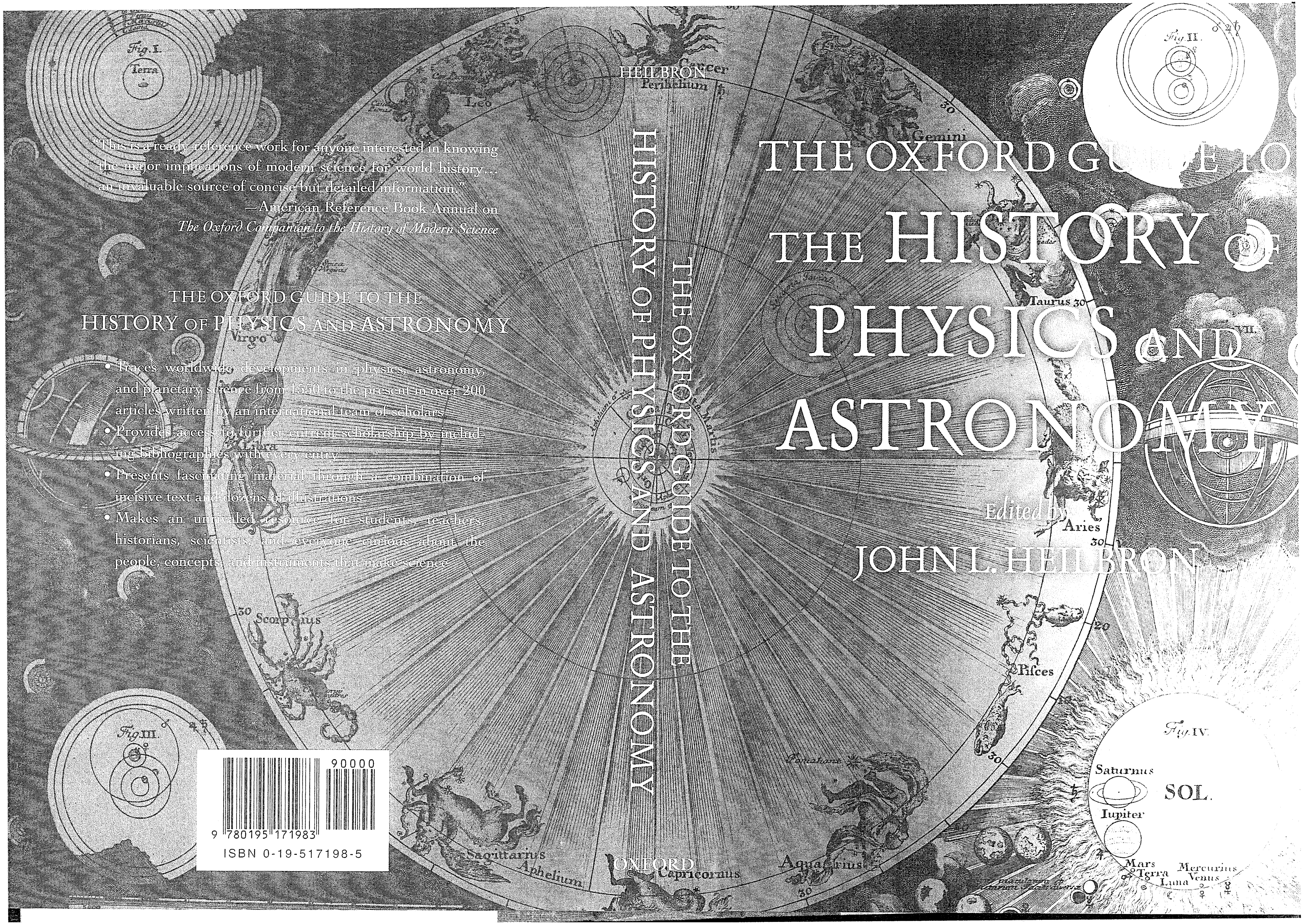

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Edited by

JOHN L. HEILBRON

ENTROPY. Many physicists and chemists quip that the second law of thermodynamics has as many formulations as there are physicists and chemists. Perhaps the most intriguing expression of the law is Ludwig *Boltzmann's paraphrase of Willard *Gibbs: "The impossibility of an uncompensated decrease in entropy seems to be reduced to improbability."

Entropy owes its birth to a paradox first pointed out by William *Thomson in 1847: energy cannot be destroyed or created, yet heat energy loses its capacity to do work (for example, to raise a weight) when it is transferred from a warm body to a cold one. In 1852 he suggested that in processes like heat conduction energy is not lost but becomes "dissipated" or unavailable. Furthermore, the dissipation, according to Thomson, amounts to a general law of nature, expressing the "directionality" of natural processes. The Scottish engineer Macquorn Rankine and Rudolf Clausius proposed a new concept, which represented the same tendency of energy towards dissipation. Initially called "thermodynamic function" by Rankine and "disgregation" by Clausius, in 1865 the latter gave the concept its definitive name, "entropy," after the Greek word for transformation. Every process that takes place in an isolated system increases the system's entropy. Clausius thus formulated the first and second laws of thermodynamics in his statement "The energy of the universe is constant, its entropy tends to a maximum." Hence, all large-scale matter will eventually reach a uniform temperature, there will be no available energy to do work, and the universe will suffer a slow "heat death."

In 1871 James Clerk *Maxwell published a thought-experiment attempting to show that heat need not always flow from a warmer to a colder body. A microscopic agent ("Maxwell's demon," as Thomson latter dubbed it), controlling a diaphragm on a wall separating a hot and a cold gas, could choose to let through only molecules of the cold gas moving faster than the average speed of the molecules of the hot gas. In that way, heat would flow from the cold to the hot gas. This thought-experiment indicated that the "dissipation" of energy was not inherent in nature, but arose from human inability to control microscopic processes. The second law of thermodynamics has only statistical validity—in macroscopic regions entropy *almost* always increases.

Boltzmann attempted to resolve a serious problem pointed out by his colleague Joseph Loschmidt in 1876, and by Thomson two years earlier, that undermined the mechanical interpretation of thermodynamics and of the second law. This law suggests that an asymmetry in times dominates natural processes; the passage of time results in an irreversible change, the increase of entropy. However, if the laws of mechanics govern the constituents of thermodynamic systems, their evolution should be reversible, since the laws of mechanics are the same whether time flows forward or backward: Newton's laws retrodict the moon's position a thousand years ago as readily as they predict its position a thousand years from now. Prima facie, there seems to be no mechanical counterpart to the second law of thermodynamics. In 1877 Boltzmann found a way out of this difficulty by interpreting the second law in the sense of Maxwell's demon. According to Boltzmann's calculus, to each macroscopic state of a system correspond many microstates (particular distributions of energy among the molecules of the system) that Boltzmann considered to be equally probable. Accordingly, the probability of a macroscopic state was determined by the number of microstates corresponding to it. Boltzmann then identified the entropy of a system with a logarithmic function of the probability of its macroscopic state. On that interpretation, the second law asserted that thermodynamic systems have the tendency to evolve toward more probable states. A decrease of entropy was unlikely, but not impossible.

In 1906 Walther Nernst formulated his heat theorem, which stated that if a chemical change took place between pure crystalline solids at absolute zero, there would be no change in entropy. Its more general formulation is accepted as the third law of thermodynamics: the maximum work obtainable from a process can be calculated from the heat evolved at temperatures close to absolute zero. More commonly the third law states that it is impossible to cool a body to absolute zero by any finite process and that at absolute zero all bodies tend to have the same constant entropy, which could be arbitrarily set to zero.

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THEODORE ARABATZIS AND
KOSTAS GAVROGLU

ERROR AND THE PERSONAL EQUATION. Since Greek times astronomers have recognized that observations were afflicted by errors, that results based on them might only be approximate, and that the quality of data varied. Astronomers in early modern Europe took the first steps toward giving reliable estimates of those errors. Johannes *Kepler, who used Tycho *Brahe's observations to derive the elliptical shape of planetary orbits, was probably the first to construct a correction term that assigned a magnitude to error, and among the first to give a theory of an instrument (the Galilean *telescope) for purposes of improving the accuracy of measurements taken with it.

During the eighteenth century steps were taken toward standardizing the analysis of measurements and understanding the conditions under which different sets of measurements could be combined. Analysts identified two types of errors: constant (affecting the instruments or the conditions of measurement) and accidental (randomly affecting the quality of the measurements themselves). Control over instrumental errors was achieved at first by codifying the behavior and demeanor of the observer, by taking into account the limitations of the human senses (especially vision), by examining how outside sources contaminate experiments, by perfecting the construction of instruments, and by developing methods for instrument calibration.

The second type of error, the random, relates to classical probability theory. Initially the criteria for the selection of good measurements rested mainly on the notion that the median or the mean of measurements reduced the effect of errors in any of them. In 1756 the mathematician Thomas Simpson countered reports that a single well-taken measurement sufficed by demonstrating the superiority of the mean; his presentation to the Royal Society of London included a discussion of the equal probability of positive and negative errors and an argument that the mean lies closer to the true value than any random measurement. But no consensus existed about the selection or combination of measurements. The first firm parameters of an error theory emerged from the consideration of observations of the Moon's motion, especially its libration; from secular inequalities in the motions of Jupiter and Saturn; and from measurements of the shape of the earth. During the second half of the eighteenth century, Johann Tobias Mayer, Leonhard *Euler, Rudjer J. Bošković, and Johann Heinrich Lambert developed ad hoc, limited, varied, but effective procedures for combining measurements made under different conditions. In 1774 Pierre-Simon *Laplace deduced a rule for the combination of measurements using probability theory.

The meridian measurements made during the French Revolution to determine the new standard of length, the meter, gave the occasion to devise the first general method for establishing an equilibrium among errors of observation by determining their "center of gravity." This method, the method of least squares, was so employed in 1805 by Adrien Marie Legendre. In 1806 Carl Friedrich *Gauss acknowledged Legendre's work but only to say that he had been using the method for years. A priority dispute ensued. Three years later Gauss published the first rigorous proof of the method of least squares; he demonstrated that if the mean is the most probable value, then the errors of measurement form a bell curve (Gaussian) distribution. The true value (which has the smallest