different amount of heat is absorbed by another heat bath, we say the bath’s temperature is correspondingly greater. These state functions showcase the full implications of the second law, providing a directionality not just to heat flow or friction, but to any process in the universe. Even if the quantum thermodynamicists one day provide us with an unambiguous definition of entropy that connects the microscopic and the macroscopic in a seamless way[§] macroscopic thermodynamics should be taught and appreciated for the elegant and self-contained theory it is. We hope that the alternative perspective provided herein will prove helpful in this regard to both teachers and their students.

[§] Unfortunately, we are inclined to quote Planck (1897): ‘At present, however, no probable limit can be set to the time which it will take to reach this goal.’ See Gemmer, Michel and Mahler (2009) for a recent review.