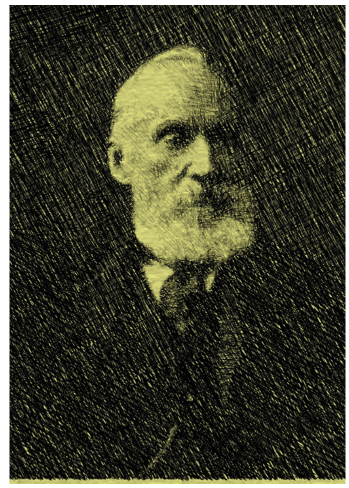
Daniel P. Sheehan

Beyond the Second Law of Thermodynamics

Rudolf Clausius



Lord Kelvin

Nicolas Sadi Carnot

Energy *makes the world go 'round in* nearly every sense. It is the lifeblood of civilization, but inexpensive, high energy density sources are rapidly being depleted, and their exploitation is severely degrading the environment. But there may be a radical solution to this environment-energy dilemma: over the last 20 years, the universality of the second law of thermodynamics has fallen into serious doubt.[1] Should it prove breakable, this could open the door to a nearly limitless reservoir of ubiquitous, clean, recyclable energy. If economical, it could precipitate paradigm shifts in energy production, utilization, and politics. Here I will summarize the current status of the second law and speculate about how its breakdown might affect both science and civilization.

Physical laws, like conservation of energy and angular momentum, govern the universe at its deepest levels. Among these, the second law of thermodynamics has often been called "the supreme law of nature."[2] The cosmos lives—and will eventually die—by it; it guides our lives from the moments of our conceptions until our deaths; and nearly every system in the universe is bound by it, from the atomic level up to the largest galactic superclusters. Even the direction of time appears authored by it.[3]

Arguably, no other physical law has been better tested. The second law has been verified in countless experiments for more than 150 years, and our technological and biological worlds rely on it. Most scientists consider it beyond reproach such that even to question it invites ridicule and professional ruin. Nevertheless, over the last 20 years it has begun to show stress—if not outright breakdown—both in theory and in laboratory experiments. During this time, more than 70 mainstream journal articles, monographs, and conference proceedings have raised several dozen challenges to its universal status—more than the sum total during its previous 150-year history.

The second law was first enunciated by Rudolf Clausius (1850) and Lord Kelvin (1851), largely based on work of Nicolas Sadi Carnot 25 years earlier. There are dozens of ways to state it formally, but for our purposes let's put it colloquially in a couple of ways:

(i) The world gets messier; and

(ii) Everything eventually runs down.

The first statement needs no explanation for anyone who's stirred cream into coffee, had to clean their house, or played 52-card pick-up. The world never spontaneously gets more organized; in fact, the more you try to tidy up your local environment the messier the world becomes overall due to the effort, sweat, and heat you generate making it so. (When I was a teenager, I once argued with my mother that I shouldn't have to clean up my room because of this fact; unfortunately, she didn't buy it. Perhaps I should have argued with my father, a physical chemist.) So relax and get used to messes, the universe likes them.

In effect, the second law is a tax on energy transactions. Ultimately, it demands that all energy must be degraded into a useless form: heat. This is why you have to eat regularly, pay power bills, and feed your cat, dog, and car. If it could be subverted, one could reconstitute heat back into useful work, thereby making energy recyclable—and thereby, effectively limitless.

Challenges to the Second Law

Over the past two decades, a number of research groups worldwide have proposed a diverse set of second law challenges. They span classical and quantum mechanical regimes; range from nanoscopic to planetary in size; operate from above the melting point of steel, down to a fraction of a degree above absolute zero. They utilize ideal gases, plasmas, semiconductors, superconductors, micro- and mesoscopic electrical circuits, chemical

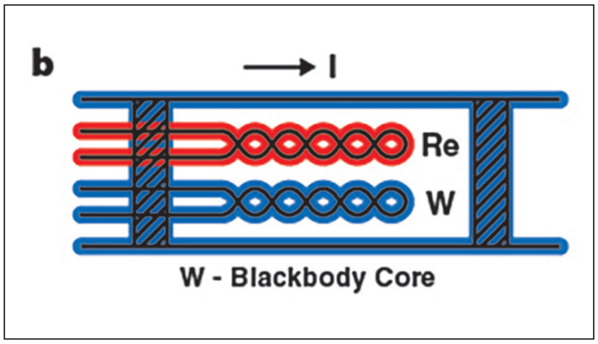


Figure 1: Schematic of second law experiment. Tungsten-coated and rhenium coated thermocouples inside high-temperature tungsten cavity. Hydrogen reactions occur on rhenium and tungsten surfaces; rhenium preferentially cools due to superior hydrogen dissociation. Thermocouples measure the temperatures of the reacting surfaces.

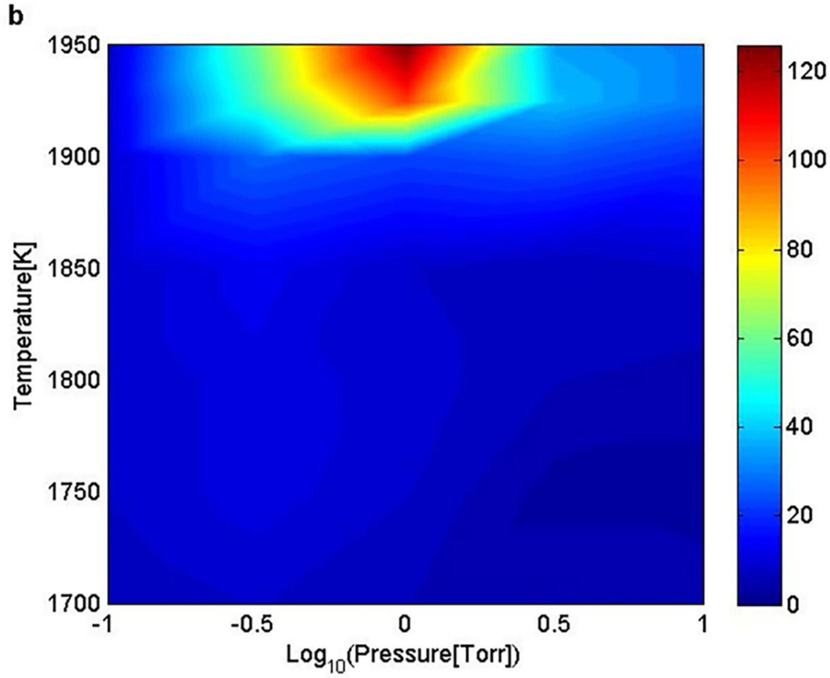


Figure 2: Second law breakdown. Temperature difference between tungsten and rhenium (color graded) versus cavity temperature (vertical axis) and hydrogen gas pressure (horizontal axis, log plot). [4] At elevated temperatures (T ≥ 1700K) and low hydrogen gas pressures (~ 1 Torr), the second-law-forbidden temperature difference between tungsten and rhenium emerges. Were the second law absolute, this plot should be monotone blue, indicating no temperature difference between tungsten and rhenium, regardless of cavity temperature and pressure.

catalysts, and biologically inspired structures. Perhaps not surprisingly, most inhabit physical regimes that were unimagined when the second law was proposed more than a century and a half ago, but which can now be easily created in the lab. Pioneers in this field include L.G.M. Gordon, J. Denur, V. Capek, et al., A. Allahverdyan and Th. Nieuwenhuizen, P. Keefe, A. Nikulov, J. Berger, and S. Miller.[1]

Here at the University of San Diego, my students and I have pursued about a half-dozen second law challenges over the past 25 years, including ones involving plasma, chemical, gravitational, biological, and solid state physics. Laboratory experiments have corroborated key mechanisms upon which they depend. These culminated in 2012–13 with a series of laboratory experiments that showed true second law breakdown.[4] The demonstration was straightforward. A small, closed, high-temperature cavity contained two metal catalysts (rhenium and tungsten), which were known to dissociate molecular hydrogen (H_2) to different degrees (Figure 1). (Rhenium dissociates hydrogen molecules into atoms better than tungsten does; conversely, tungsten recombines hydrogen atoms back into hydrogen molecules better than rhenium.) Because the dissociation reaction ($H_2 \rightarrow 2H$) is endothermic (absorbs heat), and the recombination reaction ($2H \rightarrow H_2$) is exothermic (liberates heat), when hydrogen was introduced into the cavity, the rhenium surfaces cooled (up to more than 125 K) relative to the tungsten (Figure 2). Because the hydrogen-metal reactions were ongoing in the sealed cavity, the rhenium stayed cooler than the tungsten indefinitely. This permanent temperature difference—this steady-state nonequilibrium—is expressly forbidden by the second law, not just because the system won't settle down to a single-temperature equilibrium, but because this steady-state temperature difference can, in principle, be used to drive a heat engine (or produce electricity) solely by converting heat back into work, which is a violation of one of the most fundamental statements of the second law (Kelvin-Planck formulation).[1]

Thus far, these results have been met by the scientific community with almost universal apathy; no one has pointed out any errors in the experiments or underlying theory, and yet the community has not admitted failure of the second law, remaining confident in its inviolability. As per Thomas Kuhn's insightful analysis in *The Structure of Scientific Revolutions*, these anomalous results have been insufficient to bring the second law into the crisis state necessary to precipitate a paradigm shift. To some degree this is understandable because the experiments were conducted at high temperatures and at low gas pressures, far from the conditions to which most scientists are accustomed; thus, apparently, they can be safely ignored.

Although the hydrogen-metal experiments conducted at high temperatures (almost 2000K) were encouraging, it would be better to have gas-surface reactions nearer to room temperature. Fortunately, we have recently discovered several such systems—two surfaces that differentially dissociate weakly bound gas-phase dimers at room temperature—which we hope to develop into a commercially-viable second law device (SLD).

The SLD that we are investigating is embodied as thin, bi-layered sheets that sustain large temperature gradients across them due to differential gas-surface reactions between the interior sheet surfaces. In their rudimentary form these could be used for heating or cooling homes or clothing, or for powering appliances, but in larger arrays they might help power cities, converting heat in the air or local water supplies into electricity.

The existence of SLDs raises a number of scientific questions. Perhaps dearest to most scientists is this: Is there a way to preserve the absolute status of the second law in light of working SLDs? Probably not, because laboratory experiments have now demonstrated otherwise.[4] However, if the second law is reformulated quantum mechanically, perhaps using quantum *entanglement*, then there might be hope. Entanglement is a purely quantum phenomenon whereby quantum "things" (e.g., atoms, molecules, even people) form invisible connections and correlations by interacting with one another. These unseen—often secret—correlations can be maintained, in principle, over arbitrarily large distances and times. It has been speculated that there is an inexorable increase in quantum entanglement between quantum objects as they interact, regardless of any classical entropy increase. If so, then one can perhaps reformulate the second law in terms of entanglement increase, rather than entropy increase, and thereby preserve some form of it. In other words, even a SLD should obey this quantum form of the second law involving entanglement, even though it would violate the classical form involving entropy.

The Laws of Physics

Over the centuries, many physical "laws" have been proposed—*e.g.*, ideal gas law, Kepler's laws, Newton's law of gravitation—that have later been found to be inexact or incomplete descriptions of nature. Until the recent laboratory breakdown of the second law, no law that is entirely obeyed in nature—*e.g.*, conservation of charge, conservation of linear and angular momenta—has been subverted by humans. That is, until these recent experiments,[4] humans have been unable to contrive means by which to break otherwise unbreakable natural laws. (This assumes, of course, that Nature herself does not subvert the second law; proposals for this have been made.[5]) This raises questions, for instance, (a) Are physical laws merely prescriptions rather than absolute requirements? and (b) If humans can bend the second law, might other so-called "inviolable" laws also be bent and reshaped to our liking? Might, for instance, the law of linear momentum and the nature of inertia be negotiable such as to lead to better forms of propulsion, perhaps ones suitable for interstellar travel? Ultimately, might humans be not simply observers of natural laws, but creators of them?

Since 1850, it has been realized that the cosmos as a whole should be bound by the second law, thus is condemned to an unwinding, a running down, a slow and inevitable demise, know as "heat death," in which all its usable free energy is converted into heat such that the universe arrives at a lifeless equilibrium state—thermodynamic death. Though modern inflationary cosmology modifies this fate somewhat, in general it is agreed that the second law will help orchestrate the universe's eventual demise. However, it has also been shown that, if the second law is violable, this standard fate (heat death) might be reversed or delayed by intelligent intervention, perhaps indefinitely.[1] This raises additional fundamental questions. What is the role of intelligence in the development of the cosmos? Are we just passive observers or are we active participants?

Ironically, concerning the wholesale reversal of entropy on a cosmic scale in an effort to forestall heat death, one should be careful of what one asks for. If all the heat in the universe were, in fact, converted back solely into macroscopic kinetic or potential energy, the cosmos would freeze, and die just as surely as if by heat death. As in Frost's famous poem "Fire and Ice," "Some say the world will end in fire, some say in ice," and "if it had to perish," either "would suffice."

"Until the recent laboratory breakdown of the second law, no law that is entirely obeyed in nature...has been subverted by humans."

In terms of our relationship to energy back here on Earth, subverting the second law should have a salutary effect. It is said that humans evolved with a mindset of scarcity—for food, water, land, energy—with all its attendant evils: greed, envy, violence. A limitless supply of energy might alleviate some of these scarcities, perhaps eliminating some of their attendant evils. This age-old mindset of scarcity might be replaced with a mindset of plenty.

A World in Which the Second Law is Violated

What would it mean if the second law could be broken in an economically viable manner? Simply put, it could revolutionize energy production and usage worldwide. Inasmuch as roughly 20% of the world's economy revolves around energy, one would expect that such a revolution would create both opportunities and crises. After all economies are defined by it; wars are fought over it; nations rise and fall by it. To upset this status quo is to invite change at the most fundamental levels: scientific, economic, ecological, political, military, societal.

We are surrounded by a virtually limitless sea of energy: thermal energy (heat). The total thermal energy content of the Earth's atmosphere, ocean, and upper crust is about 10,000 times greater than all the known fossil fuel and fission energy reserves. At civilization's current rate of consumption, it would take millions of years to expend this, and even then, thermal energy is constantly being generated on the earth's surface by solar radiation far faster than it is used. All the energy we could ever use already surrounds us in the form of heat; however, it is currently beyond our reach—like a mirage in the desert—because of the second law. But, this seems about to change.

Let's briefly imagine a world in which the second law is violable and in which devices exist with the high energy density predicted for them. At home, a SLD power generator might consist of a tube about the size of a coffee can. On one end could be a fan to draw the air through the tube over a series of baffles—like a radiator—packed with dozens of thin SLD panels. The SLDs convert atmospheric heat into electricity, some of which powers the fan, but the vast majority of which is available to run household appliances and utilities. (Air enters the SLD warm and leaves cooler.) For modest, self-generated air flow (5m/s) and modest heat recovery ($\Delta T \simeq 20K$), calculations indicate that this coffee-can-sized generator should produce between 1 and 2 kilowatts nonstop—roughly enough to power an average US household.

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On the road and in the sky, SLD automobiles and planes could *run on air*, taking in air at the front, passing it through internal SLD baffles, converting heat into electricity for electric motors, and finally exhausting colder air out the back. They would consume no fuel and produce no pollution, aside from trailing plumes of cool air. In principle, almost any technological device could be redesigned to be energy self-reliant. Homes, businesses, and industries could become energy self-sufficient. The power grid would become superfluous.

Thermal energy should be superior to almost any other energy resource. First, the terrestrial thermal energy reserves in the atmosphere, ocean, and crust alone exceed by orders of magnitude all presently exploited energy reserves combined (coal, oil, gas, uranium). Heat is ubiquitous—from the equator to the poles—so SLDs should operate anywhere, anytime. Unlike any other energy source, heat becomes recyclable and renewable; in this sense, it is effectively limitless. It is clean, *green* energy. Aside from the products of their manufacturing, SLDs should create no chemical wastes and no pollution since they consume no material fuel, only heat. In principle, their power flux densities suggest they should be compatible with virtually any modern mechanical or electronic device, from light bulb to locomotive.

If they prove economically competitive, SLDs could precipitate a shift in the world's energy paradigm. Unlike traditional energy sources, thermal energy does not require discovery and extraction since it is found in abundance everywhere. Large generation plants or transmission infrastructure would be unnecessary since heat-to-electricity conversion could be accomplished locally. Energy storage (*e.g.*, batteries, flywheels) would be unnecessary for all but the highest power applications. Furthermore, in principle, SLDs can generate far more power per unit area than other renewable energy sources (*e.g.*, solar, hydroelectric, or wind). And, thermal energy is not simply *renewable*, it is *perpetually recyclable*.

The short-term economic and political impacts of cheap and abundant SLDs could be dire. Vast personal, corporate, and national fortunes in mineral wealth would be wiped out. Middle Eastern energy empires would collapse as oil and gas became nearly worthless, their use restricted largely to plastics, lubricants and asphalt. The energy exploration, extraction, and delivery industries would implode; gas and oil wells, coal mines, tanker fleets, and gas stations would be idled; pipelines, refineries, power plants, and power grids would be scavenged for parts. The economic clout and political leverage derived from energy resources would largely vanish, restructuring economic and political landscapes across the globe, for instance, those between gas-rich Russia and energy-poor Europe.

Beyond the second law and these shocks, the economic, political, and ecological benefits of SLDs could be profound. The release of the world economy from the constraints of limited and expensive energy should be invigorating. Energy-shackled economies, like India and China, could flourish. Cheap and ubiquitous energy should reduce the cost of virtually all products. The costs of recycling material resources like metals, plastics, and paper should also be reduced.

Inexpensive energy should help unlock other critical resources, for instance, possibly allowing widespread desalination of seawater and its pumping over long distances to thirsty lands and populations. Recently, the world experienced a tight coupling between energy and food markets, resulting in global shortages in basic foodstuffs like rice, wheat, and corn, affecting hundreds of millions of humans. If energy can be made sufficiently inexpensive, these two markets should decouple, thereby stabilizing food supplies. (Of course, cheap energy should also reduce the cost of producing and transporting food, as well.)

Eliminating these energy-related shortages should, in turn, reduce political and economic tensions leading to war and civil strife. The necessities for military interventions to control energy reserves would end; armies could come home. Politically and militarily, there would be one less critical resource to fight over.

Pollution from fossil fuel burning and nuclear fission could be eliminated. Land scarred and ecosystems maimed by civilization's thirst for energy could be left to heal. (It has been suggested that greenhouse gases might be scrubbed from the atmosphere, but these proposals are energy-intensive. SLDs might be deployed here since scrubbing would now be an energy-neutral proposition.)

Of course, the virtues of this technology could become a vice if taken to extremes. Abundant, inexpensive energy would lift a fundamental constraint on humankind's exploitation of Nature. Mining, fishing, and logging could be conducted nonstop, further stripping the world's natural resources and accelerating environmental destruction. Wars could be conducted by tanks, ships, and planes without need of refueling. The fault of these dangers rests, of course, not in the technology but in ourselves. Even so, if history is a guide, this conversion to a heat recycling society could take decades, owing to the enormous economic and political inertias surrounding traditional energy sources.

At present the immediate specters of global food shortages, climate change, pollution, ecosystem destruction, and species extinctions, driven largely by humanity's thirst for energy, require rapid and radical solutions. If the second law can be violated in an economically and ecologically viable manner, then I believe it should be pursued vigorously.

The energy paradigm under which civilization has historically operated but which now threatens the environment and civil society—that free-energy sources are absolutely required—is now being challenged. It is hoped that recent experiments will inspire efficient, high power density, and economical second law devices. Certainly, experimental violations of the second law will fundamentally alter the landscape of physics and the pure sciences, but their potential for positive societal change is perhaps even more profound. If successful, they promise to change humankind's relationship to energy perhaps as fundamentally as it was by the taming of fire a million years ago.

Nota Bene: A patent concerning the gas-surface concepts discussed in this article has recently been granted by the USPTO. Paradigm Energy Research Corporation, which holds the patent, is seeking funding to develop it into a commercial technology.

Acknowledgements: This article, based largely on an earlier Journal of Scientific Exploration *article,[6] is dedicated to the memory of Richard Shoup.*

ENDNOTES

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DANIEL P SHEEHAN is a Professor of Physics at the University of San Diego. He earned his B.S. in chemistry at Santa Clara University in 1981, and his Ph.D. in Physics at UC Irvine in 1987, specializing in plasma physics. His research interests include the foundations of thermodynamics, the physics of time (retrocausation), non-traditional plasmas, nanotechnology, planetary formation, and Casimir physics. Over the last 25 years he has investigated several theoretical and experimental challenges to the second law of thermodynamics. In 2005 he coauthored the first mainstream scientific treatise on the subject and in 2002 organized the first international conference devoted to the limits to the second law. As a teacher one of his primary aims is to help students develop personal styles in approaching real-world physical problems using back-of-the-envelope techniques, that is, without using calculators or notes. For example, senior physics majors should be able to tackle "physics koans" such as: "I cover the golden Sun with my thumb. You disappear six kilometers away. How many fish are there in the sea?"