tum chromodynamics (QCD), for the strong nuclear force. Promising early attempts by Howard Georgi, Sheldon Glashow, and others accounted for the elementary particles of each theory—leptons for electroweak, quarks for QCD—as well as the carriers of the three forces, but experiments designed to test the theory, in particular its prediction of proton decay, failed to provide convincing evidence.

Physicists recognized that these "grand unified theories" included only three of the four forces. Gravity proved difficult to accommodate. The development in the mid-1980s of string theory, which treated constituents of matter not as particles but as strings, offered a candidate for complete unification. But string theory, while mathematically elegant, increasingly departed from experimentally verifiable predictions and, despite frequent intimations of imminent success, by the end of the century had failed to incorporate gravity with the other three forces.

A theory of everything did not imply an end to scientific research, but rather that the quest for fundamental knowledge had ended and all that remained was to fill in the details. Claims of completeness in physics echoed similar anticipations in the past—for instance, in the late 1920s after the formulation of *quantum physics, or at the end of the nineteenth century after the construction of classical physics. Theories of everything also assumed that elementary particle physics was the foundation for the rest of science, an assumption disputed by *solid-state physicists and chaos theorists, and likewise by biological scientists, for whom *quarks or string theory offered few clues to the meaning of life or consciousness. Some theoretical physicists strayed from science altogether into the realm of theology, and claimed that a theory of everything would give humankind a glimpse of the mind of God.

Steven Weinberg, *Dreams of a Final Theory* (1992). David Lindley, *The End of Physics: The Myth of a Unified Theory* (1993).

PETER J. WESTWICK

THERMODYNAMICS AND STATISTICAL MECHANICS. The development of the theory of heat in the first half of the nineteenth century, which eventually led to thermodynamics, was linked with the technology of steam engines. Their operation was originally analyzed in terms of the caloric theory, which represented heat as a conserved *imponderable fluid. In 1824 the French military engineer Sadi Carnot employed the caloric theory in his analysis of an idealized heat-engine, which aimed at improving the efficiency of real engines. On the basis of an analogy with the production of work by the fall of water in a waterwheel, Carnot assumed that a heat-engine produced work by the "fall" of caloric from a higher to a lower temperature. The analogy suggested that the work produced was proportional to the amount of caloric and the temperature difference of the two bodies between which caloric flowed. Carnot proved that no other engine could surpass his reversible ideal engine in efficiency by showing that the existence of a more efficient engine would imply the possibility of perpetual motion. In 1834 a mining engineer, Benoit-Pierre-Émile Clapeyron, reformulated Carnot's analysis, using calculus and the indicator (pressure-volume) diagram. Carnot's theory was virtually ignored, however, until its discovery in the mid-1840s, via Clapeyron's paper, by William *Thomson (Lord Kelvin), and Hermann von *Helmholtz.

James *Joule's experimental work of the 1840s, which indicated the interconversion of heat and work, undermined the caloric theory. His precise measurements supported the old idea that heat consists in the motion of the microscopic constituents of matter. The interconversion of heat and work, along with other developments spanning several fields (from theoretical mechanics to physiology), led to the formulation of the principle of energy conservation. In the early 1850s all these parallel developments were seen, with the benefit of hindsight, as "simultaneous" discoveries of energy conservation, which became the first law of thermodynamics.

Joule's experiments, however, presented a problem for Carnot's analysis of a reversible heat-engine based on the assumption of conserved heat. In the early 1850s Thomson and the German physicist Rudolf Clausius resolved the problem by introducing a second principle. Carnot's analysis could be retained, despite the rejection of the conservation of heat, because, in fact, it dealt with a quantity—the amount of heat divided by the temperature at which the heat is exchanged—that is conserved in reversible processes. During the operation of Carnot's engine, part of the heat dropped from a higher to a lower temperature and the rest became mechanical work.

In 1847 Thomson diagnosed another problem, also implicit in Carnot's analysis. Carnot had portrayed heat transfer as the cause of the production of work. In processes like conduction, however, heat flows from a warmer to a colder body without doing any work. Since the heat does not spontaneously flow from cold to hot, conduction resulted in the loss of potential for doing work. Both Joule and Thomson agreed that energy cannot perish, or, rather, that only a divine creator could destroy or create it. Thomson resolved the difficulty in 1852 by observing that in processes like conduction, energy is not lost but "dissipated," and by raising the dissipation of energy to a law of nature. "Real"—that is, irreversible—processes continually degrade energy and, in a good long time, will cause the heat-death of the universe. The Scottish engineer William Rankine and Clausius proposed a new concept that represented the same tendency of energy toward dissipation. Initially called "thermodynamic function" (by Rankine) or "disgregation" (by Clausius), it later (in 1865) received the name *"entropy" from Clausius, who grafted onto the Greek root for transformation. Every process (except ideal reversible ones) that takes place in an isolated system increases its entropy. This principle constituted the second fundamental law of thermodynamics, and its interpretation remained the subject of discussion for many years.

The dynamical conception of heat provided a link between mechanics and thermodynamics and led eventually to the introduction of statistical methods in the study of thermal phenomena. In 1857 Clausius correlated explicitly thermodynamic and mechanical concepts by identifying the quantity of heat contained in a gas with the kinetic energy (translational, rotational, and vibrational) of its molecules. He made the simplifying assumption that all the molecules of a gas had the same velocity and calculated its value, which turned out to be of the order of the speed of sound. Clausius's idealized model faced a difficulty, however, as pointed out by the Dutch meteorologist C. H. D. Buys Ballot. On the model, gases should diffuse much faster than actually observed. In 1858, in response to that difficulty, Clausius attributed the slow rate of diffusion to the molecules' collisions with each other and introduced the new concept of "mean free path," the average distance traveled by a molecule before it collides with another one.

In 1859 James Clerk *Maxwell became aware of Clausius's kinetic interpretation of thermodynamics and, in the following years, developed it further by introducing probabilistic methods. In 1860 he developed a theory in which the velocities of the molecules in a gas at equilibrium distribute according to the laws of probability. He inferred from "precarious" assumptions that the distribution followed a bell-shaped curve, the so-called normal distribution, which had been familiar from the theory of errors and the social sciences. Following up these ideas, he published in 1871 an ingenious thought experiment that he had invented four years earlier to suggest that heat need not always flow from a warmer to a colder body. In that case the second law of thermodynamics could have only a statistical validity. A microscopic agent ("Maxwell's demon," as Thomson called it), controlling a diaphragm on a wall separating a hot and a cold gas, could let through either molecules of the cold gas faster than the average speed of the molecules of the hot gas, or molecules of the hot gas slower than the average speed of the molecules of the cold gas. Heat thus would flow from the cold to the hot gas. This thought experiment indicated that the "dissipation" of energy did not lie in nature but in human inability to control microscopic processes.

Ludwig *Boltzmann carried further Maxwell's statistical probing of the foundations of thermodynamics. In 1868 he rederived, in a more general way, the distribution of molecular velocities, taking into account the forces exerted between molecules as well as the influence of external forces like gravity. In 1872 he extended the second law of thermodynamics to systems not in equilibrium by showing that there exists a mathematical function, the negative counterpart of entropy, that decreases as a system approaches thermal equilibrium. This behavior was subsequently called the "*H*-theorem."

Furthermore, Boltzmann attempted to resolve a severe problem, pointed out by Thomson in 1874 and Joseph Loschmidt in 1876, which undermined the mechanical interpretation of the second law. The law defines a time asymmetry in 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 run with equal validity toward the past and the future. *Prima facie*, there seems to be no mechanical counterpart to the second law of thermodynamics.

Boltzmann eluded the difficulty in 1877 by construing the second law probabilistically. To each macroscopic state of a system correspond many microstates (particular distributions of energy among the constituents of the system), which Boltzmann ranked as equally probable. He defined the probability of each macroscopic state by the number of microstates corresponding to it and identified the entropy of a system with a simple logarithmic function of the probability of its macroscopic state. On that interpretation of entropy, the second law asserted that thermodynamic systems have a tendency to evolve toward more probable states. The interpretation came at the cost of demoting the law. A decrease of entropy was unlikely, but not impossible.

Maxwell's and Boltzmann's statistical approach to thermodynamics was developed further by J. Willard *Gibbs, who avoided hypotheses concerning the molecular constitution of matter. He formulated statistical mechanics, which analyzed the statistical properties of an ensemble, a collection of mechanical systems. This more general treatment proved to be very useful for the investigation of systems other than those studied by the kinetic theory of gases, like electrons in metals or ions in solutions.

D. S. L. Cardwell, *From Watt to Clausius: The Rise of Thermodynamics in the Early Industrial Age* (1971). S. G. Brush, *The Kind of Motion We Call Heat: A History of the Kinetic Theory of Gases in the 19th Century*, 2 vols. (1976). Lawrence Sklar, *Physics and Chance: Philosophical Issues in the Foundations of Statistical Mechanics* (1993). Crosbie Smith, *The Science of Energy* (1998).

THEODORE ARABATZIS

THERMOMETER. The notion of a scale or degrees of heat and cold dates back at least to the second-century physician Galen, as does the idea of using a standard—such as a mixture of ice and boiling water—as a fixed point for the scale. Ancient philosophers' experiments, such as Hero of Alexandria's "fountain that drips in the sun," demonstrated the expansion of air with heat, and were known among natural philosophers of the sixteenth century. In the second decade of the seventeenth century, *Galileo, Santorio Santorio, and others began to use long-necked glass flasks partially filled with air and inverted in water to measure temperature, applying them to medical and physical experiments and keeping meteorological records. The first sealed liquid-in-glass thermometers, filled with spirit of wine, were constructed for the Accademia del Cimento in Florence in 1654 by the artisan Mariani; though not calibrated from fixed points, his thermometers agreed very closely among themselves.

The succeeding century saw experimentation with thermometric liquids, among which spirit of wine was favored for its quick response and because no cold then known would freeze it. Several natural philosophers, including Robert *Hooke, Christiaan *Huygens, and Edme Mariotte, worked out methods for graduating their instruments from a single fixed point, typically the freezing or boiling point of water. Toward the end of the seventeenth century, Italian investigators began using two fixed points, as did the Dutch instrument maker Daniel Fahrenheit in the first few decades of the eighteenth century. Fahrenheit's ex-