Tracing the Second Law
Modern thermodynamics owes a debt to the contributions of a line of researchers extending back more than a century. By Howard W. Butler

While man learned to control and use fire many thousands of years ago, only in the last 300 years has the nature of heat been given serious consideration. In this short time, it has been explained as phlogiston, a mysterious fluid created by fire, and as caloric, a material fluid flowing from hot to cold. The modern view, that heat is a convertible form of energy, is fewer than 200 years old.

In the 19th century, James Joule, an English physicist, experimented with converting mechanical energy into thermal effect. He discovered the equivalence of heat and work, and the First Law of Thermodynamics was firmly established. His tombstone is inscribed with a number, 722.55, which was his approximation to the now-accepted 778 foot-pounds per British thermal unit. In his honor, the units for energy in the S.I. system are designated in joules.

The Second Law developed in phases over some 125 years. It is one of the most abstract laws of physical science, and is the bane of students and others who try to understand its complexity. A professor once observed that all engineers could be divided into three groups: those who knew all about entropy, those who used it anyway, and those carefree souls into whose lives it never intrudes. Blissful ignorance, however, simply ignores the universal influence of the Second Law on every natural process. Even the simple act of taking a step would be impossible without the intrusion of an entropic effect.

The first phase in the evolution of the Second Law is older than Joule’s work and is due to Sadi Carnot. A graduate of the famous École Polytechnique in Paris, he joined the French Army Corps of Engineers. In this capacity, he became fascinated with the development of the steam engine. He was also impressed that such useful machines could be developed in the total absence of guiding principles or analysis, but on empirical reasoning alone. His technical background gave him the incentive and preparation to try to remedy this condition, but he soon discovered that a major obstacle was the inability to give mathematical precision to the many irreversible events occurring in the operation. This led to his two most significant discoveries.

The first was the observation that all irreversible processes have associated with them an ideal process that is the limiting case when the irreversibility is progressively reduced to zero. This ideal case is amenable to mathematical analysis, using the appropriate available principles. The other discovery was the idea of combining a sequence of ideal processes so that the last one ended where the first one began, and the concept of a cycle was born. This was quite
novel, since no steam engine operated on such a cycle.

By combining these two ideas, Carnot was able to analyze a number of cycles in which caloric flowed in and out of a cycle while producing useful work. His most famous cycle has the caloric added to the system at a constant high temperature and leaving the system at a constant lower temperature. For this cycle, he demonstrated that the efficiency depended only on the temperatures of the sources and sinks of the caloric, and was independent of the nature of the thermodynamic medium.


His work was done despite two major defects. One was that the prevailing temperature scale was based on the freezing and boiling points of water; the other was the prevailing concept of heat as a caloric fluid that had to be conserved during the cycle. His later writings indicate he was dissatisfied with the caloric theory and, had he not died in 1832, Carnot might have preempted Joule in rejecting it.

The second phase in the evolution of the Second Law took place in 1849, when William Thomson (later Lord Kelvin) studied Carnot’s work. Being familiar with the recent development of the first law, he discovered and corrected the error due to the caloric theory, which led him to his discovery of an absolute temperature scale. With this, he showed that the heat discharged to the low-temperature reservoir was only a fraction of the heat from the high-temperature source, leading to the relation,

\[ Q_d/T_3 = Q_i/T_i \]

where \( Q_d \) is the heat added at the temperature \( T_d \), and \( Q_i \) is the heat removed at the temperature \( T_i \), the difference between \( Q_d \) and \( Q_i \) is the work delivered by the ideal cycle.

The third phase of the evolution of the Second Law was carried out by a German professor of mathematical physics, Rudolf Clausius, who became aware of the work of Carnot, Joule, and Kelvin in 1850. He modified Kelvin’s formula in two ways—first, by adopting the convention that heat added is considered to be positive, and heat removed negative; second, he recognized that heat might be added and removed at several points during the cycle. His revision took the form:

\[ Q_1/T_1 + Q_2/T_2 + Q_3/T_3 + \ldots = 0 \]

where \( Q \) may be positive and negative. He then recognized that a more general form of this relation for all ideal cycles could be stated in a simple calculus form as:

\[ \int \frac{dQ}{T} = 0 \]

where \( T \) is the temperature at the surface across which the small quantities of heat flow.

During the next 15 years, Clausius undertook an investigation into the logic used by Carnot in his ideal cycle analysis to see if any general rule could be found for the form of the cyclic integral if an unspecified type and amount of irreversibility occurred during the cycle. His study was rewarded by the discovery of his famous inequality:

\[ \int \frac{dQ}{T} \leq 0 \]

where the equality to zero holds for ideal cycles, and the negative inequality for all irreversible cycles. Clausius recognized that when the integral of a quantity around a complete cycle is zero, the integral of that quantity between different states is independent of the process and depends only on the change of a related property of the system. The simple steps required to demonstrate this are shown in all textbooks. When this is applied to the first law:

\[ \int \delta Q - \delta W = 0, \text{ then } \int \delta Q - \delta W = \int \delta E = E_2 - E_1 \]

where \( Q \) and \( W \) are the heat and work, and \( E \) is the internal energy property.

In order to apply this procedure to his inequality, Clausius devised a clever scheme to convert it into an equality. He postulated that when heat was added to the cycle, it was “given a small amplification \( \delta Q' \), but when heat left the cycle, it was unchanged. He called \( \delta Q' \) the ‘uncompensated heat,’ and expressed equation 4 as:

\[ \frac{\delta Q}{T} + \frac{\delta Q'}{T} = 0, \text{ where } \delta Q' > 0. \]

There is no record of this idea ever having been taken seriously, but it did allow him to discover the property \( S \), which he gave the name “entropy” in his 1865 paper. Willard Gibbs wrote a world-renowned book, *On the Equilibrium of Heterogeneous Substances*, in 1878, and completely ignored the inequality.

A fourth phase in the development of the Second Law was carried out by Lars Onsager in 1931. As an assistant professor of chemistry at Brown University, he became interested in applying the ideas of the earlier discoverers to chemically reacting systems. He devised an ingenious type of Carnot cycle in which a series of three chemical reac-
tions were arranged in a cycle. He was able to analyze these reactions in sufficient detail to discover a chemical equivalent to Clausius’s uncompensated heat. For reactions taking place irreversibly, he derived a quantity he called dissipation, designated $\phi$, which was produced by the irreversibility. For reversible reactions, this quantity is always zero. The positive-definite quality of this quantity enabled him to discover his famous reciprocal relations, $Lij = Lji$. He was awarded the Nobel Prize in 1975 for this work. His form of the Clausius inequality was:

$$ \int \delta Q / T + \delta Q / T = 0, \text{ with } \phi > 0. $$

The fifth phase in the evolution of the Second Law was developed by Ilya Prigogine in 1945. As a doctoral student at the Free University of Brussels, he became interested in the new field of irreversible thermodynamics, where the properties of the system are allowed to vary from point to point as well as with time. To apply the laws to such systems, it is necessary to invoke the principle of local equilibrium, which states the specific dependent properties retain their dependence on the independent properties at a point as they do for a quasistatic system. Fortunately, many processes of practical importance conform to this condition, such as heat conduction, diffusion, and Newtonian viscous fluids. However, the flow through strong shock waves, violent chemical reactions, turbulence, and chaotic processes are “too” irreversible to be in this class.

Prigogine modified Clausius’s equation 6 by splitting the change in the entropy into two parts, one of which replaced the uncompensated heat. This gave him a form of the Second Law that yielded clusters of terms for a general dissipation function, with each containing pairs of terms for a particular irreversibility. He called these pairs products of generalized forces and fluxes, and since either can be positive or negative, the product is only positive. In order to meet this requirement, the forces are linearly related to the fluxes. As an example, for simple heat conduction, $Q = -k \frac{dT}{dx} \geq 0$, setting $q = -k \frac{dT}{dx}$ gives $\phi = k (\frac{dT}{dx})^2 \geq 0$ and the Second Law prescribes that heat can only flow down a temperature gradient. Similarly, more complex relations are found for natural processes. Prigogine was also awarded a Nobel Prize in 1977.

At this point, it is appropriate to show that the Clausius inequality can be transformed into an equality without resorting to strained justifications. All that is needed is the recognition that the magnitude of the negativity of Clausius’s inequality is monotonically related to the intensity of the irreversibility, and that the irreversibility may manifest itself at any point around the cycle. The first makes it possible to express equation 4 as:

$$ \int \delta Q / T + \delta Q / T = 0, \text{ with } \sigma > 0, $$

where $\sigma$ is the magnitude of the negative value of the integral for the entire cycle. Secondly, this total accumulates bit-by-bit throughout the cycle and is simply the sum of the bits, i.e.:

$$ \sigma = \int \delta Q / T $$

Combining this with the above relation gives:

$$ \int \delta Q / T + \delta Q / T = 0, \text{ with } \sigma > 0. $$

This is now in the proper form to be converted to a single process, as:

$$ \int \delta Q / T + \delta Q / T = \int dS = S_2 - S_1 $$

With equation 11 as the basic form of the Second Law for closed systems, simple math requires each term be expressed in the same units, but there is no recognized name for them, like joules for the energy terms in the First Law.

**Clarifying Terms**

I propose that the units be called carnots, in honor of the originator. Second, that the unifying concept of the Second Law be called entropy, in honor of the contributions of Clausius, who coined the term. Third, that the property $S$ be renamed the internal entropy by analogy with the internal energy of the First Law. The quantity $Q / T$ is the entropy flow yoked to the heat flow. Last, the positive-definite quantity $\sigma$ be called the entropy creation, as a recognition of its source in irreversible effects. It is the one term that makes the Second Law unique in the physical world. If individual terms for the concepts could be adopted, much of the confusion of the Second Law would be mitigated.

The Second Law is a statement that the entropy content of a system may be increased or decreased by entropy exchanges with the environment, but may only be increased as irreversibilities cause entropy creation. It is not a conservation law, but simply a balancing of several entropic effects. Since real processes are irreversible, the 1865 statement by Clausius, “The entropy of the universe tends always toward a maximum,” is certainly an ultimate truth.