



RESEARCH
ARTICLE

Beyond the Thermodynamic Limit: Template for Second Law Violators

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SUBMITTED April 24, 2022
ACCEPTED August 6, 2022
PUBLISHED October 22, 2022

<https://doi.org/10.31275/20222593>

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HIGHLIGHTS

Several of the most promising second law challenges currently in the literature follow a standard physical template; an exemplar is discussed.

ABSTRACT

For 150 years the second law of thermodynamics has been considered inviolable by the general scientific community; however, over the last three decades its absolute status has been challenged by dozens of theoretical and experimental counterexamples. This study explores commonalities between some of the most potent of these and reveals a common template that involves broken physical–thermodynamic symmetries and reservoirs of work-exploitable thermal energy stored at system boundaries. Commercially successful second law devices could disrupt the current energy economy and help support a sustainable energy future. This article expands on a talk presented at *Advanced Energy Concepts Challenging the Second Law of Thermodynamics*, a symposium hosted as part of the 4th Annual Advanced Propulsion and Energy Workshop (22 January 2022).

KEYWORDS

Second law of thermodynamics, Maxwell's demon, sustainable energy

I. INTRODUCTION

Among the principles of Nature, perhaps none is more consequential and intimately tied to the human condition than the second law of thermodynamics (Čápek & Sheehan, 2005). It guides almost every natural process from the size of nuclei up to the scale of the cosmos. It began with the Big Bang and will likely help decide the ultimate fate of the universe. The second law is believed to largely underwrite the very passage of time.

The second law conditions virtually everything we do. We are born, live (too briefly), and die by it. It weighs on our psyches as we grapple with disorder around us, endure the decay of all things, toil against the dissipation of our efforts, finally succumb to ageing, and are reduced to dust. It's been called a neurosis of Western Civilization (Čápek & Sheehan, 2005). The second law is, arguably, the most de-

pressing of all physical laws. For these reasons and more, it has been called *the supreme law of nature* (Eddington, 1929).

Despite its downsides, the second law is essential to our existence. It mediates the mixing of chemicals in our bodies and the completion of biochemical reactions; its molecular chaos keeps us warm and contributes to the oblivion that allows the world (and us) to forget so that new things can arise. As Picasso said, "Every act of creation is first an act of destruction." The second law seems destructive, but it is essential to creation for that reason.

One of its most ringing endorsements is the following (Einstein, 1970): "[Classical] thermodynamics is the only physical theory of universal content concerning which I am convinced that, *within the framework of applicability of its basic concepts*, it will never be overthrown [emphasis added].



While this statement is regularly offered for the centrality of thermodynamics and the inviolability of the second law, in fact, its italicised clause renders Einstein's endorsement a tautology: *Thermodynamics is correct when it's correct*. It follows, then, that *thermodynamics (and the second law) is not correct when it's not correct*. This paper concerns this thesis.

II. A LITTLE THERMODYNAMICS

A. Thermodynamic Law

But what is this *second law of thermodynamics*? To begin, *thermodynamics* is the field of science concerned with the interplay between *work* and *heat*, the two basic types of energy in the universe. *Work* is high-grade, organized energy, while *heat* is low-grade, disorganized energy. *Energy is the currency of change*—nothing can happen without it—therefore, thermodynamics is central not just to physics, engineering, biology, chemistry, but to economics, industry, geopolitics, and every sphere of human activity. If *energy makes the world go 'round*, then the second law is its lord and master.

Thermodynamics is governed by four laws, designated 0, 1, 2, and 3. The zeroth and third laws are almost throw-aways; they cover ways to define equilibrium and entropy, respectively. Both could be abolished and most scientists and engineers would neither care nor notice. Not so for the first and second laws: they are respected like nitroglycerin. They are the flesh and bone of thermodynamics.

The first law, conservation of energy, stipulates that the total mass–energy content of a closed system cannot change. Various forms of energy can interconvert—e.g., radiative, rest mass, chemical, gravitational, kinetic, thermal—but the total sum cannot change; in other words, there's no free lunch and you don't get anything for nothing. While this all seems quite fair and physically reasonable and, thus, worthy of a law of nature, in fact, the first law should not be considered a law at all, rather just a handy accounting scheme for energy. In a practical sense, this 'law' cannot be violated because if an apparent violation (loophole) were to appear—that is, some new type of energy were to be discovered that unbalanced the books—well then, *the books can be cooked*. In other words, it is always possible to invent a new form of energy to cover up any discrepancy, close any loophole, and null out any suspected violation to preserve the first law as inviolate.¹ As such, the first law violates Karl Popper's Principle of Falsification, which asserts that for a physical theory (or law) to be legitimate, it must be able to be tested and potentially be proven false. The first law does not satisfy this criterion, therefore, if it is a law, it is a peculiar one. Not so with the

second law. If a violation of it is found, the law cannot be easily rejiggered to remain inviolate. In principle, it can be falsified and in recent years it has been.

There are a number of misconceptions concerning the second law, two of the most common of which are that: i) it cannot be violated, even in principle; and ii) it has been theoretically proven. Both spring from epistemological errors. *Physical laws are scientific postulates (axioms), and postulates by definition cannot be proven; they are either accepted or not accepted*. (Think, for instance, of the five postulates in Euclidean geometry.) Physical laws are statements about nature that are assumed to be true because they have been always observed to be so. However, one can never test a law in every possible physical scenario, therefore, one must always leave open the possibility that a counterexample might turn up. Its status, thus, is *contingent* and subject to Popperian falsifiability. Even a single violation is significant, for although it does not invalidate the law under circumstances where it does apply it vanquishes the law's absolute status, perhaps making it a subcase of a more general law.

Misconception (ii)—the second law can be rigorously derived (theoretically proven)—is also an epistemological error. The second law is an axiom, not a theorem. Were it theoretically provable, it would be a mere theorem, reliant on deeper axioms for its support. 'Proving' the second law would also violate Popper's falsifiability principle.

These misconceptions have multiple causes, some defensible, others less so. Certainly, the second law rings true, validating by our experience of the world that disorder tends to increase. Furthermore, its statement is simple, snappy, easy to use and comprehend. These misconceptions can also be traced in part to the tendency of physicists to hang their beliefs on idealized models, what T. S. Kuhn has called *exemplars*. One of the most seductive is the ideal gas: a collection of non-interacting point masses with kinetic (thermal) energy. This model provides wonderful insights and good physical approximations into the behaviors of many real gases. Equally seductive, it can be derived simply and exactly. Capping it off, it provides an ideal test case for the second law, one that can be proven rigorously, which it passes *summa cum thermodynamically*. From there, it seems intuitive to extrapolate this theoretical triumph for an ideal gas to real gases and from there on to every other thermodynamic system in the universe.

It is the experience of this author that a plurality of physicists turn to the ideal gas both for intuition and justification for the second law's behavior and absolute status. Unfortunately, the universe is neither simple nor ideal. As Mark Twain noted, *What gets us into trouble is not what we don't know. It's what we know for sure that just ain't so*. This tendency to extrapolate from simple, idealized cases to

more complex ones, even though lacking sufficient justification, will be called the *Ideal Gas Syndrome* (IGS). When it comes to the second law, the IGS courts trouble in spades.

B. The Second Law

If the first law of thermodynamics is not a real law and the zeroth and third are ignorable, then one might say that thermodynamics really has only one significant law: the second. Fortunately, what it lacks in number, it makes up for in formulations. There are more than a dozen standard ways to state the second law, all of which are more than a century old and most of which were developed in the 19th century, during the age of steam engines. Here we will focus on two of the most prominent and useful.

The *Kelvin–Planck* formulation is considered by many to be the gold standard: *It is impossible to convert a quantity of heat solely into work in a thermodynamic cycle.*² The second law embodies one of the starkest asymmetries in Nature. Work can be turned wholly into heat, but the reverse is not possible. That is, heat cannot be turned back wholly into work in a thermodynamic cycle. As a demonstration, rub your hands together. They warm up. Now rub them in reverse. They just warm up more. The heat in your hands contains the energy of the work you did rubbing them, but you'll not get it back as motion of your hands. (The same thing happens to almost all the energy you will ever use, it will end up as unrecoverable heat in the environment.)

Heat generation can be viewed as a physical tax paid by every working system, a form of energy that can never be fully redeemed back into work. The original energy (in the form of work) isn't lost—the first law guarantees this—but it is reduced to a less usable, less effective form: heat. On the everyday level this means that useful (work) energy (e.g., electricity, carbon fuels, solar, wind, or nuclear) must be constantly supplied to offset losses from heat generation. Taxes are higher in some places than in others. For an electric heater the tax is high and immediate, which is a good thing for staying warm, while for a sleek electric car the tax is deferred long enough for efficient transportation. In the end, however, for both cases the tax paid is almost always 100 percent.

The second formulation of the law, the *Planck* form, reflects a view of thermodynamics incorporating entropy and statistical mechanics: *For any spontaneous process, the entropy change of the universe is never negative.* If entropy is taken to be a measure of disorder, then the Planck formulation says that for anything that happens (a spontaneous process) the overall disorder of the world must increase or remain the same, but it will never decrease. This validates what we understand intuitively and viscerally: messes never clean themselves up and, left to their own devices, sys-

tems tend to become more disorganized. When it comes to holding back entropy generation, the best one can hope for is accomplished by doing nothing at all because every act of cleaning up, though it might reduce entropy (disorder) locally, must increase the overall entropy of the universe. If you're really intent on not messing up the universe, kill yourself, and you won't generate entropy through your biochemical reactions and other life activities.

In sum, the second law is a thermodynamic ratchet system that inexorably degrades high quality energy (work) into lower quality energy (heat), reducing order to disorder, marking our time as it *creeps in this petty pace from day to day to the last syllable of recorded time . . . pointing the way to dusty death* (Shakespeare). Let us now turn to some approximations and oversights that have contributed to this thermodynamic fatalism and set the stage for the law's overthrow.

C. Boundaries and the Thermodynamic Limit

Like any well-developed field, thermodynamics is replete with technical terms and approximations that embody its viewpoint and ethos. Among the most widely applied is the *thermodynamic limit*. This idea and handy approximation streamlines analysis and leverages intuition, but, sadly, it is also a mindset and a classic case of the IGS, which appears to have blinded the scientific community to the limits of the second law for at least a century.

As a technical term, the thermodynamic limit refers to an approximation in which the number of particles (atoms/molecules) in a system (N) is taken mathematically to go to infinity ($N \rightarrow \infty$), while at the same time the volume of the system (V) is also taken to go to infinity ($V \rightarrow \infty$) in such a way that their ratio, the number density ($n = N/V$) remains finite. This handy approximation streamlines calculations of bulk thermodynamically quantities—e.g., specific heat, various free energies, thermal diffusivity, pressure, latent heats of vaporization and fusion—without having to deal with often unwanted, complex, or physically intractable implications of boundary surfaces.

The utility of the thermodynamic limit is unquestioned, but it has led to a general mindset within much of the scientific community that, somehow, boundaries and surfaces have limited thermodynamic significance, that they can be ignored with perhaps only minor consequence or even with impunity. Few beliefs could be further from the truth and few assumptions have greater consequence.

In fact, boundaries are essential to physical reality. They define the physical world, allowing us to differentiate one object or region from another. When we interact with the world, it is usually through boundary surfaces: the ground we stand on; the surface of a table; the printed

word on a page; the colorful skins of fruits. Without them, the universe would be an undifferentiated blur.

Thermodynamically, *boundaries are where the action is* because most physical interactions occur there. Entire fields of study are defined by them. At the boundary of a plasma, for example, is a *Debye sheath*, where the electron and ion energies are anomalously high, where temperature is not well defined, and strong electric fields are found. At equilibrium, the electrostatic potential of an entire plasma can be determined by its boundary. Transistors, diodes, LEDs, and other semiconductor technology depend on the intricate physics at the microscopically thin boundaries between n- and p-doped semiconductors that make them up. Heterogeneous catalysis, which is the beating heart of industrial chemistry and which touches 90% or more of all manufactured products in some way, is defined by surface reactions. And, of course, living cells and their organelles are bounded by membranes that regulate the influx and efflux of chemicals and ions necessary for life. (Roughly half the total metabolic energy of a typical cell is devoted to membrane processes.) Indeed, boundaries are ignored at one's peril.³

For our purposes, boundaries represent broken physical or chemical symmetries in a system, discontinuities in chemical potential, pressure, or temperature, any one of which can, in principle, be tapped to perform work. As such, boundaries represent reservoirs of free energy. So long as there are surfaces, the universe cannot be at full thermodynamic equilibrium and there will always be something left to happen. Under certain circumstances, this boundary energy can be tapped cyclically for work. If it is derived from ambient, single-temperature thermal energy, the system might violate the second law.

D. Second Law Renaissance

Over the last 25–30 years there has been a renaissance in investigations of potential violations of the second law (Cápek & Sheehan, 2005). It began quietly in the 1980s with theoretical proposals by Lyndsay Gordon and Jack Denur. By the mid-1990s, several university research teams had picked up the scent and began nipping at the second law's heels. By the early 2000s the interest had grown sufficiently to motivate several international conferences devoted to the challenges to the law (Sheehan, 2002, 2007, 2011). The first scientific monograph on the subject was published in 2005 (Cápek & Sheehan, 2005). For the next 10 years theoretical proposals continued to mount and were soon joined by experiments that increasingly demonstrated deficiencies in the law. Now, in the early 2020s intellectual property is being amassed in anticipation of commercializable *second law devices* (SLD). In total, over the last 30 years more than four dozen second

law challenges have advanced into the mainstream scientific literature, more than the total over the previous 150 years combined. The latest challenges are experimentally testable, some potentially commercializable.

The span of physical regimes encompassed by the various challenges is bracing. In size they range over at least 14 orders of magnitude, from the dimension of cell membranes (0.1 microns) up to that of compact planetary systems (10,000 kilometers); in mass they span 42 orders of magnitude. Operating temperatures range from just above absolute zero up to several thousand degrees, the melting points of ceramics and refractory metals. All four standard phases of matter are represented (solid, liquid, gas, and plasma), as are both classical and quantum regimes.

E. Maxwell's Demon

One of the most unfortunate diversions in the 170-year history of the second law has been the preoccupation with Maxwell's demon (Leff & Rex, 1990, 2002). The demon is an imaginary *heat fairy*, a theoretical microscopic creature who, by sharp observation and quick action, is able to sort molecules on an individual basis so as to create temperature or pressure differences that can be used to perform work, thereby subverting the second law.

In Figure 1, Maxwell's demon is imagined as a microscopic version of the mischievous Calvin (from the cartoon *Calvin and Hobbes*) who operates a trap door in a box of molecules. By opening the door at precisely the right moments, Calvin can preferentially direct molecules into one side of the box rather than the other. Eventually, molecules accumulate on one side and a pressure difference builds up between the two sides of the partition. This is then harnessed to do pressure-volume work, much like as is done in an automobile engine. Once the work is completed and the pressure difference is exhausted, Calvin starts over and separates the molecules again. If this scheme actually worked, it would constitute a second law violator. Regret-

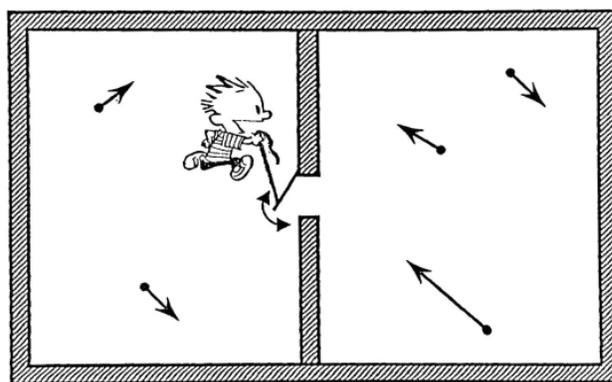


Figure 1. Maxwell's demon imagined as that lil' devil, Calvin.

tably, like all purported SLDs thus far that rely on manipulating molecules on an individual basis or that attempt to exploit their natural fluctuations, the Calvin demon fails—as do most of Calvin’s schemes in the comics.

Maxwell’s demon’s shortcomings are so numerous that it’s remarkable that so much ink has been spilt over them. The demon is microscopic and, even after more than 150 years of discussion, it remains unknown how it could be constructed. A sighted demon is rendered effectively blind because in a blackbody cavity everything has the same color, thus, it could not discriminate between the radiation emitted by the walls, the atoms it’s trying to sort, and the radiation output of its own eyes. Its microscopic fingers would shake uncontrollably, just like the molecules it attempts to handle, so sorting molecules would be nearly impossible. Its final fatal flaw, however, comes from thinking too much. In order to complete a full thermodynamic cycle, the demon must forget what it knows about the molecules it sorts, in other words, it must clear its memory banks. However, information theory has shown that this forgetting automatically creates enough entropy to offset any work (or entropy decrease) that it may have done. In all, it appears that Maxwell’s demon was, is, and probably always will be a straw man. And yet, this hasn’t diminished the scientific community’s fixation with it. Perhaps the community should pick on someone more its own size, rather than on a hapless, hopeless theoretical construct from the 19th century. Enter the Maxwell zombie (Sheehan, 2018).

II. TEMPLATE FOR SECOND LAW CHALLENGES

Many of the most promising and potent second law devices (SLD) have been found to share a common template (Lee, 2021; Thibado et al., 2020; D’Abramo, 2012; Moddel et al., 2021; Sheehan et al., 2022; Sheehan, 2022; Sheehan & Means, 1998, Sheehan et al., 2005; Sheehan et al., 2014). Several were discussed at the symposium upon which this special issue is based.⁴ The template consists of the following four physical conditions.⁵

1) Physical/Thermodynamic Asymmetry at Boundaries: *The system’s physical boundaries have strong thermodynamic activity or properties. In particular, they have one or more physical and/or thermodynamic asymmetries built into them that create a discontinuity in chemical potential, temperature or pressures in the system.*

Every surface is thermodynamically active to some degree, but some are more active than others. For instance, liquid helium or a piece of room-temperature teflon is thermodynamically active but far less so than, say, an oxy-

gen plasma or a slab of tungsten metal heated to 2000 K. Surfaces are notoriously complex entities—entire fields of physics and chemistry are devoted to them. By its very existence, a surface represents a discontinuity in chemical potential, which in principle might be used to do work, but how much, how well, and how fast must be determined on a case-by-case basis. For an SLD, its asymmetry must generate an asymmetry in some type of flux (e.g., electric current, gas particles, chemical species) that can convey or be converted into work (high quality, organized energy). Without this asymmetry, there can be no net directional flux, therefore, no capacity to conduct work. Note, the critical flux need not be generated at the location of the SLD asymmetry itself.

2) Thermal Energy Reservoir: *The asymmetry in 1) creates a macroscopic reservoir of thermally generated free energy at or near a boundary.*

The thermal energy of an individual molecule is minute and randomly oriented and, therefore, unsuitable for performing work. To be suitable, the energy must be macroscopic (forming a reservoir) and ordered. The thermodynamically active boundaries perform this role: They organize, amass, and direct the thermal energy of individual molecules. By analogy, an aimless mob might have the same number of persons as an army, but the army is the more structured entity and thus can be more effective for conducting organized operations. The system boundaries are the recruiters, the drill sergeants, and the generals who organize, mobilize, and direct the army of molecules such that they can perform work. Together, they might have no more total energy than they did as individuals, however, because they operate en masse, they can direct their thermal energy to perform macroscopic work—and perhaps break the second law.

The energy reservoir can consist of pressure, temperature, or chemical concentration differences, even electric or magnetic fields. Such reservoirs constitute a nonequilibrium state than can be harnessed to do work. In everyday circumstances, such energy reservoirs power the world. For instance, terrestrial temperature differences create atmospheric pressure differences, which in turn create the weather. Temperature differences between the Earth’s mantle and crust drive plate tectonics; in the Sun they drive energy from the core to the surface, where it is radiated away as sunlight. Electric fields induce electric currents that make electronics possible. Concentration differences are part-and-parcel of living organisms, especially in and around membranes. Life is a decidedly *non-equilibrium* process.⁶ Thermodynamically, life is one of the second law’s best friends.

3) Independent (‘Orthogonal’) Work Extraction: *The*

system has a means by which to extract macroscopic work from this boundary energy reservoir. This energy extraction mechanism is independent of (i.e., operationally orthogonal) to the thermal energy collection mechanism.

Criteria (1) and (2) account for the accumulation of thermally derived energy into a potentially useful form, but by themselves they are not sufficient for an SLD.

There must also be a mechanism to harvest this energy as work. *Independent* and *operationally orthogonal* mean that the mechanism by which the thermal energy reservoir is tapped is distinct from the processes which created the reservoir in the first place. This precludes or reduces the possibility that the organized boundary energy will backslide into its original, random, thermal form. It decouples the energy storage and energy use processes. A later example will make this clearer.

4) Resettable Metastable Configuration: *Once macroscopic work has been extracted, the system spontaneously returns to its original physical/thermodynamic state via the absorption of heat from its surroundings.*

This step completes the thermodynamic work cycle. The original state of the system involves a macroscopic energy reservoir that has accumulated at boundaries due to the spontaneous thermodynamic rearrangement and marshalling of thermal energy. The extraction of work by the independent/operationally orthogonal process produces useful work, however, by the first law (conservation of energy), this must put the system into a lower energy state than it was before the work was extracted. This lower energy manifests itself as cooling of the system. Ironically, now that the system is cooler than its surroundings (recall that it starts off at the same temperature),⁵ the Clausius form of the second law⁷ guarantees that heat conducts from the surroundings into the system until it returns to its original thermodynamic equilibrium.

If the system successfully completes these four steps, it has completed a thermodynamic cycle in which heat has been converted solely into work, a cycle strictly forbidden by the Kelvin–Planck form of the second law. Several points are noteworthy.

First, the fact that the original equilibrium state of the system is able to produce work and, therefore, go into a lower energy state, implies that it is, in fact, a high-energy metastable state. The universe is replete with such metastable states—actually, it can persuasively be argued that every system in the universe is a metastable state of some sort because one can always find a way to reduce it to a higher entropy, lower energy configuration. However, only a select few systems can amass macroscopic energy stores by thermal means, fewer still are coupled to independent/

orthogonal energy extraction subsystems, and even fewer are able to return to their original states by absorbing heat from their environments. Second law devices can.

Second, most of these four conditions are similar to those operating in everyday work-producing, second-law-abiding devices. Consider, for instance, a gasoline engine. It has boundaries and asymmetries built into it. The piston and cylinders have walls upon which high pressure gases (created by the ignition of the gasoline–oxygen mix) exert forces and produce net work when the piston moves smoothly and asymmetrically in one direction along the inside of its matching cylinder. Work is extracted by an ‘independent/orthogonal’ device: a mechanical crank that converts the pressure force into rotational motion that is eventually coupled to the wheels. And, once the piston returns to its original position in the cylinder, the system resets and the thermodynamic cycle repeats. And off you go!

In all, one sees shades of Criteria 1, 3, and 4 in everyday thermodynamic cycles. What distinguishes the SLDs from everyday work-producing systems is that their energy does not derive from external free energy sources (e.g., gasoline, wind, solar, fission), but rather, from ambient thermal energy, Criterion 2.

Third, the second law applies to virtually every multi-particle system in the universe—even to SLDs. For example, in Condition (4) the SLD cools when it performs work, but the Clausius form guarantees that it warms back up.⁷ Nonetheless, for its full thermodynamic cycle the SLD violates the Kelvin–Planck form of the law. This ambivalence of the SLD toward the second law suggests that the various forms of the law might not be equivalent or that they are internally inconsistent (self-contradicting) in some circumstances.

III. THERMAL BATTERY

As a demonstration of these four criteria (§II), let’s consider the *asymmetric membrane concentration cell* (AMCC), which for simplicity will be called the *thermal battery* (Sheehan et al., 2022; Sheehan, 2022). This device converts environmental heat into electricity using spatially asymmetric electrochemical diffusion.

A. A Taste for Chocolate

Electrochemistry is one of the most challenging scientific fields, drawing widely from physics, chemistry, and engineering (Newman & Thomas-Alyea, 2004; Bockris & Reddy, 2002; Hibbert, 1993). To understand the key thermodynamic processes driving the thermal battery, consider the following edible scenario. Imagine a long narrow corridor (length L , width w , Figure 2) with crowds of

chocolate lovers (CL) milling about randomly, occasionally running into the corridor walls, and sometimes bumping into each other. No one speaks or communicates; everyone acts independently.⁸ Along the walls are boxes of chocolates. They are arranged in a special way. On the left side of the corridor (Figure 2) the boxes are relatively scarce (widely spaced) and the chocolate is relatively lousy (e.g., Hershey's), but as one proceeds to the right, the quality of chocolate and the density of boxes steadily increase, such that at the far right side of the corridor it's wall-to-wall Läderach (better than Ferrero Rocher, Ghirardelli, Lindt, or Godiva). The rules about eating the chocolate are simple: (i) upon colliding with a wall, if a CL encounters a box, he must pick a piece of chocolate and consume it entirely, but if there is no box, he simply reflects and continues randomly walking about the corridor; (ii) the chocolate can only be eaten at the wall; (iii) the CL cannot leave a spot on the wall until he finishes the piece selected; (iv) a CL spends longer eating a piece of high quality chocolate than eating a low quality one; and (v) after consuming the piece and leaving, the CL must re-enter the corridor and resume wandering aimlessly about until colliding with another wall.

Given these rules, it's not hard to deduce that, over

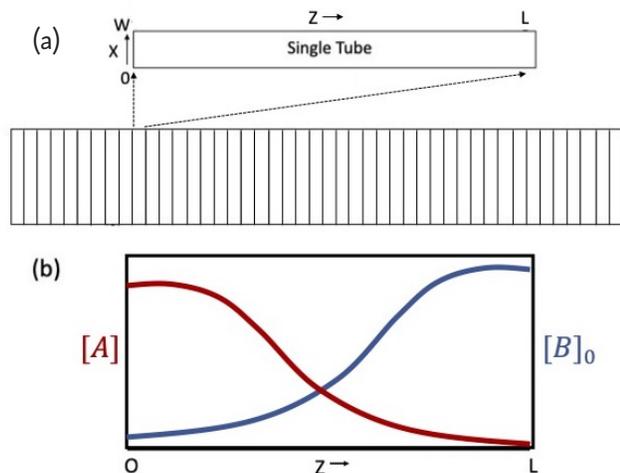


Figure 2. Depictions of thermal battery membrane, tube, and species concentration profiles in tube. **(a)** Membrane as array of microscopic tubes and magnified single tube extracted from the membrane. **(b)** Distribution of binding sites (or chocolate boxes), $[B(z)]_0$ in blue) and resulting concentration of solute A (or chocolate lovers), $[A(z)]$ in red) inside tube. Note inverse spatial relationship between $[A]$ and $[B]_0$.

time the chocolate lovers will accumulate on the walls near the right side of the corridor (i.e., the solid phase of CLs) be-

cause, even if their wanderings are entirely random, there are more sites there with which to attach and they spend longer times at each site eating. This, however, counts only CLs attached to the corridor walls. If one instead considers where the most chocolate lovers are wandering around freely in the space within the corridor, between the walls (i.e., in the liquid phase of CLs), the opposite is true: They accumulate primarily on the left end of the corridor—after all, they aren't spending much time stuck to the wall eating.⁹ This is depicted in Figure 2b. To be clear, the wall surface (linear) density of chocolate lovers (CL/m) is highest on the right side of the corridor (blue curve), but their liquid (areal) density (CL/m²) is highest on the left side (red curve). The latter result can have consequences.

Let's say that after the diffusion of CLs has leveled off and come to an equilibrium, a game of tug-of-war is arranged in which: (a) contestants are drawn exclusively from the liquid phase of chocolate lovers at the two ends of the corridor; and (b) the team that pulls the hardest wins a prize.¹⁰ Because the left corridor has a higher liquid density of players, their end of the tugging rope has many more contestants than the right end of the rope and, as a result, they win the game.¹¹

After the game of tug-of-war is concluded and the spoils divided, everyone is brought back to the middle of the corridor and the sorting begins again. This cycle of sorting, tugging, and winning repeats ad infinitum. This metaphorical scenario describes the essential features of the thermal battery.

B. Thermal Battery

The thermal battery consists of two subsystems: (1) the *asymmetric membrane separator* (AMS), which separates a solution of A into two distinct concentrations with concentration difference $\Delta[A] \equiv [A]_{\text{high}} - [A]_{\text{low}}$, thereby fulfilling Criteria (1, 2); and (2) the concentration cell (CC), which exploits the $\Delta[A]$ to generate electricity, thereby satisfying Criterion (3). It is depicted in Figure 3. The AMS consists of two thin liquid reservoirs separated by a chemically asymmetric membrane (Figure 2a). Here the membrane is modeled as an array of large aspect ratio microscopic tubes bundled together lengthwise and filled with species A dissolved in a solvent. Individual tubes are microscopic; typical dimensions are in the range: $10^{-6} \text{ m} \leq L \leq 10^{-4} \text{ m}$ and $10^{-8} \text{ m} \leq w \leq 10^{-6} \text{ m}$. Billions or trillions of tubes comprise a single AMS membrane. They are modeled as straight and uniform. The tubes are identical, therefore to understand the physical chemistry of a single tube is to understand that of the entire membrane. The AMS membrane in Figure 3a is represented by such a single tube, as in Figure 2a.

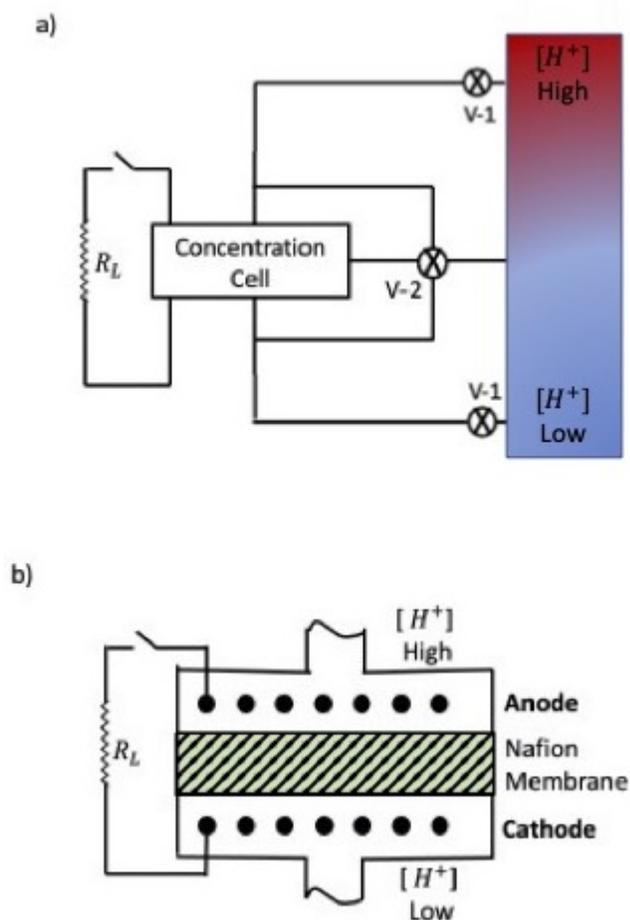
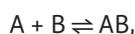


Figure 3. Schematic of thermal battery. (a) AMS with valves, plumbing, and concentration cell. (b) Concentration cell magnified. V-1 open/V-2 closed configuration admits solutions into concentration cell for electricity generation; V-1 closed/V-2 open configuration returns solutions to AMS for reparation. Note: The AMS in this figure is a representation of the membrane tube in Figure 2a.

The solute molecules A randomly diffuse in the solvent, analogously to the aimless wanderings of the chocolate lovers, and temporarily attach to the binding sites on the tube wall (B), following in the simple chemical reaction:



for which the chemical equilibrium constant is:

$$K_{\text{eq}} = \frac{[AB]}{[A][B]}. \quad (1)$$

Here $[A]$, $[B]$ and $[AB]$ are the normalized volume and surface concentrations of species A, B, and AB.

It is shown elsewhere (Sheehan et al., 2022; Sheehan, 2022) that if $[B]$ and K_{eq} (a proxy for the A-B binding strength) are made to vary along the length of the tube, then $[A]$ will also vary. This is analogous to the variation of the quality of chocolate and number density of boxes in the chocolate tasting corridor (§III.A). The results for the two scenarios are similar, as depicted in Figure 2b. Because of the differential binding of A to B, at equilibrium there is a concentration gradient of A created across the width of the membrane. As with the chocolate example, this has consequences.

For laboratory experiments conducted at University of San Diego (USD), custom membranes were fabricated to separate hydrogen ions (H^+) in hydrochloric acid (HCl) into different concentrations. The $[\text{H}^+]$ gradient created a matching chloride ion (Cl^-) concentration gradient (in order to satisfy the requirement for electrostatic quasi-neutrality). The chloride ion concentration gradient was used to power a new type of electrochemical cell, the *asymmetric membrane concentration cell* (AMCC), the thermal battery depicted in Figure 3.

The concentration cell is non-controversial; it has been well understood and studied for a century or more (Newman & Thomas-Alyea, 2004; Bockris & Reddy, 2002; Hibbert, 1993). It is the AMS that renders the AMCC a second law device.

There are several types of electrochemical cell. Everyday batteries (e.g., dry cells, alkaline, lead-acid, Li ion rechargeables), also known as *voltaic cells*, rely on the transfer of electrons between *disparate* chemical species to generate electricity. A lesser-known type, the *concentration cell*, generates electricity using a single chemical species, but at two distinct concentrations, like those generated by the AMS. Ironically, the energy derived from the AMCC is due to the entropy of mixing the two distinct single-species concentrations—a classic application of the second law. In the USD experiments, the concentration cell was driven by the difference in the chloride concentration across the width of the membrane.

The electromotive force (voltage) generated by single concentration cells is usually small, typically 10–100 mV, however, they can be added in series. Because the AMS membranes and concentration cell electrodes can, in principle, be made micron-thin, in theory, a multi-volt AMCC can be made paper-thin. Their theoretical energy densities are sizable, though still 1–2 orders of magnitude less than those of standard voltaic cells. The reason for this is that the characteristic energy of individual species in a thermal battery is of the order of a thermal energy unit, kT , where k is the Boltzmann constant (1.38×10^{-23} J/K) and T is the absolute temperature (Kelvin, K). In contrast, the energy associated with species in a traditional voltaic cell is that of a standard chemical reaction, on the order of 100 kT .

C. Thermal Battery and Template Criteria

Let's examine how the thermal battery meets the four criterion in §III.

Criterion 1: The heart of the AMCC is the AMS. As its name suggests, the AMS has a built-in chemical asymmetry with respect to the binding sites, B, both in terms of surface number density and binding strength. These two asymmetries generate a spatially reciprocal asymmetry in the solute concentration, $[A]$. In the USD experiments, the AMS binding sites were carboxylic (COO^-) and sulfonic (SO^-) moieties, while the solute species were the hydrogen ion (H^+) and chloride ion (Cl^-).

Criterion 2: The concentration difference across the AMS membrane ($\Delta[A] = \Delta[\text{H}^+]$) is derived from particle diffusion, hence from ambient thermal energy (kT). The $\Delta[A]$ in the AMS is a metastable equilibrium state of the solute. It is also a macroscopic reservoir of thermally generated free energy because it can be used to power a concentration cell. In the USD experiments, $\Delta[A] = \Delta[\text{Cl}^-]$.

Criterion 3: The free energy inherent in $\Delta[A]$ is extracted by the electrodes on opposite sides of the AMS (Figure 3a). These concentration cell reactions are 'orthogonal' and independent of the reactions in the AMS that created the original $\Delta[A]$. In the USD experiments, the AMS separates $[\text{H}^+]$ and the $[\text{Cl}^-]$ comes along for the ride. The concentration cell exploits the chloride ion concentration gradient using Ag/AgCl electrodes (Figure 3b).¹²

Criterion 4: The AMCC expends its $\Delta[A]$ to generate electricity. As $\Delta[A]$ declines to zero, so does the concentration cell voltage. When the concentration cell is switched off, the AMS re-separates species A and restores the $\Delta[A]$ to its original equilibrium value, in which case it can be used again. Actually, because the AMS and concentration cell are chemically 'orthogonal,' they can be operated simultaneously, allowing the AMCC to operate continuously.

The primary advantage of the thermal battery over voltaic cells is not its energy density, but rather its rechargeability. If an AMCC can be recharged several hundred times via thermal energy alone, then its effective energy density could be considered on par with or greater than that of a standard voltaic cell.

IV. IMPLICATIONS OF SLDS

The current trajectory of world energy use is unsustainable and, if not corrected, will probably precipitate climatic, ecological, and societal catastrophes (Andrews & Jelley, 2017; Bressler, 2021). Even strict compliance with

the Paris Climate Accord will, at best, avert only the most serious effects. Much of this peril is due to the effects of carbon fuel consumption (i.e., coal, oil, and natural gas).

The world's dependence on carbon fuels is understandable. They offer tremendously high energy densities (~50 MJ/kg), are relatively inexpensive (e.g., gasoline is often cheaper than bottled water in the US), and the technologies for their discovery, extraction, purification, and use are well-honed, having been sharpened for more than two centuries. In all, the "energy business"—e.g., the discovery, extraction, processing, transportation, use, remediation of fossil (carbon) fuels—constitutes upward of 10% of the global economy.

Alternative energy sources face daunting competition. Even if SLDS are proven viable in the laboratory, it is unclear whether they could be made economically competitive against standard energy sources. Scientific viability and economic competitiveness are two different issues. If successful, however, their ramifications might be profound, salutary, and disruptive in almost every sense. Let's consider the relative magnitude of energy reserves. SLDS utilize heat (thermal energy). The total thermal energy content of the world's ocean, atmosphere, and upper crust is roughly 10,000 times greater than the world's known carbon fuel reserves. Anything with a temperature above absolute zero possesses it. Thermal energy surrounds us, it's free, and it's non-polluting. SLDS do not make energy merely renewable, they make it recyclable. Energy can be used again and again in an endless cycle.

To understand the magnitude of this thermal energy reserve, consider a couple of domestic examples. Consider a cubic meter of air, a volume roughly half that of a typical office desk. The mass of that air is roughly 1.2 kg. The average speed of the air molecules is roughly 500 m/s, which is nearly 1.5 times the speed of sound, or roughly that of a medium-speed bullet. Now imagine being hit by such a bullet weighing about two-and-a-half pounds—what a mess! The kinetic energy of this cubic meter of air is roughly equivalent to the energy liberated in detonating 60 grams of the high explosive TNT. Water is even richer in thermal energy. The heat liberated in cooling a cubic meter of water from room temperature ($T = 20\text{ }^\circ\text{C}$) down to its freezing point ($T = 0\text{ }^\circ\text{C}$) and then freezing it is equivalent to the chemical energy released in detonating about 100 kg of TNT—enough to blow up a house.

The significance is this: There's virtually unlimited thermal energy in our environment, but it's generally overlooked because we don't see or feel it. In everyday scenarios, molecular motions are randomly oriented, working against each other—negating each other for purposes of doing work. (The second law sees to this.) Furthermore, we've learned to overlook the possibilities of thermal energy be-

cause of our belief in the second law's absolute status.

SLDs utilize ambient thermal energy so their fuel is free and effectively limitless. They emit no greenhouse gases and should be non-polluting, aside from the products used in their manufacture and retirement. Some proposed SLDs would use common and benign household chemicals. Overall, economically competitive SLDs would probably be positively disruptive. Their technology, of course, would have to be developed and adapted to the current uses for carbon fuels. History suggests that this conversion might take at least 3 to 4 decades.

In summary, a number of second law challenges share a common template. In theory, some offer high energy densities and other attractive features. It remains an open question, however, whether any can be translated into commercially viable technologies. Much may depend on the answer to this question.

NOTES

- ¹ An example of this occurred in 1998 when it was discovered that the cosmos is expanding faster than it ought. Because something was *changing* that could not be accounted for with known types of energy, a new type of energy was posited: *dark energy*. Indeed, this might be a new type of energy—although other explanations have been advanced—but in the interests of the first law, it was invented.
- ² Like many religious commandments, the second law is often stated as a prohibition rather than as a permission or directive.
- ³ The renowned 20th-century physicist Wolfgang Pauli famously quipped, *God made the bulk; surfaces were invented by the devil*. Given the historical significance of Maxwell's demon with the respect to the second law and the current role of surfaces in its downfall, Pauli's statement is ironic and prescient.
- ⁴ It is emphasized that not all SLDs share this template. For example, some supradegenerate and ideal gas systems rely on bulk processes to drive their SLD behaviors, rather than surface-boundary thermodynamic asymmetries (Item (1)).
- ⁵ It is presumed that the systems start in thermal equilibrium with their environments (assumed infinite in extent and in thermal energy content).
- ⁶ When an organism dies these concentrations differences relax, between parts of the cell, between inside and outside the cell, as the organism's molecules glide toward thermodynamic equilibrium with the environment.
- ⁷ *No device is possible that operates in a cycle and whose sole net effect is to transfer heat from a cooler body to a hotter body*. In the colloquial: *Heat spontaneously conducts from*

hot to cold, not vice versa. For example, one often sees ice melt in a hot drink, but one never sees cold tea spontaneously heat up while just sitting around.

- ⁸ Think of a boring art exhibit attended by mutual strangers.
- ⁹ There they are probably dearly hoping they won't run into a wall and be forced to eat another white chocolate Hershey kiss with a stale almond at the center. Unfortunately, their walks are random so they have no control over whether or when they hit another wall—rules are rules, after all. Fortunately, the boxes are scarce at the left end of the corridor.
- ¹⁰ This might be a dumpster full of valuable Star Wars memorabilia (Lisbeth Accomando, private communication, 2022).
- ¹¹ Now the left-corridor unfortunates, who had to endure eating white chocolate Hershey kisses with stale almond centers, have won their reward and, at the very least, they can now afford some decent chocolate.
- ¹² A critical aspect of the AMCC is that its anode grows (precipitates AgCl), while its cathode corrodes (loses AgCl). For the system to behave as a true SLD, the anode and cathode must be regularly flipped in order for them to maintain their masses.

ACKNOWLEDGMENTS

The author gratefully acknowledges the insights, comments, and assistance of D. Miller, T. Zawlacki, T. Welsh, A. Watson, G. Hathaway, A. B. Accomando, P. C. Sheehan, and W. F. Sheehan. Technical support for this article was provided by C. Ibarra. The author thanks G. Moddel and C. Chase for inviting this article and the two reviewers for their helpful suggestions. This research was partially supported by the Laney and Pasha Thornton Foundation.

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