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Entropy is the handmaiden of the second law, not its peer.

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This quote, taken from Section 1.5 of *Challenges to the Second Law of Thermodynamics* by Vladislav Capek and Daniel P. Sheehan, is the theme for this month’s blog providing both an admonition and the capstone of much of the past year’s worth of posts.

Over a year ago (15 months to be more exact – in the post entitled [An Invitation to Entropy](http://underthehood.blogwyrm.com/?p=1553)) I asserted that no physical concept was as poorly understood as entropy. I based that claim on a similar statement by Swendsen, who presented 9 pairs of contradictory statements about entropy in an article for the American Journal of Physics. Over the intervening months, this column has explored various ways of looking at entropy and the second law as a way of testing this assertion. It did this mostly by following the logic of Enrico Fermi’s book *Thermodynamics* or, a text clearly influenced by it, Ashley Carter’s *Classical and Statistical Thermodynamics*.

Fermi’s approach (here I also include Carter) had a clear plan of showing the logical equivalence of three different articulations of the second law: Kelvin-Planck, Clausius, and Carnot and then using them (predominantly Carnot’s theorem) to introduce entropy as a state variable, a discovery that was one of the great triumphs of nineteenth century physics.

This approach is powerful in its cohesion but it is not powerful enough to have persuaded every physicist, or even a majority of them, as to its completeness and universality. Anyone who doubts that conclusion need only consult Chapter 1 of Capek and Sheehan in which they say “[o]nce established, it settled in and multiplied wantonly; the second law has more common formulations than any other physical law.” In that chapter, they present an excellent history of the thinking about the second law in order to set the stage for the various challenges that follow. They also present ‘21’ different expressions of second law along with the assurance that not all of them are logically equivalent. The following table lists the various ones provided by Capek and Sheehan roughly grouped by the categorization scheme they use.

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| Category | Name | Formulation |
| Device and Process Impossibilities | [Kelvin-Planck](http://underthehood.blogwyrm.com/?p=1626) | No device, operating in a cycle, can produce the sole effect of extraction a quantity of heat from a heat reservoir and the performance of an equal quantity of work. |
| [Clausius Heat](http://underthehood.blogwyrm.com/?p=1626) | No process is possible for which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at higher temperature. |
| Perpetual Motion | Perpetuum mobile of the second type (i.e., conventional perpetual motion machines that can convert heat to work perfectly) are impossible. |
| [Refrigerators](http://underthehood.blogwyrm.com/?p=1640) | Perfectly efficient refrigerators are impossible. |
| Irreversibility | All natural processes are irreversible or it is impossible to find a natural process that is reversible |
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| [Heat Engines](http://underthehood.blogwyrm.com/?p=1640) | Perfectly efficient heat engines ($\eta = 1$) are impossible. |
| Engines | [Carnot Theorem](http://underthehood.blogwyrm.com/?p=1640) | All Carnot engines operating between the same two temperatures have the same efficiency. |
| [Efficiency](http://underthehood.blogwyrm.com/?p=1640) | All Carnot engines have efficiencies satisfying: $0 <\eta< 1$. |
| [Cycle Theorem](http://underthehood.blogwyrm.com/?p=1689) | Any physically realizable heat engine that operates in a cycle must satisfy: $\oint \frac{\{\tilde d} Q}{T} \leq 0$ where the equality holds only for reversible processes. |
| Equilibrium States | Reversibility | All normal quasi-static processes are reversible, and conversely |
| Free Expansion | Adiabatic free expansion of a perfect gas is an irreversible process |
| Equilibrium | The macroscopic properties of an isolated nonstatic system eventually assume static values. |
| Gyftopolous & Beretta | Among all the states of a system – with given values of energy, the amounts of constituents and the parameters – there is one and only one stable equilibrium state. Moreover, starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrary specified values of amounts of constituents and parameters by means of a reversible weight process. |
| Macdonald | It is impossible to transfer an arbitrarily large amount of heat from a standard heat source with processes terminating at a fixed state of $Z$. |
| Thomson Equilibrium | No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source. |
| Entropy | [Clausius Entropy](http://underthehood.blogwyrm.com/?p=1689) | An adiabatically isolated system ${\tilde d} Q = 0$ that moves from one equilibrium state to another there is a state function, called the entropy, such that its change between any two states is given by $\Delta S = S\_b - S\_a \geq \int\_a^b \frac{ {\tilde d} Q}{T} = 0$ where the equality holds for reversible processes. |
| Planck | Every physical or chemical process occurring in nature proceeds in such a way that the sum of the entropies of all bodies which participate in any way in the process is increased. In the limiting case, for reversible processes, the sum remains unchanged. |
| Gibbs | Thermodynamic equilibrium for an isolated system is the state of maximum entropy. |
| Entropy Properties | Every thermodynamic system has ast least two properties (and perhaps others): an intensive one, called the absolute temperature $T({\vec x},t)$, that may vary spatially and temporally in the system and an extensive one, called the entropy $S$ to which it is conjugate. Together they satisfy the following three conditions: (i) The entropy change $dS$ during time interval $dt$ is the sum $dS = dS\_e + dS\_i$, where $dS\_e$ is the flow of entropy through the boundary of the system and $dS\_I$ is the entropy production within the system; (ii) Heat flux ${\tilde d}Q$ through a boundary at uniform temperature $T$ results in entropy change $dS\_e = {\tilde d} Q T$. (iii) $dS\_i \geq 0$ where the equality holds for reversible processes and the inequality for irreversible ones. |
| Mathematical Sets and Spaces | Caratheodory (Born Version) | In every neighborhood of each state $s$ there are states $\{t\}$ that are inaccessible by means of adiabatic changes of state. |
| Caratheodory Principle | In every open neighborhood $U\_s \sub \Gamma$ of an arbitrarily chosen state $s$ there are states $\{t\}$ such that for some open neighborhood \cup t of t$: all states $r$ within $\cup t$ cannot be reached adiabatically from $s$. |

Capek and Sheehan go to great pains to stress that this list is by no means exhaustive. They offer the following in way of explaining just why there are so many inequivalent ways of looking at the second law:

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Despite — or perhaps because of — its fundamental importance, no single formulation has risen to dominance. This is a reflection of its many facets and applications, its protean nature, its colorful and confused history, but also its many unresolved foundational issues.

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In the same chapter they also present 21 non-equivalent definitions of entropy ranging from Clausius’ original statement of $S$ as a state variable to Boltzmann’s notion of relating it to the natural logarithm of the number of microstates to modern quantum and information theoretic points-of-view. They notes that:

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[t]here is no completely satisfactory definition of entropy. To some degree, every definition is predicated on physical ignorance of the system it describes and, therefore, must rely on powerful ad hoc assumptions to close the explanatory gap. These limit their scopes of validity.

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Capek and Sheehan provide a number of insights and thought-provoking (and often witty) points. They present an excellent critique demonstrating how the ambiguity in the definition of equilibrium state is strongly linked to the level of abstraction one employs in describing nature. But the primary scientific utility they provide is drawing a clear distinction between the second law and entropy (hence the introductory quote). Sheehan goes so far as to opine that the concept of entropy, despite its historic and current usefulness, must eventually be abandoned in favor of concepts more in line with the systems being studies.

Capek and Sheehan have done a great service in compiling this summary and by drawing sharper distinctions in a subject that encourages fuzzy thinking. I’ll leave this month’s post by quoting them again as the impress on the reader just how far we have to go with understanding nature, thermodynamics, and the second law:

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In summary, the laws of thermodynamics are not as sacrosanct as one might hope. The third law has been violated experimentally (in at least one form); the zeroth law has a warrant out for its arrest; and the first law can’t be violated because it’s effectively tautological. The second law is intact (for now), but as we will discuss, it is under heavy attack both experimentally and theoretically.

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