

# CONNECTING ENERGY DISPERSAL AND THE CLASSICAL DEFINITION OF ENTROPY

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## INTRODUCTION

Entropy is a measure of the spread of energy. To quote Lambert, “Energy’s diffusion, dissipation, or dispersion in a final state compared to an initial state is the driving force in chemistry. Entropy is the index of that dispersal within a system and between the system and its surroundings.”<sup>[1]</sup> Similar ideas have been expressed elsewhere;<sup>[2–5]</sup> motivating entropy as the index of energy dispersal is intuitive and theoretically sound.

Unfortunately, it is not simple to connect the notion of energy dispersal to entropy’s classical, quantitative definition:

$$dS = \frac{\delta Q_{\text{rev}}}{T} \quad (1)$$

where  $S$  and  $T$  are the entropy and temperature of a closed system, respectively, and  $Q_{\text{rev}}$  is heat energy reversibly entering the system. Leff<sup>[4]</sup> provides a justification for the notion that entropy is a measure of energy dispersal, but his arguments are based upon Callen’s postulational approach, rather than entropy’s traditional definition, as shown in Eq. (1).<sup>[6]</sup> Bhattacharyya and Dawlaty<sup>[5]</sup> provide a useful 1D model that connects Eq. (1) to Boltzmann’s entropy formula, but they do not discuss the connection with energy dispersal in depth. The “energy dispersal” interpretation of entropy is increasingly popular – see, for instance, recent additions of Atkins’<sup>[7]</sup> physical chemistry text and other popular resources.<sup>[8,9,10,11]</sup> However, there remains a need for concrete arguments connecting the quantitative definition of entropy, Eq. (1), and the qualitative notion of energy dispersion. Without such a connection, the notion of entropy as “energy dispersal” remains little more than a useful qualitative intuition, comparable to entropy as “disorder” or “mixed-up-ness.”<sup>[12]</sup>

In this article, we demonstrate that the traditional definition of entropy, Eq. (1), defines a state function that quanti-

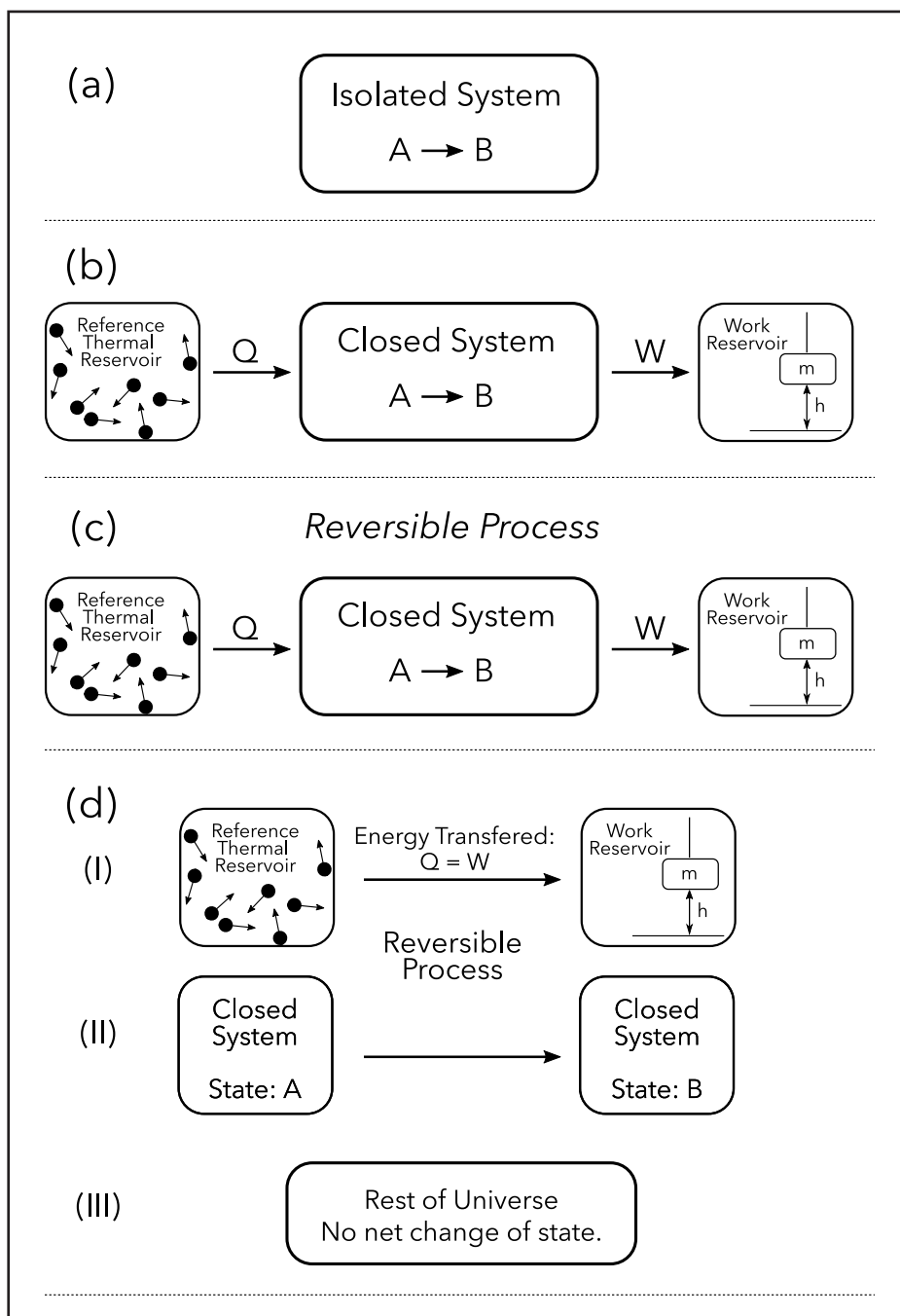
fies the change in energy dispersal for an arbitrary process occurring in an isolated system. We present the argument as a physical *interpretation* of entropy, which may be used to provide intuition for the concept after it has been defined. We briefly discuss how this approach may instead be used to *define* entropy and prove its basic properties. We present the arguments and figures in an order suited to a lecture or tutorial session, and in the Appendix we present the arguments in the form of a guided problem set.

## ENTROPY AS A MEASURE OF ENERGY DISPERSION

We are interested in developing a physically plausible interpretation of the entropy state function, which we have formally defined by Eq. (1). To begin, we consider an arbitrary process  $A \rightarrow B$  occurring in an *isolated* system (Figure 1a.) This process could be as simple or as complex as we like. However, the fact that it occurs in an isolated system tells us something: the First Law implies that there is no change in internal energy, such that  $\Delta U = U_B - U_A = 0$ .

The same change of state  $A \rightarrow B$  could also be made to occur in other ways. For example, in Figure 1b, we imagine the  $A \rightarrow B$  now occurs in a *closed* system, so that heat energy  $Q$

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**Figure 1.** Heat and work flows are not always path dependent. (a) An isolated system transforms from state  $A$  to state  $B$ . (b) The same process occurs in a closed system while heat energy,  $Q$ , is withdrawn from a reference thermal reservoir, and work energy,  $W$ , is withdrawn from a work reservoir. Note that  $\Delta U = 0$  implies  $Q = W$ . (c) The same process occurs in a reversible manner. (d) Alternative visualization of process shown in Figure 1c, explicitly showing all transformations within the universe: (I) energy  $Q = W$  is moved from a reference thermal reservoir to a work reservoir; (II) a closed system changes from state  $A$  to state  $B$ ; and (III) the initial and final states of the rest of the universe are identical.

may be removed from some reference thermal reservoir, and work energy  $W$  may be added to some work reservoir. For concreteness, we may imagine the work reservoir to be a weight that may be raised or lowered, and the thermal reservoir to be a very large bath of water at its triple point (the reference for the Kelvin temperature scale) at a reference temperature  $T_0$  (conventionally,  $T_0$  is given the thermodynamically-arbitrary value of 273.16 K). We may now ask: in Figure 1b, are  $Q$  and  $W$  path functions or state functions? The answer is a truism of elementary thermodynamics:  $\Delta U$  (which in this case equals zero) depends only on the initial and final states  $A$  and  $B$ , so it is a state function, while  $Q$  and  $W$  depend on the process by which  $A$  is transformed into  $B$ , so they are path functions. In this case, the fact that  $\Delta U = 0$  implies that  $Q = W$ , but their value remains path dependent.

We now make a small change to Figure 1b: let's assume that the process can be made to occur *reversibly* (Figure 1c). Later, we'll discuss how this could in principle be achieved for quite a general transformation  $A \rightarrow B$ . Are  $Q$  and  $W$  still path functions? In this case, the answer is *no*. In Figure 1c,  $Q$  and  $W$  depend only on the initial and final states  $A$  and  $B$ . This was previously observed by Pal,<sup>[13]</sup> and it may be proven in two ways. First, it may be proven as a direct consequence of the Second Law, without any mention of entropy; we sketch the proof in Figure 2. However, as we are interested in developing an interpretation of entropy (which has been previously defined in Eq. (1)), we may also conduct a conventional entropy balance, which gives:

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{thermal reservoir}} + \Delta S_{\text{work reservoir}} = 0 \quad (2a)$$

$$\Delta S + \left(-\frac{Q}{T_0}\right) + 0 = 0 \quad (2b)$$

$$Q = T_0 \Delta S = T_0 (S_B - S_A) \quad (2c)$$

where  $\Delta S$  is the change in entropy of the closed system. We see that  $Q$  is indeed path independent: it is proportional to the change in entropy of the closed system,  $\Delta S$ , with the proportionality constant being the arbitrary temperature of the reference thermal reservoir,  $T_0$ . As  $Q$  and  $\Delta S$  are equivalent up to an arbitrary multiplicative constant, an intuitive explanation for why  $Q$  is path independent, and a physical interpretation of what  $Q$  represents in terms of the initial and final states of the system,  $A$  and  $B$ , will apply equally to  $\Delta S$ .

Why would we expect  $Q$  in Figure 1c to depend only on the states  $A$  and  $B$ ? And what does this new state function physically represent – what does it tell us about the states  $A$  and  $B$ ? To answer these questions, we begin by redrawing Figure 1c in an equivalent but more systematic form. Figure 1d explicitly lists all the changes of states that occur in Figure 1c: (I) some quantity of energy is removed from a thermal reservoir, and an equal quantity of energy is added to a work reservoir (or vice versa); (II) a closed system undergoes an isoenergetic ( $\Delta U = 0$ ) transformation  $A \rightarrow B$ ; (III) the initial and final states of the rest of the universe are identical (note, we don't explicitly forbid intermediate changes of state within the rest of the universe; we only require any processes that may occur in the rest of the universe be cyclic, so there is no net change of state). We stress that (I) to (III) are not sequential processes. Figure 1d is just an enumerated list of all the things that occur in Figure 1c: energy is transferred to/from some work/thermal reservoirs, a closed system's state is changed, and the state of the rest of the universe is unaltered.

Process (I) is familiar: the interconversion of work energy and thermal energy. Recall that Kelvin's statement of the Second Law places a severe restriction on this process when it is the only transformation occurring in the universe:

**Kelvin's Statement of the Second Law:** No process may have the sole effect of transferring some quantity of energy from a thermal reservoir to a work reservoir.

Of course, Figure 1d does not contradict the Second Law, as process (I) is not the only transformation within the universe; it is accompanied by the transformation in process (II).

Let's take a moment to build some intuition for *why* Kelvin's statement of the Second Law is reasonable. Why would we never expect heat energy to spontaneously and completely transform into work energy, while the reverse is possible? A concrete example may help. When a pendulum is bumped, it will swing for a time before eventually coming

to a standstill. The kinetic energy (a form of work) spontaneously transforms, via friction, into thermal energy (the pendulum will now be ever-so-slightly warmer). Have you ever seen the opposite occur? Could a stationary pendulum spontaneously cool just a little, drawing thermal energy from its surroundings, and begin swinging? We can't say we've seen this happen. It wouldn't contradict the First Law, but it does contradict Kelvin's statement of the Second Law. A reasonable explanation for why this hypothetical process is impossible is that thermal energy is *disperse* – it is energy spread over trillions and trillions of microscopic degrees of freedom – while work energy is *concentrated* in a handful of macroscopic degrees of freedom, such as the angle and velocity of the pendulum. It is extraordinarily unlikely that dispersed thermal energy would spontaneously concentrate itself into the uniform motion of a pendulum. It is appealing to imagine this may be generalized in the following way:

**Plausible Intuition:** A spontaneous process can never cause a net concentration of energy within the universe as a whole, accounting for changes in all systems.

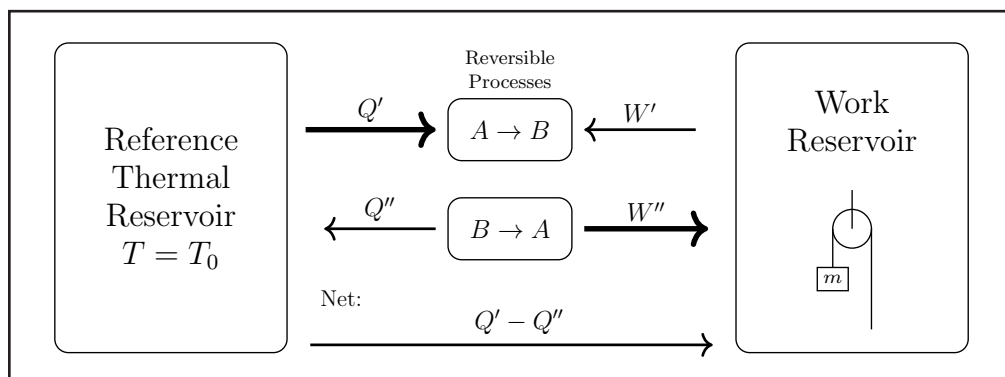
This statement is consistent with daily experience: coffee cools, friction disperses kinetic energy. Lambert<sup>[1]</sup> discusses how this intuition may be applied to a broad range of transformations, including some which, at first glance, appear to involve concentration of energy. We refer to it as a "plausible intuition," as we have not expressed it in a quantitative manner, though it may be justified by statistical or combinatorial arguments, as dispersed states are more numerous than concentrated states.<sup>[14]</sup> It also implies an important corollary about processes that can be completely reversed. Because neither the forward nor the reverse process can involve energy concentration, the following must be true:

**Corollary:** A reversible process must involve no net concentration *or* dispersion of energy within the universe as a whole, accounting for changes in all systems.

We may now return to Figure 1d, and to the question of why we expect  $Q$  to be a state function, and what it (and in turn,  $\Delta S$ ) physically represents. Note the following about Figure 1d:

1. The process is conducted reversibly, so taken together processes (I) & (II) must involve no net dispersion or concentration of energy.
2. Process (I) is the quintessential energy-concentrating process, referenced by Kelvin's statement of the Second Law: the transformation of a quantity of dispersed thermal energy into concentrated work energy.

If the processes (I) and (II) together involve no net dispersion or concentration of energy, then the concentration of energy occurring in (I) must be offset by an equal-and-



**Figure 2.** Proof from first principles that  $Q$  is a function of the initial and final states of the closed system,  $A$  and  $B$ . Suppose it were not, so that  $Q$  could take two different values,  $Q'$  and  $Q''$ , satisfying  $Q' > Q''$ . Then by running  $A \rightarrow B$ , and then restoring the closed system to its original state via  $B \rightarrow A$  (this is possible, as both processes are reversible), we could construct a process whose sole effect on the universe would be to convert heat directly into work, contradicting Kelvin's statement of the Second Law. Bold arrows indicated greater energy flows.

opposite dispersion of energy in (II). The larger the value of  $Q$ , the more energy is concentrated in process (I), and the more energy is dispersed in process (II). In other words, the larger the value of  $\Delta S$ , the more dispersed is the energy in state  $B$  compared with state  $A$ .

This, then, is our intuitive explanation for why  $Q$ , and in turn  $\Delta S$ , depends only on the initial and final states  $A$  and  $B$ . For any process  $A \rightarrow B$  that is isoenergetic (so that  $\Delta U = 0$ ),  $\Delta S$  is a quantitative measure of the difference in energy dispersion between states  $A$  and  $B$ . The reversibility of the process in Figure 1c/d allows for a comparison test: energy dispersal in the process  $A \rightarrow B$  may be directly compared with energy dispersal in an elementary dispersive process: the conversion of concentrated energy (work) into disperse energy (thermal energy in a reference reservoir). Process (I) may be thought of as the *reference* process by which energy dispersion can be quantified, and Figure 1d allows the energy dispersal in another transformation  $A \rightarrow B$  to be quantitatively compared with this reference.

## DISCUSSION AND CONCLUSION

The discussion above provides a connection between the intuitive notion of energy dispersion and the quantitative definition of entropy, Eq. (1). It relies on the plausible assumptions that (a) energy tends to disperse over time, and (b) the conversion of work into heat is a dispersive process, which may be used as a reference by which energy dispersion in other processes may be quantified. It may be presented in the order above in a lecture or tutorial format, with Figure 1a progressively transformed into Figure 1c on a whiteboard or slides. The dictum that “internal energy is a state function, but heat and work are path functions” is drilled into

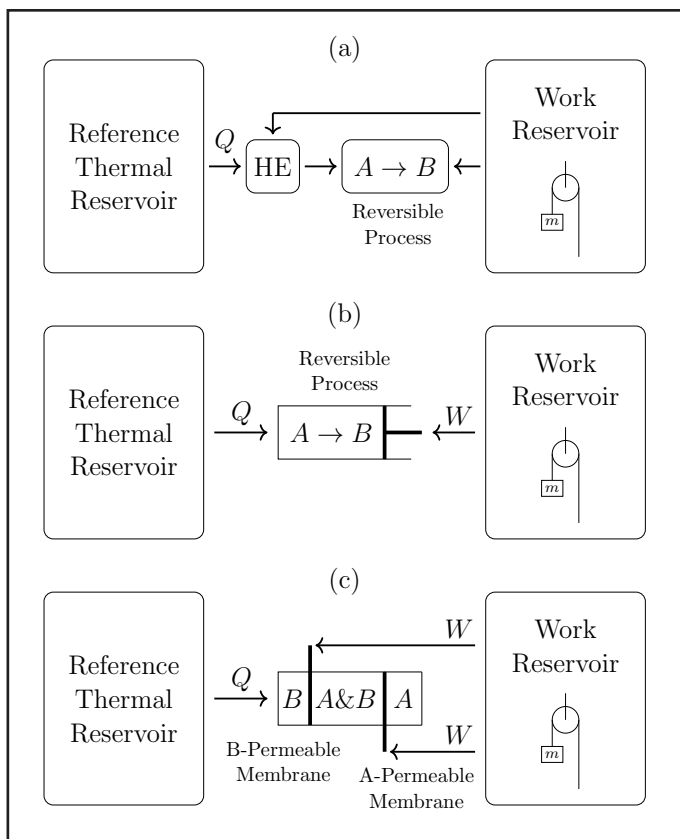
the heads of undergraduate thermodynamics students, so in a graduate class most students correctly identify that  $Q$  and  $W$  are path functions in Figure 1b. The change in behavior of  $Q$  and  $W$  in Figure 1c often comes as a surprise to students. Seeing entropy pop out of a figure as familiar as Figure 1b (which is typically only used when discussing the First Law) is satisfying and may help consolidate the role of reversibility in the measurement of entropy. As an alternative to the lecture format, the arguments may

be presented through a guided problem set (an example is provided in the Appendix). Some prior exposure to entropy is assumed in this approach, and it may be best used to provide motivation for the topic in an advanced undergraduate or graduate course.

Rather than using the discussion above to provide *physical intuition* for entropy, Figures 1c and Eq. (2) may instead be used as the *definition* of the change in entropy of a closed system. In this case, the restriction that  $\Delta U = 0$  should be removed. We have already proven from first principles that the entropy so defined is a path independent quantity (see Figure 2). Other properties of entropy may also be shown to be a direct consequence of the Second Law, such as the fact that entropy cannot decrease in an isolated system – a property that would be expected for a state function that quantifies energy dispersion. This definition is also more general than it first appears, as cyclic tools such as reversible heat engines located in the “rest of the universe” (process (III) in Figure 1d) may be used to enact a very wide range of transformations (see Figure 3). Finally, temperature may be defined in a manner consistent with Eq. (1). This approach is quite abstract, but it allows entropy and temperature to be introduced, and their properties proved, without a detailed analysis of heat engines, and with a strong emphasis on entropy's connection with energy dispersion, all of which is attractive in a chemical thermodynamics course. It may be suitable for a graduate course where the subject is developed rigorously, at the level of the presentation of Denbigh<sup>[15]</sup> or Fermi.<sup>[16]</sup> Contact the author at moore260@llnl.gov for further details.

Interestingly, this argument also reveals a limitation of the “energy dispersal” interpretation of entropy: it only applies to isoenergetic transformations, for which  $\Delta U = 0$ . This is unsurprising, as it is unclear how one could meaningfully





**Figure 3.** Examples of concrete reversible processes enabling various changes of state in a manner consistent with Figure 1c and 1d. (a) A reversible heat engine, ‘HE’, is used to supply/remove heat of arbitrary quality (i.e., temperature), enabling reversible heating/cooling of a system. (b) A piston is used to reversibly and isothermally recover/supply volume expansion work. (c) A set of semi-permeable membranes may be used to reversibly mix/separate two gases. Note that, in each case, the rest of the universe undergoes at most a cyclic transformation, consistent with process (III) in Figure 1d.

quantify how the energy in a system is dispersed or concentrated if the total amount of energy is itself changing. The interpretation of entropy as a measure of energy dispersal *does* hold for processes occurring in an isolated system, and for such processes energy will tend to disperse over time, and entropy can only increase. Furthermore, for *any* process, the change in entropy of the universe (i.e., the system and its surroundings) is always non-negative and represents the change in energy dispersion of the universe as a whole.

Finally, this approach reveals a striking symmetry between the First and Second Laws. As Joule famously showed, when an *adiabatic* process draws *work* from a single *work reservoir*, the *work energy* withdrawn is path independent. Analogously, we have seen that when a *reversible* process draws *heat* from a

reference *thermal reservoir*, the *heat energy* withdrawn is path independent. Joule’s observation implies the existence of a state function – the internal energy – that quantifies the energy content of the system. Our observation implies the existence of another state function – the entropy – that quantifies the degree of energy dispersion for isoenergetic changes within the system.

## ACKNOWLEDGMENT

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## APPENDIX: GUIDED PROBLEM SET

1. Figure 1a shows an arbitrary process  $A \rightarrow B$  occurring in an isolated system. What can be said about the change in internal energy,  $\Delta U = U_B - U_A = 0$ , and the change in entropy  $\Delta S = S_B - S_A$ ?
2. Figure 1b shows the *same* process  $A \rightarrow B$ , now occurring in a closed system, capable of exchanging energy with its surroundings. A quantity of heat energy,  $Q$ , is removed from a reference thermal reservoir at temperature  $T_0$ , containing water at its triple point, and a quantity of work energy,  $W$ , is added to a work reservoir. Given that  $\Delta U = 0$ , are  $Q$  and  $W$  independent of each other? If not, how are they related?
3. In Figure 1b, are  $Q$  and  $W$  state functions or path functions? In other words, does knowledge of the states  $A$  and  $B$  determine the values of  $Q$  and  $W$ ?
4. Figure 1c is identical to Figure 1b, except now we require that the transformation be conducted *reversibly*. Demonstrate that the quantity of energy removed from the reference thermal reservoir,  $Q$ , is now a state function, depending only on states  $A$  and  $B$ . Demonstrate that  $Q$  is proportional to  $\Delta S = S_B - S_A$ .
5. Figure 1d shows all changes of state occurring in Figure 1c: a quantity of energy is removed from a reference thermal reservoir and an equal quantity of energy is added to a work reservoir (we call this ‘process (I)’), the closed system is transformed from  $A \rightarrow B$  (process (II)), and the initial and final states of the rest of the universe are identical (process (III)). Explain why the presence of process (I) (the conversion of thermal energy to work energy) does not contradict Kelvin’s statement of the Second Law.
6. Let us take as given that spontaneous processes cause a net dispersion of energy (or at least, no net concentration of energy) within the universe as a whole, accounting for changes in all systems (we will refer to this as *Statement A*). For example, a sliding block will eventually come to a stop, its kinetic energy dispersing via friction into septillions of random molecular motions (thermal energy) in the environment. The opposite never occurs: stationary blocks never move of their own accord, spontaneously increasing their kinetic energy by concentrating disperse thermal energy from their environment. Show that Kelvin’s statement of the Second Law may be interpreted as forbidding one particular energy-concentrating process.
7. Why does Statement A in question 6 imply that a reversible process must involve no net concentration or dispersion of energy within the universe as a whole, accounting for changes in all systems.
8. Figure 1d is a reversible process in which two transformations occur, the energy-concentrating process (I), and process (II). What does the reversibility of the overall process imply about the concentration or dispersion of energy in process (II)? Show how  $Q$ , and in turn  $\Delta S = S_B - S_A$ , may be interpreted as a quantitative measure of the difference in energy dispersion between states  $B$  and  $A$ .