4.5 Heat and Energy

4.5.1 *The Thermometer*

On the one side, philosophy; on the other, technology—with such support, the nineteenth century discovered the most basic law of physics, one that was only strengthened by the later "one–two punch" of quantum mechanics and relativity—the law of conservation of energy.

Romantic natural philosophy aroused in the hearts of physicists the wish to discover what was common and consistent in the relationships among the variety of phenomena and transformations while technological advances led to questions about the efficiency of engines. It is not surprising, then, that progress in knowledge about the nature of heat was closely related to the development of the concept of energy. The importance of "living force," which today is called kinetic energy, was surmised already at the end of the seventeenth century, except that its disappearance during an inelastic collision or due to friction was a very confusing fact. LEIBNIZ already recognized that in these cases the living force is transformed into the living forces of the particles that constitute the given object. The main argument leading to the law of conservation of energy is in this way connected with questions about the nature of heat. Naturally, as shown in Figure 4.116, other fragments of physical knowledge also had important roles, for example, the connection between electrical phenomena and heat, or the heat generated by chemical reactions, as well as the relationship between electrical and chemical phenomena.

One would expect that ideas concerning the nature of heat would have been based on a conception that was already widespread at the end of the seventeenth century, namely, that heat has its origin in the motion of the particles that make up a material body. This would then have led directly to the connection between the two forms of energy: heat and kinetic energy. However, that is not what happened. In a seemingly superfluous and at first glance surprising detour in the history of physics, the kinetic theory of heat was abandoned, and in its place a theory of heat substance (*caloricum*) was adopted. It is only the result of our hasty judgment about what should have happened that names such as JOSEPH BLACK have fallen into obscurity, although we owe our thanks to him for such quantitative concepts as heat quantity, specific heat, latent heat, melting point, and boiling point. It has also been forgotten that findings in CARNOT's and FOURIER's theory of heat that are seen today as fundamental and used in teaching are based on the theory of the *caloricum*.

We must immediately add that these results, arrived at by using the most up-to-date mathematical apparatus of the time, actually hindered the development of the kinetic theory of heat, which was mired down in its search for quantitative conclusions from its qualitative ideas. For this reason the detour was necessary; only in this roundabout way could the qualitative notions be introduced whose measurements then would allow for the formulation of the simplest laws.

It was already clear in the Middle Ages that in connection with heat, two fundamentally different quantities had to be considered: one is an *intensity* and the other is a *quantity*. Naturally, all this was expressed only vaguely. But they could sense that, for example, a flame somehow possesses a greater heat intensity than a piece of warm iron, whereas in the piece of iron the quantity of heat is greater than in the flame. Today, we call these temperature and heat quantity.

The measurements were made possible by the development in the seventeenth century of the most important instrument for the theory of heat: the thermometer.

◀ **Figure 4.116** Road-map leading to the law of conservation of energy.

◀ **Figure 4.117** The barothermoscope, attributed to GALILEO, whose readings depend on temperature and also on barometric pressure.
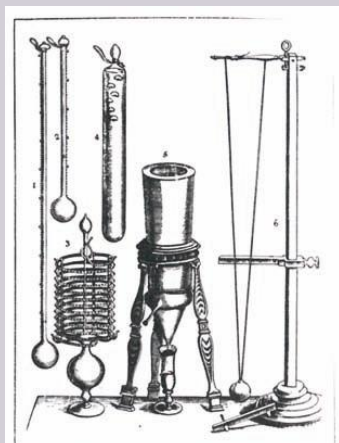
◀ **Figure 4.118** Thermometers and other scientific instruments from the second half of the seventeenth century.

As mentioned in Section 1.4, the fact that air expands when heated was known and used already in Alexandria. However, this phenomenon was not employed for the measurement of temperature until the beginning of the seventeenth century. Figure 4.117 shows an apparatus whose construction is attributed to GALILEO, although he himself did not describe it in detail. This measuring instrument is called the barothermoscope because its reading depends on the air pressure as well as on the temperature. The first enclosed alcohol thermometer (Figure 4.118) is ascribed to FERDINANDO II DE' MEDICI, grand duke of Tuscany. In Florence, under the auspices of the Accademia del Cimento (Academy of Experiment), 1657–1667, a variety of glass masterpieces were produced with scales formed of colored glass beads. It is worthwhile to especially draw attention to thermometer #4 in the illustration. An alcohol-filled ampoule contains a number of small, hollow glass spheres. The weights of the spheres are adjusted in such a way that as the density of alcohol decreases with rising temperature, one sphere after the other—at different given temperatures—sinks to the bottom.

The eighteenth century brought nothing essentially new to the construction of the thermometer. However, reproducibility of temperature measurements was achieved by temperature scales between two set scale values corresponding to two easily achievable phenomena. The temperature scale that was to become most widely used was introduced by the Swedish astronomer ANDERS CELSIUS (1701–1744). The zero point of this scale corresponds to the temperature of melting ice, and the boiling point of water is designated the second fixed point on the scale with the value of 100 ºC. In Figure 4.119, alongside the Celsius scale we can see the Fahrenheit scale, which was introduced around the same time, and also the "absolute" (Kelvin) temperature scale, which was established in the second half of the nineteenth century.

4.5.2 *Progressive in Its Day: The Caloricum Theory of Joseph Black*

With the introduction of the thermometer, a quantitative formulation of the fundamental laws of thermodynamics was made possible. This was accomplished by JOSEPH BLACK (1728–1799).

BLACK was a professor of chemistry and medical sciences, first in Glasgow (from 1756 until 1766) and then in Edinburgh (1766 up to his death). His most important discoveries in the field of thermodynamics date from his time in Glasgow. BLACK himself wrote no books; we know of his theory primarily because of a book written in 1803 by his student ROBISON, in which BLACK's lectures are reproduced (Figure 4.120). Intriguingly, ROBISON dedicated this book to JAMES WATT, as the most talented and famous of BLACK's students (Quotation 4.38).

A quotation from this book (Quotation 4.39) makes it clear how little the concepts of temperature and heat quantity were understood in BLACK's time. By taking measurements, BLACK confirmed the fact, previously known, that bodies in contact tend to assume the same temperature. This phenomenon was interpreted by BLACK as the result of equal distribution of heat among the various bodies. BLACK accurately called this state heat *equilibrium* of the bodies and concluded that anyone talking about heat *equality* was confusing two quantities, namely temperature and heat quantity.

Through his investigations into the heat quantities needed to achieve equal increase in temperature in bodies of equal mass but different chemical composition, BLACK introduced the notion of specific heat. He refuted the generally accepted opinion that this quantity should be proportional to the mass for bodies of equal

volume, in other words, to their density. Black believed that his measurements contradicted the kinetic theory of heat: From the kinetic theory, it would follow—at least at first glance—that when more particles or heavier particles move, their living force will be greater. Black added, "I see little possibility of refuting this counterargument." As things turned out, the answer was only provided 100 years later, with the aid of the equipartition principle (Quotation 4.40).
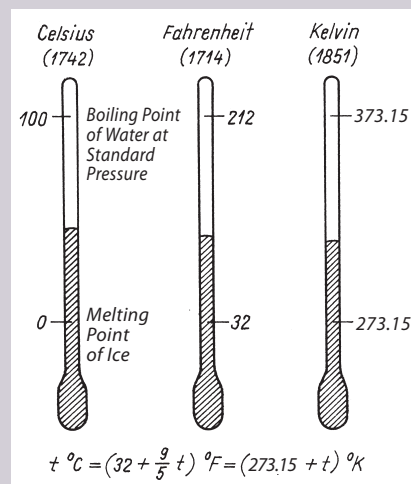
Black's train of thought with regard to latent heat is so clear and convincing that it could be transcribed verbatim into our high school physics texts (Quotation 4.41). His final conclusion—specifically that heat is a substance—is no longer accepted. It is remarkable, however, how cautiously he set forth his hypotheses. In the last lines of the quotation, we hear from the true experimental physicist who suggests the limited practical use for hypotheses arrived at through an overabundance of imagination.

What did Black or his contemporary, the important chemist Lavoisier, understand by *caloricum* or "heat substance"? Black himself refers to Cleghorn, who in 1779 summarized the properties of heat substance as follows: The *caloricum* is an elastic liquid, a *fluidum*, whose particles are mutually repellent, being simultaneously attracted by the particles of ordinary ponderable (weighable) matter, where the attractive force depends on the quality of the material and its aggregate state. This *fluidum* can be neither created nor destroyed; like ponderable matter, it satisfies the conservation law. The *caloricum* can be present both measurably and latently in ponderable matter. In the latter case, the heat substance forms to some extent a chemical bond with the ponderable matter.

There was no universal agreement as to the weight of the heat substance. Many researchers attempted to decide this question on the basis of measurements. Yet we may easily imagine the difficulties and the many sources of error that arose in measurements taken when the material present in one pan of the balance had to be heated after the pans had been balanced. Measurements seemed to indicate
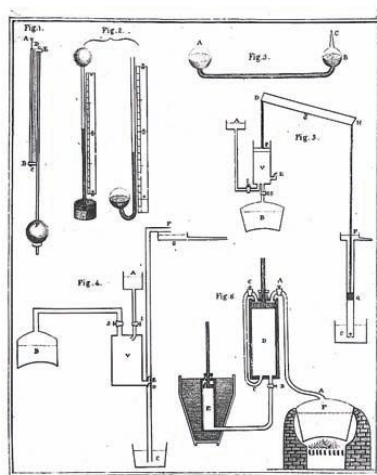
$$t \; ^{\circ}C = \left(32 + \frac{9}{5}\, t\right)\, ^{\circ}F = (273.15 + t)\, ^{\circ}K$$

▲ **Figure 4.119** Three important temperature scales.

Quotation 4.38

Fortunately for Dr. Black, and for the world, he had now gotten a pupil who was as keenly interested in the scientific question as the Professor. This was Mr. James Watt, then employed in fitting up the instruments in the McFarlane Observatory of the University; a philosopher in the most exalted sense of the word, who never could be satisfied with a conjectural knowledge of any subject, and who grudged no labor or study to acquire certainty in his researches. He chanced to have in his hands, for repairs, a model of Newcomen's steam engine, belonging to the Natural Philosophy Class, and was delighted with the opportunity which this small machine gave him for trying experiments connected with the theory of ebullition, which he had just learned from Dr. Black. These he prosecuted in a most happy train of success and did not stop, till his steam engine was rendered more like the most docile of animals, than a frame of lifeless matter; so that, while its power is competent to the lifting a house from its place, a child of ten years old shall, with a touch of his hand, make it go fast or slow, forwards or backwards, and act either forcefully or feebly. This gentleman attached to Dr. Black by every tie of respect, esteem, and affection, supplied him with proofs and illustrations in abundance, of all the points on which the professor wanted information. These were always recited in the class, with the most cordial acknowledgment of obligation to Mr. Watt.

—John Robison's editor's preface to Joseph Black's *Lectures on the Elements of Chemistry*

▲ **Figure 4.120** Black's lectures in German. Title page and a typical page of drawings. (Library of the University for Heavy Industry, Miskolc.)

that the *caloricum* had some weight, though very small in comparison to the total weight of the object containing it. There were also measurements according to which a negative weight would have had to be assigned to the *caloricum*. The idea of a weightless substance—imponderable matter—would have caused no particular difficulties; physicists had already become accustomed to it in the case of light as well as that of the electric *fluidum*.

4.5.3 *Rumford: But Heat Is Still a Form of Motion!*

Declaring that heat is a form of motion, Count RUMFORD (BENJAMIN THOMPSON, 1753–1814) took up the fight against the substance theory of heat. In the course of an adventurous life, RUMFORD worked in a wide variety of fields and left behind contributions not only to science but also to other realms of human endeavor. In 1800, for example, he founded the English Royal Institution, whose first director was DAVY and which later became famous through the work of FARADAY. RUMFORD's scientific work was done in Munich, where he served as advisor to the Bavarian king and later as director of the military arsenal. He also founded social institutions and a state employment agency; and to this day, his name lives on in Rumford soup and the Rumford fireplace.

RUMFORD first set himself the task of verifying and completing the measurements relating to the weight of the heat substance. He noticed that latent heat was a suitable object of these measurements because, for example, a relatively large amount of heat is required for the melting of ice, and the same quantity of heat is liberated when water freezes without a change in its temperature. This method allowed for the elimination of the sources of error resulting from differences in temperature. With carefully executed experiments, in which he investigated the influence of even the smallest possible differences in temperature on the balance arm, RUMFORD was able to prove unambiguously that the heat substance, if indeed it existed, must have a vanishingly small weight. According to RUMFORD, he achieved such a degree of precision in his weighing that he would have been able to detect a deviation of one part in a million in the weight of an object. RUMFORD's description of his measurements can be found in Quotation 4.42, together with a cautious note that his results are almost self-evident if one considers heat not as a substance, but as motion.

The weakest point of the substance theory was its inability to provide a plausible explanation for the creation of heat through friction. Within the framework of substance theory, it was necessary to assume that friction so alters the state of a body that its heat capacity is reduced, with the result that the unchanged quantity of heat substance can raise its temperature. By examining the heat generated by the process of boring cannon barrels in great detail, RUMFORD intended to deal a death-blow to this theory. He was first able to prove that the specific heat of the shavings from the barrel remained unchanged. Then he was able to establish that from a given body kept warm by friction we can extract a heat quantity proportional to time; in other words, we can extract as much heat from it as we want. From these observations, RUMFORD drew confidently his final conclusions: Heat cannot be a substance, because if it were, then one would not be able to remove an unlimited quantity from a body. Heat can be nothing other than motion that can be continually recreated by mechanical friction, so that one can draw off heat from a body as long as this heat is created by mechanical work (Quotation 4.43). Quotation 4.44, from RUMFORD's article, shows that he came quite close to recogniz-

ing the equivalence of mechanical energy and heat energy. From the results of his measurements, with hindsight, we can even determine a value for the equivalence, which will play an important role later.

In saying farewell to RUMFORD, we must mention that he saw his investigations as basic research without immediate practical application and therefore had no expectation of material support. He writes in self-justification that the cannon barrels used in his experiments did not go to waste, but were put to use for their intended purpose.

From today's vantage point of the complete triumph of the kinetic theory, we would be inclined to see RUMFORD's conclusions as definitive. However, such was not the case at the beginning of the nineteenth century. RUMFORD's experimental results were accepted, to be sure, but the attempt was made to interpret them on the basis of heat substance. The fact, for example, that one can remove an inexhaustible quantity of heat from a body was interpreted to mean that in such cases the body serves only as a conduit; in reality, the heat substance flows into the body from the environment, which constitutes a practically inexhaustible reservoir.

To be sure, the kinetic theory also had its difficulties in the quantitative—and also qualitative—explanation of certain phenomena.

The following table summarizes the most important phenomena as well as commentary as to which of the two theories—heat-substance theory and kinetic theory—can more convincingly explain them.

	Heat conduction	Thermal radiation	Latent heat	Frictional heat	Quantitative conclusion possible?
Heat substance theory	yes	yes	yes	no	yes
Kinetic theory	yes	no	no	yes	no

To this table it must be added that the flow of heat substance (thermal conduction) could be presented as a very simple analogy to fluid flow, whereas with the kinetic theory, conduction was very difficult to describe because knowledge of the statistical nature of collision processes would have been needed. Nevertheless, in the table we state that the kinetic theory would eventually be able to accomplish this task. The *caloricum* theory can easily explain thermal radiation, that is, transmission of heat through a vacuum, as a flow of imponderable heat substance through a vacuum. The kinetic theory is helpless in the face of this phenomenon. Today we say that, in this situation, heat is transmitted from one body to another as electromagnetic radiation, that is, in a form of motion different from the usual motion of matter.

Looking at the above table, it is not difficult to understand why the great majority of scholars in the first decades of the nineteenth century still accepted the substance theory—not with full conviction, but as a useful working hypothesis.

4.5.4 *Fourier's Theory of Heat Conduction*

One of the most important successes of heat substance theory was achieved by FOURIER with his mathematical theory of heat conduction.

JEAN BAPTISTE JOSEPH FOURIER (Figure 4.121) came from a poor family. It was thanks to the French Revolution—and, following it, NAPOLEON—that he had

Quotation 4.40, *continued*

matter in each, but in proportions widely different from this, and for which no general principle or reason can yet be assigned. ...

Quicksilver, therefore, has less *capacity* for the matter of heat than water (if I may be allowed to use this expression) has; it requires a smaller quantity of it to raise its temperature by the same number of degrees. ... We must, therefore, conclude that different bodies, although they be of the same size, or even of the same weight, when they are reduced to the same temperature or degree of heat, whatever that be, may contain very different quantities of the matter of heat; which different quantities are necessary to bring them to this level, or equilibrium, with one another.

It may have been remarked that the discoveries which have been made in this way are very unfavorable to one of the opinions which have been formed of the nature of heat. Many have supposed that heat is a tremulous, or other, motion of the particles of matter, which tremendous motion they imagined to be communicated from one body to another. But, if this were true, we must admit that the communication would be in conformity with our general experience of the communication of tremulous motion. We are not at liberty to feign laws of motion different from those already admitted, otherwise we can make any supposition account for any phenomena that we please. The denser substances ought surely to be the most powerful in communicating heat to others, or exciting it in them. The fact, however, in a great many examples, and yet not in all, is just the reverse. Such an opinion is therefore totally inconsistent with the phenomena. I do not see how this objection can be evaded.

—JOSEPH BLACK, *Lectures on the Elements of Chemistry* [pp. 76, 77, 80]

Quotation 4.41

Fluidity was universally considered as produced by a small addition to the quantity of heat which a body contains, when it is once heated up to its melting point; and the return of such a body to a solid state as depending on a very small diminution of the quantity of heat after it is cooled to the same degree; that a solid body, when it is changed into a fluid, receives no greater addition to the heat within it than what is measured by the elevation of temperature indicated after fusion by the thermometer; and that, when the melted body is again made to congeal, by a diminution of its heat, it suffers no greater loss of heat than what is indicated also by the simple application to it of the same instrument.

the opportunity to develop his talents. He had begun his investigations related to thermal conduction as early as 1807, but their publication was at first rejected by the strict referees Lagrange, Laplace, and Legendre. Fourier's results finally appeared in 1822, in the book *Théorie analytique de la chaleur*, in which he starts out with a very clear physical description of the problem and proceeds to offer an illuminative presentation of the mathematical issues involved.

For the following discussion, let us imagine a body with an arbitrary initial temperature distribution. We could picture this by using tiny thermometers applied to various locations on the body. Each thermometer would at the outset show a particular value, perhaps all identical. From its surface, the body gives off heat, which passes into the environment, while heat flows from the interior of the body toward the surface. We can therefore expect that the thermometers located at various positions around the body, at any given time, will show different temperatures (Figure 4.122). The goal of the mathematical investigation is then to determine the temperatures displayed by the thermometers as a function of position and time.

Fourier's research was of fundamental importance for the development of both mathematics and physics. Fourier found that the solution to the mathematical form of the problem, at least in its simplest case where the temperature is sought as a function of position, can be represented by combinations of sine functions with various arguments. Since the initial condition, that is, the temperature distribution at the beginning of the experiment, can be prescribed arbitrarily, it is natural to ask, *how can an arbitrary function be built up just from sine functions?* In the language of mathematics, this question relates to the representation of arbitrary functions by what are now called Fourier series. Thus, Fourier's approach opened up an entire new branch of mathematics, the theory of Fourier series, and physicists also found the Fourier series an extraordinarily effective method for solving many of their problems.

In the following, we stick to Fourier's description of the problem and, for the sake of simplicity, confine our attention to the one-dimensional case.

As shown in Figure 4.123, suppose we are given, at time $t = 0$, the temperature distribution $T(x,0)$ in a rod that runs along the x-axis. Furthermore, suppose that for all future times $t > 0$, the two ends of the rod are held at a fixed temperature, for example 0º C. This can be realized in practice by placing the ends of the rod in thermal contact with a very large container filled with water at 0º C. We assume that the heat capacity of this container is so great that the heat flowing from the rod into the heat sink causes no change in the container's temperature. We assume that the cylindrical rod is covered by a heat-insulating layer, so that heat can only flow along the axis of the rod. Fourier was already aware, or, to put it more accurately, correctly assumed, that the heat flow J is proportional to the difference in temperature per unit length, or equivalently, the temperature gradient $\partial T/\partial x$, and flows in the direction of decreasing temperature. With this assumption, Fourier arrived at the relationship

$$J = -\kappa \frac{\partial T}{\partial x},$$

where κ is the so-called thermal conductivity constant. Moreover, Fourier took into account that the heat content of a segment of the rod of length ∂x can vary over time, since the quantities of heat flowing in or out of the two lateral surfaces do not have to be equal. This yields the second equation,

$$\frac{\partial J}{\partial x} = -\rho c \frac{\partial T}{\partial t},$$

where c is the specific heat and ρ is the thickness of the rod. (For the sake of simplicity, we have set the cross-sectional area of the rod equal to 1.) Combining the two equations, we immediately obtain the following differential equation for thermal conduction:

$$\frac{\partial^2 T}{\partial x^2} = \frac{\rho c}{\kappa} \frac{\partial T}{\partial t} = k^2 \frac{\partial T}{\partial t}. \qquad (1)$$

Even today, differential equations of this type are called heat equations, even though we meet them in other branches of physics as well, such as the theory of long-distance electrical transmission and the theory of diffusion processes. We therefore seek the function

$$T = T(x,t)$$

that satisfies the above differential equation, with the boundary conditions

$$T(0,t) = 0, \quad T(l,t) = 0, \quad t > 0,$$

and the initial condition

$$T(x,0) = f(x),$$

where $f(x)$ is some prescribed function.

FOURIER solved equation (1) by applying the usual method of separation of variables. He assumed that the desired function could be represented as the product of two functions, one of them a function of x alone and the other a function of t alone:

$$T(x,t) = \Phi(x)\Psi(t).$$

If we substitute this product into the initial differential equation,

$$\Psi(t)\frac{d^2\Phi(x)}{dx^2} = k^2\Phi(x)\frac{d\Psi(t)}{dt},$$

we obtain, after a bit of manipulation,

$$\frac{1}{k^2\Phi(x)}\frac{d^2\Phi(x)}{dx^2} = \frac{1}{\Psi(t)}\frac{d\Psi(t)}{dt} = -\lambda.$$

One side of this equation depends only on the variable x, whereas the other side depends only on t, so the equation can only be satisfied if both sides are equal to some constant. (This constant, denoted by λ, is called the separation constant.) If this is the case, then the initial differential equation, which is a partial differential equation, decomposes into two ordinary differential equations

$$\frac{d^2\Phi(x)}{dx^2} + \lambda k\Phi(x) = 0, \quad \frac{d\Psi(t)}{dt} + \lambda\Psi(t) = 0,$$

whose solutions can be written at once:

$$\Phi(x) = b\sin\left(\sqrt{\lambda}kx + c\right), \quad \Psi(t) = a\,e^{-\lambda t}.$$

The boundary conditions are satisfied when we require of the function $\Phi(x)$ that

$$\Phi(0) = \Phi(l) = 0.$$

These conditions are satisfied if we have

$$c = 0, \quad \sqrt{\lambda}kl = \pi v, \quad v = 1,2,\ldots,$$

and so the separation constant assumes the value

$$\lambda_v = \left(\frac{\pi v}{kl}\right)^2.$$

Taking into account the time-dependent term, we obtain

$$T(x,t) = \sum_v T_v(x,t) = \sum_v c_v \exp\left[-\left(\frac{\pi v}{kl}\right)^2 t\right]\sin\frac{v\pi x}{l} \quad (c_v = ab_v),$$

where we have taken into consideration the fact that for the linear differential equation (1), the sum of solutions is again a solution.

◀ **Figure 4.121** JOSEPH FOURIER (1768–1830): 1796: professor at the École Polytechnique. 1816: member of the French Academy. His *Théorie analytique de la chaleur*, in which the theory of the Fourier series also appears, was published in 1822. He also investigated problems of measurement errors.
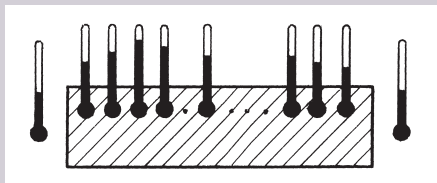
▲ Figure 4.122 Fourier's problem: At time $t = 0$, a certain temperature distribution in a body is given. How will the temperature change at various points in the body as a function of time?

$$T(x,0) = f(x)$$
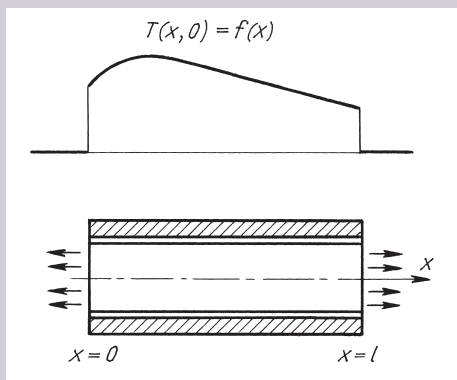
▲ Figure 4.123 The one-dimensional heat-conduction problem: We are investigating the cooling of the rod given the initial temperature distribution and given that the rod can transmit heat to the environment only at its end surfaces.

◄ Figure 4.124

Joseph-Louis Gay-Lussac (1778–1850): After his studies at the École Polytechnique, worked as a chemist in Berthollet's laboratory (in Arcueil), then was associated for a time with Humboldt (who also belonged to the Arcueil circle; the director of the physics department of the laboratory was Laplace).

1809–1832: professor of chemistry at the École Polytechnique and professor of physics at the Sorbonne.

Two laws are associated with his name: 1802, investigation of the expansion of gases under constant pressure, where he obtained the relation

$$V = V_0\left[1 + \alpha(t - t_0)\right].$$

The coefficient of expansion a in this formula is the same for all gases to very good approximation. Gay-Lussac also measured its value, and for $t = 0°$C he obtained the excellent result a = $(1/267)$ K^{-1} (the exact value being $1/273.15$ K^{-1}).

The mathematical problem of representing an arbitrary function by a Fourier series arises in the attempt to satisfy the initial conditions. If we set $t = 0$ in the general solution procedure, we obtain the relationship

$$T(x,0) = f(x) = \sum_{v=1}^{\infty} c_v \sin\frac{v\pi x}{l}.$$

On the left-hand side of this equation, we have an arbitrary function, and on the right-hand side, we have an infinite series of sine functions.

In order to determine the unknown coefficients c_v associated with the function $f(x)$, Fourier at first offered a very complicated method that was extremely questionable with respect to mathematical rigor. He developed the sine functions into the power series

$$\sin vx = \sum_{n=1}^{\infty} \frac{(-1)^{n-1} v^{2n-1}}{(2n-1)!} x^{2n-1}.$$

He then interchanged the order of summation, thereby obtaining

$$f(x) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(2n-1)!} \left(\sum_{v=1}^{\infty} v^{2n-1} c_v\right) x^{2n-1}.$$

Fourier then compared the resulting power series with the Maclaurin series of the function $f(x)$:

$$f(x) = \sum_{k=0}^{\infty} \frac{1}{k!} f^{(k)}(0) x^k,$$

finally obtaining the following algebraic system of infinitely many equations in an infinite number of unknowns c_v:

$$\sum_{v=1}^{\infty} v^{2n-1} c_v = (-1)^{n-1} f^{(2n-1)}(0), \quad n = 1,2,3\ldots.$$

Later, Fourier also found the relationship, familiar to us today,

$$c_v = \frac{2}{\pi} \int_0^{\pi} f(s)\sin vs\, d s.$$

In studying this relationship, Fourier determined that the value of the integral can be interpreted geometrically as the area under the graph of the function $f(s)\sin vs$ over the interval from 0 to π, and therefore one can carry out the transformation as well for the case of "arbitrary" functions that are not analytic in the sense of Lagrange. This way, whether he intended or not, Fourier contributed to the extension of the notion of function.

4.5.5 *Caloricum and the State Equation*

The theory of the *caloricum* was able to produce useful results even beyond the connection with heat flow. Laplace attempted also to derive the state equations for gases on the basis of this theory. Reading his works today, one cannot help but be amazed by the ability of this brilliant mathematician to juggle hypotheses and formulas. Laplace begins with the assumption that due to the heat substance that surrounds the particles of mater like a cloud, a repulsive force emerges between the particles that can be expressed by the relationship

$$F = Hc^2\varphi(r),$$

where H is a constant, c the density of the *caloricum*, and $\varphi(r)$ a function that decreases rapidly with the distance between the particles. (We note, in this discussion, that we are assuming for the first time the action of short-range forces.) By considering the sum of such forces, Laplace derives the formula

$$P = 2\pi HK \rho^2 c^2$$

for the pressure of the gas. The constant K describes the resultant of all forces acting on a single particle. This constant has a finite value even in the case of infinitely many particles because of the above-mentioned short range of interaction between the particles. However, the derived formula is obviously incorrect because the gas density ρ appears to the second power instead of to the correct first. This issue was explained away effortlessly by Laplace by arguing that the density of the material and the density of the

caloricum are not independent of each other—indeed, that as a consequence of the radiative equilibrium between them, there must exist a dependence of the form

$$\rho c^2 = \Pi(u),$$

in which the right-hand side depends solely on the temperature u. With this assumption, Laplace finally obtains

$$P \sim \rho \Pi(u),$$

which is the correct result: The equation has the same form of Gay-Lussac's law if, like Laplace, we use the quantity $\Pi(u)$ that depends only on the temperature instead of the temperature itself (Figure 4.124).

The greatest accomplishment of Laplace's theory is the derivation, in which he uses the method described above, of the state equation for the adiabatic change of state:

$$pV^\kappa = \text{constant}.$$

4.5.6 *The Carnot Cycle*

Efforts to increase the efficiency of heat engines led to the recognition—especially by James Watt (Figure 4.125)—of the necessity to merge theory with practical application. The experiments of Sadi Carnot (Figure 4.126) were also dedicated to this task. Carnot envisioned the mode of operation of a heat engine as being similar to that of a water-powered engine, whereby water (in itself incapable of being transformed into work) cascades from a higher to a lower level, thereby producing mechanical work. In the case of heat engines, one can think of the water level as being replaced by the temperature, and the flowing mass of water by the heat substance that, like the water, is neither created nor destroyed. If one accepts this analogy in calculating the efficiency of a steam engine, then the result is

$$\eta = \frac{Q(T_1 - T_2)}{Q T_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}.$$

This example demonstrates both the heuristic value of analogical thinking and the dangers of its uncritical application. If we compare, following Figure 4.127, the operating principles of a water-powered engine, a heat engine, and a direct-current motor, we can see that in all three cases, work is performed by a flow from a higher level (a higher potential) to a lower, assuming, however, that the quantities of electricity and heat remain unchanged. The analogy between the water-wheel and the electric motor works, in the sense that in both cases the inflow per unit time of substance (water or electric charge) at the higher level is equal to the outflow per unit time at the lower level. However, Carnot erroneously believed the heat substance to be conserved, when, in fact, the amount of heat at a lower temperature flowing out of a heat engine is less than the amount at a higher temperature flowing in. Part of the heat is transformed in the machine into mechanical work. Such cannot be said about either water or electric charge, that some part of the water or some of the charge were somehow turned into mechanical work.

The surprising fact is that the Carnot formula for efficiency is still correct and is still in use today. But there is a simple explanation for this: if in a given time interval we supply Q_1 heat at temperature T_1 to the engine, and at the same time remove Q_2 heat and temperature T_2, then, in the ideal case, the difference $Q_1 - Q_2$ is turned into mechanical work, so the efficiency will be

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

Figure 4.124 *continued*

1808: publication of the results of several years of research, according to which the volumes of chemically reacting gases and the gaseous reaction products are in the proportions of whole numbers that tend to be small. For example, if a unit volume of hydrogen reacts with a unit volume of chlorine, then after the reaction, there will be two unit volumes of hydrochloric acid: $H_2 + Cl_2 = 2HCl$. Dalton propounded the law of simple and multiple proportions around this time. Dalton and Gay-Lussac did not get along, so it was only later that Amadeo Avogadro was able to unite their results, by pointing out the difference between atoms and molecules and thereby formulating the law that bears his name.

Of interest are also the balloon ascents that Gay-Lussac made in 1804 with Biot for measuring Earth's magnetic field (Figure 4.88). Later, Gay-Lussac ascended alone to a height of 7000 meters to measure air pressure and temperature and take air samples at various altitudes.

An important result of Gay-Lussac's multifaceted work in the area of chemistry is the discovery (together with Thénard) of the element boron.

We should mention as well that Jacques-Alexandre-César Charles, in part before Gay-Lussac and in part at the same time, but independently, also discovered the law of the thermal expansion of gases.

Putting together the laws of Boyle–Mariotte and Gay-Lussac yields the state equation for ideal gases, and after the introduction of absolute temperature $T = t + 273.15$, the formula $pV = RT$ for this law becomes obvious. Clapeyron gave the state equation in this form, but it was a long journey before W. Thomson (Lord Kelvin) introduced the thermodynamic temperature scale named for him (1848), which is independent of the properties of the ideal gas.

Quotation 4.44

As the machinery used in this experiment could easily be carried round by the force of one horse (though, to render the work lighter, two horses were actually employed in doing it), these computations show further how large a quantity of heat might be produced, by proper mechanical contrivance, merely by the strength of a horse, without either fire, light, combustion, or chemical decomposition; and, in a case of necessity, the heat thus produced might be used in cooking victuals.

But no circumstances can be imagined, in which this method of procuring heat would not be disadvantageous; for, more heat might be obtained by using the fodder necessary for the support of a horse, as fuel …

For fear I should be suspected of prodigality in the prosecution of my philosophical researches, I think it is necessary to inform the Society, that the cannon I made use of in this experiment was not sacrificed to it. The short hollow cylinder which was formed at the end of it … called in the German language the *verlorner Kopf* … the head of the cannon to be thrown away.

—Count Rumford, "An Inquiry Concerning the Source of the Heat Which Is Excited by Friction" [p. 95]
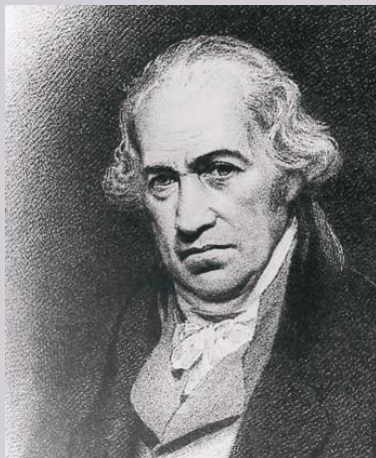
◀ Figure 4.125

JAMES WATT (1736–1819): Son of a well-to-do shipwright. Unable to attend school regularly because of his health. In 1757, opened in Glasgow a mechanical workshop affiliated with the university, and here, in addition to his skills as a toolmaker, acquired the theoretical knowledge that turned him from a technician into a scientist. In 1763, he began the repairs to a model of a Newcomen engine that belonged to the university. 1765: the condensing steam engine is born. The centrifugal regulator and the indicator for measuring steam pressure in the cylinder are also his inventions. WATT's significant contributions are twofold: He brought the steam engine into a practical form and helped it thereby to achieve the role that it would play in the course of the Industrial Revolution, while also giving impetus to scientifically based investigation into increasing the engine's efficiency, on which the foundations of thermodynamics were laid.

◀ Figure 4.126

NICOLAS LÉONARD SADI CARNOT (1796–1832): Engineering officer. Wrote his famous treatise *Réflexion sur la puissance motrice de feu et sur les machines propres à développer cette puissance* (published in Paris in 1824) in 1821 while fleeing the Bourbons. In this work, CARNOT still supports the existence of a heat substance (*caloricum*); however, from notes that he wrote shortly before his death, it is clear that he had recognized the kinetic theory as a possible alternative. One can even find in his ideas hints of the principle of conservation of energy.

Today we know that, in the case of the process investigated by CARNOT, the so called *Carnot cycle* (Figure 4.128), the following relationship holds:

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2},$$

In other words,

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1}.$$

This means that Carnot's formula, even though it was derived on the basis of incorrect assumptions, happens to be completely correct. In his later years—as it is evident from his correspondence and notes—CARNOT saw the relationship between heat and mechanical work more clearly. His untimely death prevented him from taking the decisive step, but the following quotation shows just how close he had come to the principle of conservation of energy.

It may be objected at this point that perpetual motion, which has been shown to be impossible for purely mechanical processes, may not be so where the effects of heat or electricity are concerned. But is it conceivable that the phenomena of heat or electricity are [not] due to ... some kind of motion and hence that they are not governed by the general laws of mechanics? Moreover, do we not know from experience that every attempt to produce perpetual motion has been futile, whatever method has been used, and that no one has ever managed to generate motion that is truly perpetual, in other words, motion that would continue without any effect on the materials being used to create it?

It has sometimes been suggested that the electrical generating apparatus (Volta's pile) could be a source of perpetual motion, and attempts have been made to achieve this by constructing dry piles which are claimed to undergo no changes. But, no matter what procedure has been adopted, the devices have always deteriorated quite markedly, whenever they have been used at all vigorously and for any length of time.

In a broad philosophical sense, the words "perpetual motion" should not be taken simply to mean motion that will continue indefinitely, following some initial impetus. They refer to the effect produced by a device, or any apparatus, that is capable of yielding unlimited quantities of motive power, capable of successively disturbing the state of rest of all those objects in nature that are not in motion and of overcoming their principle of inertia. Such a device would even possess the force necessary to move the entire universe and to sustain and constantly accelerate its motion. This is what we mean by the true creation of motive power. If such creation was possible, we would have no need to seek motive power in air currents, water, or combustible materials. We would have at our disposal a limitless supply on which we could draw infinitely.

—SADI CARNOT, *Reflexions on the Motive Power of Fire* [pp. 69–70]

4.5.7 The Kinetic Theory of Heat: First Steps

With CARNOT's results, the theory of heat substance reached the limits of its explanatory power. While in the first half of the nineteenth century this theory continued to serve as the background for investigations into the physics of heat, even its most successful proponents, such as CARNOT and LAPLACE, were already considering the possibility that heat is, in fact, a form of motion of the particles of

matter. The only problem was that proceeding from this point of view, they were not able to derive quantitative laws.

As we mentioned before, the kinetic theory already had a long history. Indeed, Bacon (Section 3.4) had categorically declared that there must exist a close relationship between heat and motion. This idea was generally accepted throughout the seventeenth century. However, the quantitative formulation of the theory was first taken up seriously by the "Basel school." Jakob Hermann (1678–1733) had claimed in 1716, although without any justification, that heat is proportional to the density of a body and the square of its motion. As in so many other areas, here, too, Euler contributed pioneering work: He arrived at a numerical value for the speed of the particles: $v \approx 477$ ms^{-1}. In the year 1738, Daniel Bernoulli, in his work on hydrodynamics, derived the relationship

$$p \sim nmv^2,$$

where he began with assumptions that are very similar to those underlying today's kinetic theory of gases. Figure 4.129 is taken from his book. Bernoulli surmised that the pressure exerted by a gas is the result of collisions of particles bouncing about as they try to move on a straight path. As can be seen in the figure, Bernoulli pictured the particles of matter neither as identical shapes nor as geometrically regular. Bernoulli's quantitative theories were not immediately taken note of, and they were forgotten for almost a century. The first time we encounter Bernoulli's ideas again is in 1816, in the work of John Herapath (1790–1868), who, however, made no further progress and indeed, contrary to Bernoulli, incorrectly associated temperature with the *impulse* of the particles. Thus it was easy for his opponents, among them no less an authority than Davy, to silence him.

Significant progress was made at the beginning of the 1840s in the theory derived by John James Waterston (1811–1883). The fate of Waterston's investigations is most instructive. An unknown neophyte among professional physicists, he sent his work from Bombay to the Royal Society. His article was turned over to two referees who were recognized specialists. Only one of the two found anything remotely positive to say in an otherwise negative review, while the other declared the entire work to be nothing but nonsense (Quotation 4.45).

Waterston's work, and indeed his very name, would have faded into obscurity had it not been possible for him finally to publish a short extract from his work and had not Lord Rayleigh discovered, in 1891, the original manuscript in the archives of the Royal Society. As a result, Waterston's article eventually appeared in the journal of the Royal Society after a delay of half a century. In connection with this story, Lord Rayleigh's advice to young physicists is particularly noteworthy: "A young author who believes himself capable of great things would usually do well to secure the favourable recognition of the scientific world by work whose scope is limited, and whose value is easily judged, before embarking on higher flights" (see Quotation 4.45). And Lord Rayleigh meant this completely seriously.

Quotation 4.46 reproduces Waterston's article almost completely, summarizing his theory. The author's "peculiar theory" has an entirely modern tone. We may judge Waterston's most important accomplishment to be that he succeeded in formulating with greater precision the findings of the earlier kinetic theories. Furthermore, he was the first to formulate a special case of the equipartition principle, namely that every atom of two gases at temperature equilibrium has the same average kinetic energy. We shall have more to say about the role of the equipartition theorem when we treat classical statistical theory. Here we mention only that
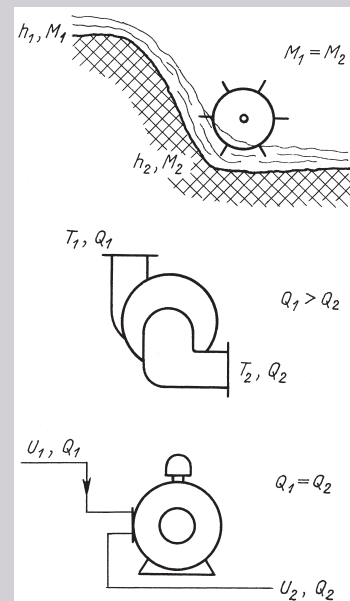
▲ **Figure 4.127** How work is extracted by a water wheel, a heat engine, and a direct-current motor. The water wheel and the electric motor work analogously, but the pattern breaks down with the heat engine because though the heat flows from a higher level to a lower one, it changes in its quantity. This was first noticed by Joule. Carnot did not yet realize the problem in his *Réflexion…* .

We may rightly compare the moving force of heat with that of a waterfall. The moving force of the latter depends on the height and on the quantity of fluid: the moving force of heat depends on the applied quantity of *caloricum* and—what could be called the height of fall—on the temperature difference that exists between the heat-exchanging bodies.
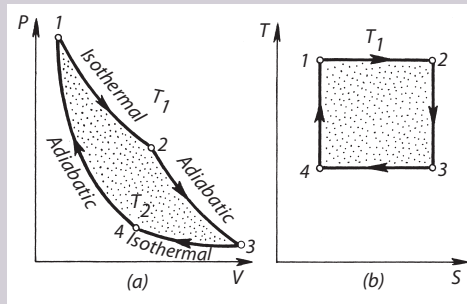
▲ **Figure 4.128** The Carnot cycle, represented in **(a)** a *V-P* and in **(b)** an *S-T* coordinate system.
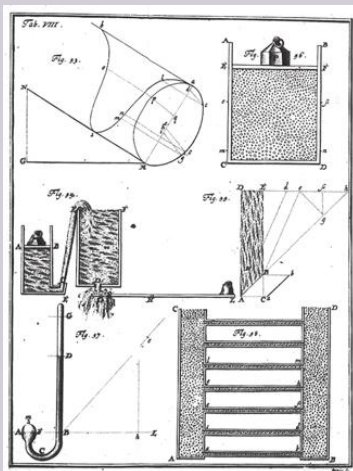
◀ **Figure 4.129** An illustration in BERNOULLI'S work on the kinetic theory of gases (Fig. 96). (Library of the University for Heavy Industry, Miskolc.)

Quotation 4.45

It is difficult to put oneself in imagination into the position of the reader of 1845, and one can understand that the substance of the memoir should have appeared speculative and that its mathematical style should have failed to attract. But it is startling to find a referee expressing the opinion that "the paper is nothing but nonsense, unfit even for reading before the Society." Another remarks "that the whole investigation is confessedly founded on a principle entirely hypothetical, from which it is the object to deduce a mathematical representation of the phenomena of elastic media. It exhibits much skill and many remarkable accordances with the general facts, as well as numerical values furnished by observation.... The original principle itself involves an assumption which seems to me very difficult to admit, and by no means a satisfactory basis for a mathematical theory, viz., that the elasticity of a medium is to be measured by supposing its molecules in vertical motion, and making a succession of impacts against an elastic gravitating plane." ... [The history of this paper suggests that] highly speculative investigations, especially by an unknown author, are best brought before the world through some other channel than a scientific society, which naturally hesitates to admit into its printed records matter of uncertain value. ... [Perhaps one may go further and say that] a young author who believes himself capable of great things would usually do well to secure the favourable recognition of the scientific world by work whose scope is limited, and whose value is easily judged, before embarking on higher flights.

—Lord RAYLEIGH, Introduction to J. J. WATERSTON, "On the Physics of Media that Are Composed of Free and Perfectly Elastic Molecules in a State of Motion"

WATERSTON was the first to succeed in answering BLACK's question as to why the kinetic theory did not necessarily imply a proportionality between the specific heat of a body and its density.

Given all this, we can well understand why WATERSTON had absolutely no influence on the further development of the kinetic theory. It was not in England, but in Germany a decade later, that the theory was advanced, or more precisely, restarted from a somewhat more basic level than where WATERSTON started.

4.5.8 *The Law of Conservation of Energy*

Meanwhile, by the beginning of the 1840s, the time had become ripe for a formulation of the law of conservation of energy.

The discovery of this law is usually linked to three names: JULIUS ROBERT MAYER (1814–1878, Figure 4.130), JAMES PRESCOTT JOULE (1818–1889, Figure 4.131), and HERMANN VON HELMHOLTZ (1821–1894, Figure 4.132). However, we should add that similar ideas had occurred to many other researchers. Thus, for example, JUSTUS LIEBIG wrote about the connection between heat energy and chemistry as well as the role of energy in biological processes.

ROBERT MAYER, too, was led to his own research by certain physiological phenomena. As a naval physician, he noticed that the blood drawn from the veins of sailors was of a brighter red in the tropics than what was usual in their chillier home climate. He correctly concluded that in the tropics, the oxidation processes of an organism proceed with lesser intensity because part of the heat required by life functions is supplied by the environment. His 1842 paper entitled *Bemerkungen über die Kräfte der unbelebten Natur* (Remarks on the Forces of the Inorganic Nature) was strongly influenced by natural philosophy, and it is therefore no great surprise that it was rejected for publication by the leading physics journal of the time, *Annalen der Physik*. Eventually, LIEBIG helped to place the article in the journal *Annalen der Chemie*. In reading the introduction (Quotation 4.47), we can understand the unease of the physicists with a work in which every claim is derived from the basic axiom that *causa aequat effectum*, meaning the cause is to be equated with its effect. Of a similar nature is the strange argument with which ROBERT MAYER tries to make it plausible that falling bodies increase in temperature. He starts from the experience that when we compress a body, that is, when we decrease its volume, heat is created. Let's consider a stone falling from a high place: as it falls, the volume of Earth to which the stone also, after all, belongs will thereby be reduced; hence, the temperature will rise …

At the end of his article, almost unexpectedly, we find the correct conclusion that when a body falls from a given height, its temperature must rise by a corresponding definite amount. This is posed in the form of a question: from what height must a body fall in order to achieve an increase in temperature of one degree? Although MAYER, as we would expect, did not carry out the experiment, he nevertheless gives an answer: Using the relationship of the specific heat of gases under constant pressure and volume, he estimates the mechanical equivalent for heat and obtains a numerical value of about 360 kpm. This value is far from the 425 kpm measured by JOULE, which is today considered valid. Nonetheless, the order of magnitude of the result and the theoretical approach were both entirely correct.

In 1841, JOULE published the law that is today named for him regarding the heat effect of electric current, whereby the heat generated by current flowing through

a resistor is proportional to the square of the current, the resistance, and the time:

$$Q \sim I^2 Rt.$$

His seminal work on the law of conservation of energy was published in 1845 with the title *On the Existence of an Equivalent Relation between Heat and the Ordinary Forms of Mechanical Power*. The method he used for taking measurements and the measuring device employed are today part and parcel of the standard high school physics curriculum (Figure 4.133). The potential energy of a body of a given weight is transformed into heat as the descent of the weight drives stirring paddles in some liquid. Of course, the measurements must be made with great care. Joule's first measurements did not yield the value that is considered correct today. However, with a refinement of his techniques, elimination of sources of error, or compensating for them, he arrived at a value for the mechanical equivalent of heat that is very close to what is in use today: 1 kcal ≈ 425 kpm.

Helmholtz's work on the conservation of energy was published in 1847 under the title *Über die Erhaltung der Kraft* (*On the Conservation of Force*). Although Helmholtz's style also exhibits the influence of Romantic natural philosophy, his arguments are presented in a form that would completely satisfy the tastes of today's physicists.

Because of the importance of the law of conservation of energy, it is worth taking the time to read some of the reminiscences of those who participated in its discovery, and here we are thinking primarily of the sober, realistic Joule, who was raised in the tradition of English empiricism. We learn from the memoirs he wrote in 1850, that he, too, was of the opinion that the time was ripe for an articulation of the law of conservation of energy. Nevertheless, this was accepted only with great hesitation by the scientists of the time. Joule's first report met with complete indifference except for one enthusiastic young man who did pay attention to it—with skepticism, to be sure, but nonetheless sensing the importance of the discovery. This was William Thomson, the future Lord Kelvin (Quotation 4.48).

4.5.9 *The Kinetic Theory of Gases*

After the formulation of the law of conservation of energy, the kinetic theory of matter, at first in the form of a kinetic theory of gases, came back into the limelight. More to the point, we should say that this theory was discovered anew, and now nothing stood in the way of its general acknowledgment. Referring to Herapath, in 1848 Joule himself had attempted to calculate the velocity of a hydrogen molecule and the specific heat of a gas under constant volume. His work was published in 1851 but did not arouse any particular attention.

The breakthrough in this approach came thanks to August Karl Krönig (1822–1879). While his brief 1856 article contained no new ideas, because it was the opinion of a noted professor, it gave the long-overdue impetus to the field. From this time on, macroscopic thermodynamics, the kinetic theory of gases, and classical statistics mutually reinforced their parallel development. Among those associated with this era were the likes of Rudolf Clausius (Figure 4.134), J. C. Maxwell, William Thomson (Figure 4.135), and Ludwig Boltzmann (Figure 4.136), to mention only the most important names.

It was Clausius who laid the cornerstone of both the macroscopic and microscopic theories. In his 1857 *Annalen der Physik* article *Über die Art der Bewegung, welche wir Wärme nennen* (On the form of motion that we call heat), he derives

▲ **Figure 4.130** Julius Robert Mayer (1814–1878): His observations on the color of blood in Surabaya (Java), while serving as a ship's surgeon in 1840, provided an impetus to the formulation of the energy conservation law. In 1841, the journal *Annalen der Physik* declined to publish his work, and it appeared a year later in the *Annalen der Chemie* with the title *Bemerkungen über die Kräfte der unbelebten Natur*. In 1845, Mayer thoroughly investigated, in a way that is convincing even to today's physicists, the relationship between the work of expansion of a gas and the participating heat quantity. In 1848, he conjectured that the heat of the Sun stems from the kinetic and gravitational energy of the meteors that strike it. Physicists were slowly becoming aware of the law of conservation of energy, but they considered Joule and Helmholtz as its discoverers. Mayer fought long in vain for recognition of his contribution, suffered a nervous breakdown, and in 1850 attempted suicide. Tyndall, in an 1862 lecture to the Royal Institution, finally conceded that Robert Mayer should be granted first place among the discoverers of the energy conservation law.

Quotation 4.46

The author deduces the properties of gases, with respect to heat and elasticity, from a peculiar form of the theory which regards heat as consisting in small but rapid motions of the particles of matter. He conceives that the atoms of a gas, being perfectly elastic, are in continual motion in all directions, being restrained within a limited space by their collisions with each other, and with the particles of surrounding bodies. The *vis viva* of those motions in a given portion of gas constitutes the quantity of heat contained in it.

He shows that the result of this state of motion must be to give the gas an elasticity proportional to the mean square of the velocity of the molecular motions, and to the total mass of the atoms contained in unity of bulk; that is to say, to the density of the medium.

◀ **Figure 4.131** James Prescott Joule (1818–1899): Owner of a brewery, perhaps the last autodidact who made a significant contribution to science. His strength was a finely honed measurement technique. In recognition of his scientific accomplishments, he was named president of the Literary and Philosophical Society of Manchester. In 1840, he worked out the laws for the heat generated by an electric current. 1843: measurement of the heat equivalent of mechanical work. Over three decades, he determined the numerical conversion factors for energy transformation with various techniques; these experiments contributed decisively to the general recognition of the concept of energy and the energy conservation law. His friendship with Thomson (later Lord Kelvin) had a great influence on his work: The Joule–Thomson effect is the change in temperature that occurs in the expansion of a gas without doing work and while kept insulated so that no heat exchange with the environment occurs. At room temperature, all gases—with the exception of hydrogen, helium, and neon—will cool under these conditions, so that this effect can be used for the liquefaction of gases. At very low temperatures, hydrogen and helium can also be cooled this way.

the state equation

$$pv = \frac{nmu^2}{3},$$

where u^2 is mean square velocity of the molecules. His derivation is similar to what appears in today's textbooks on theoretical physics. Clausius determined that the pressure of a gas is a function of the energy of the translational motion of the molecules. The translational energy is a portion of the internal energy of the gas, to which other energies may also contribute. Thus, with increasing complexity of the molecules, the energy contribution resulting from the vibrational motion of the atoms within the molecules increases as well. Clausius derived the following relationship between the kinetic energy of the translational motion E_k and the total heat q:

$$\frac{E_k}{q} = \frac{3}{2}\frac{c_v - c_p}{c_p},$$

where c_v is the specific (related to the volume unit) heat of the gas at constant volume, and c_p is the specific heat under constant pressure.

Clausius also introduced the notion of free path length into the theory and explained the apparent contradiction between the extraordinarily high velocities of the gas particles (for hydrogen, it is 1800 ms⁻¹) and the small speed of diffusion.

For Maxwell, the kinetic gas theory was an interesting exercise in mechanics. In a letter, Maxwell writes that it would be worthwhile to investigate, independently of the kinetic theory of gases, the behavior of a large number of elastic spheres interacting exclusively by collision processes. The main result of his 1860 work is the derivation of the velocity distribution function that now bears his name. Using it, one can determine the number of particles with velocities in the interval from v to $v + dv$ (Figure 4.137) via

$$\frac{dN}{N} = \frac{4}{\alpha^3 \sqrt{\pi}} v^2\, e^{-v^2/\alpha^2}\, dv,$$

where α^2, defined by $\overline{v^2} = \frac{3}{2}\alpha^2$, is a quantity proportional to the mean square velocity.

Also of importance is Maxwell's conclusion that for a mixture of gases in thermodynamic equilibrium, every molecule possesses the same average kinetic energy (equipartition theorem). This principle was generalized by Maxwell in the same article: the same energy is associated with each degree of freedom of the gas particles. But equal average energy is also additionally allotted to every degree of freedom that is bound to a potential energy. This average energy is equal to $\frac{1}{2}kT$, where T is the absolute temperature and

$$k = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}} = 1.38 \times 10^{-16}\ \mathrm{erg\,K^{-1}}$$

is one of the universal constants of physics (the Boltzmann constant).

Maxwell then calls attention to the fact that the theoretical values thus derived for the specific heats differ from the experimental results by more than the margin of error in the experiments (Figure 4.138).
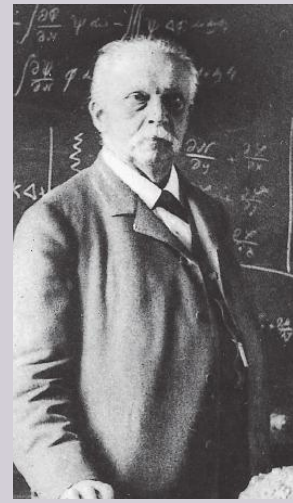
In 1866, Maxwell derived the following general relationship that would later become so significant: $c_p / c_v = (f + 2)/f$, where f is the number of degrees of freedom of the gas molecules.
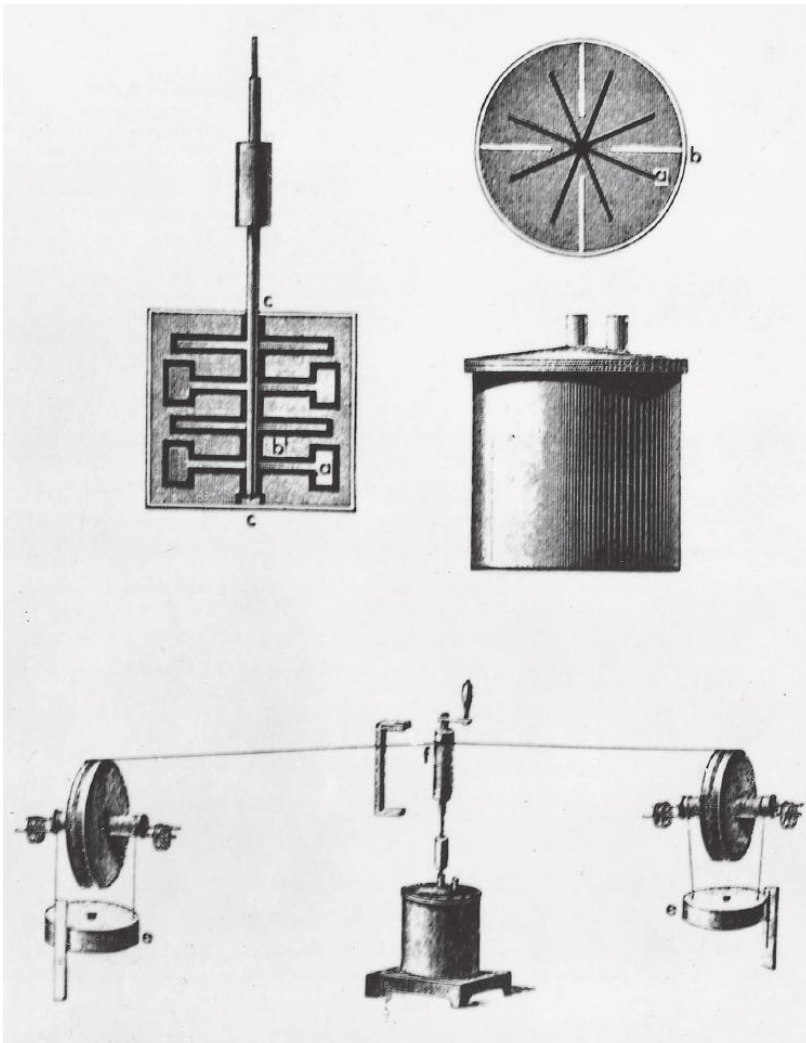
▲ **Figure 4.133** Joule's experimental apparatus for determining the mechanical equivalent of heat.

4.5.10 *The Second Law of Thermodynamics*

In macroscopic thermodynamics, Clausius again takes center stage. Having accepted the equivalence of heat and mechanical work, or, more generally, the principle of conservation of energy, he noticed that for an explanation of thermodynamic phenomena, yet another concept was also needed. He began with the 1854 axiom that heat cannot of its own accord pass from a colder body to a warmer one. This axiom is a generally understandable way of stating the second law of thermodynamics (Figure 4.139(a)). An axiom equivalent to this is the following: it is impossible to construct a perpetual motion machine of the second type, by which is meant an apparatus that without violating the law of conservation of energy, nevertheless completely (with 100% efficiency) transforms heat into mechanical work (Figure 4.139(b)).

Quotation 4.47

Forces are causes; therefore, the following fundamental law applies: *causa aequat effectum*. If cause *c* has effect *e*, then *c* = *e*. If *e* is itself the cause of another effect *f*, then *e* = *f*, etc., *c* = *e* = *f* = ... = *c*. In a chain of causes and effects, as is illuminated from the nature of an equation, a term or a part of a term can never become zero. This first property of all causes we call *indestructibility*.

If the given cause *c* has caused the like effect *e*, then *c* has ceased to be; *c* has become *e*; if after the creation of *e*, *c* remains in whole or in part, then a further effect would have to correspond to this remaining cause, and the effect of *c* must therefore be > *e*, which contradicts the assumption *c* = *e*. Since therefore *c* changes into *e*, *e* into *f*, etc., these quantities must be seen as different manifestations of one and the same object. The capacity of being able to assume different forms is the second significant property of all causes. Summarizing both properties, we say, causes are (quantitatively) *indestructible* and (qualitatively) *changeable objects*.

Two categories of causes are to be found in nature between which, according to experience, no transformations take place. One category consists of the causes to which are associated the property of ponderability and impenetrability—matter. The others are the causes that do not have these properties—forces that we may call imponderable in recognition of a property that they lack. Forces

are therefore these: *indestructible, changeable, imponderable objects*.

It is now agreed that for vanishing motion in many cases (*exceptio confirmat regulam*), no other effect can be found than heat, for the created heat no other cause than motion; we therefore prefer the assumption that heat results from motion to the assumption of a cause without effect and an effect without cause, like a chemist establishing a connection between H and O on the one hand and water on the other instead of unquestioningly allowing H and O to vanish and water to appear in an unexplained manner.

We may clarify the natural relationship that arises among gravitational force, motion, and heat in the following way. We know that heat appears when the individual mass elements of a body move closer together; compression creates heat; now, what holds for the smallest mass elements and their smallest interstices must hold as well for large masses and measurable volumes. The falling of a weight is an actual reduction in the volume of the Earth, and therefore must be related to the resulting heat; this heat must be precisely proportional to the size of the weight and its (original) distance. ...

We close our theses, which arise necessarily from the fundamental law *causa aequat effectum* and stand in full accord with all natural phenomena with a practical consequence. ...

We must find how high a given weight must be raised above the Earth's surface so that its gravitational force is equivalent to the heating of an equal weight of water from 0° to 1° C. That such an equation can actually be established in nature can be considered the summary of what we have said above.

Using the established theorems on the heat and volume relationships of gases, one finds the sinking of a column of mercury compressing a gas to be equal to the heat quantity released by the compression, and it turns out—the relative powers of the capacities of atmospheric air under equal pressure and volume = 1.421—that the falling of a weight from a height of about 365 m corresponds to a warming of an equal weight of water from 0° to 1°. If one compares the power of our best steam engines with this result, one sees how only a small portion of the heat generated in the boiler is actually converted into motion or lifting power, and this could serve as justification for searching for other ways to represent motion fruitfully than the sacrifice of the chemical difference of C and O, namely through transformation of electricity created by chemical means into motion.

—Robert Mayer, "Bemerkungen über die Kräfte der unbelebten Natur," 1842

We arrive at the notion of entropy and thereby a mathematical formulation of the second law of thermodynamics in the following way: In an ideal reversible Carnot cycle, we have $Q_1 / T_1 = Q_2 / T_2$, or equivalently, $Q_1 / T_1 - Q_2 / T_2 = 0$. More generally, we may write $\sum Q_i / T_i = 0$, where the quantities of heat flowing into the system are taken as positive, and those flowing out as negative. Given a general ideal reversible cycle, it can be broken down into small "elementary" cycles. For each of these, the above equation holds with the incoming or outgoing heat quantity dQ and with the (variable) temperature T. Thus, in 1865, it was established by Clausius that for an arbitrary reversible cycle that is run to completion, one has the equation $\oint dQ / T = 0$.

From this, it follows that the quantity dQ / T is a total differential. The value of the line integral for a process that does not return to its original state therefore depends only on the initial and final states:

$$\frac{dQ}{T} = dS, \quad \int_A^B \frac{dQ}{T} = S_B - S_A.$$

If the point A is held fixed, then one has a quantity that depends only on the state B. This new quantity of state is the entropy of the material. For irreversible cyclical processes, Clausius was able to prove the equation

$$\oint \frac{dQ}{T} < 0,$$

where heat flowing into the system must be taken as positive.

From this, it follows that the entropy of a closed system cannot decrease (Figure 4.139(c)).

The two laws of thermodynamics can now be written as

$$dU = dQ + dA$$

and

$$dQ \leq T\, dS,$$

or equivalently:

1. The energy of a closed system is constant.
2. The entropy of a closed system can only increase or remain constant.

The work of the chemist Walther Nernst (1864–1941) and the physicist Max Planck then led (in 1904 and 1911, respectively) to the formulation of the third law of thermodynamics:

3. The entropy of a system in thermodynamic equilibrium approaches zero as the temperature approaches absolute zero.

The further development of phenomenological thermodynamics and its extension to heterogeneous systems in the 1880s is due primarily to Helmholtz and Gibbs. Then in the twentieth century, the focus of interest moved to irreversible processes, with particular emphasis on biological phenomena (Prigogine, Onsager, Gyarmati).

At first glance, entropy appears to be a totally abstract quantity, of interest solely in theoretical physics. However, entropy is a quantity of state just like pressure, volume, and temperature, so it has practical engineering applications, for example, in the design of steam engines with temperature/entropy diagrams (see Figure 4.128).

Many of the phenomena in daily life can be related through the concept of entropy. It makes it possible to describe quantitatively simple laws: for example, if we have in a closed system of bodies at different temperatures, sooner or later their temperatures will come into equilibrium.

This conclusion was projected to the whole universe in the so-called heat death theory, according to which the universe at present is in a state of relatively low entropy, which means that we can find bodies in it with widely differing temperatures. But every process that takes place in the universe leads to an increase in its total entropy, so the universe must eventually reach a state of maximal entropy in which all temperature differences have been equalized, and thus one in which the possibility for life no longer exists. From the standpoint of physics, however, this conclusion is incorrect for two reasons. The first is that the law of increase in

entropy holds true only for closed, finite systems; the second objection relates to the probabilistic nature of the second law, which describes the probable course of events, from which, even if only with a small probability, deviations are possible.

It was KELVIN who, in 1852, first emphasized that in natural processes, there is a general tendency for all forms of energy to be transformed eventually into heat, equalizing any temperature differences. The pessimism of SCHOPENHAUER, which came into fashion at this time, provided the philosophical background for these fresh scientific theories.

The vision of the French poet JULES LAFORGUE (1860–1887) in *Funeral March for the Death of the Earth* (Quotation 4.49) is just as viable today as it was then, but at the time the catastrophe was going to be due to the blind laws of nature; today, however, it is human nature (or perhaps the blind laws of human nature) that is responsible for what will come.

Furthermore, from what we now know, it seems that the laws of nature are more likely to incinerate us than to freeze us: After a few billion years, our Sun will be transformed into a red giant and will eventually become so large as to encompass Earth's orbit.

4.5.11 *Entropy and Probability*

By the mid-1860s, the two laws of macroscopic (phenomenological) thermodynamics had firmly taken root; following the interpretation of the state equation, the kinetic theory of gases successfully dealt with the problems of heat conduction and viscosity (MAXWELL, *On the Dynamical Theory of Gases*, 1866–1868).

The state equation and even the first law of thermodynamics had been derived from simple mechanical laws (conservation of momentum and energy), so it is no wonder that the need immediately arose to interpret the second law of thermodynamics in terms of the kinetic theory. Entropy plays a central role in the mathematical formulation of the second law, so the first serious efforts were directed toward proving within the framework of the kinetic theory—by investigating reversible processes—that the expression $\mathrm{d}S = \mathrm{d}Q\,/\,T$ is a complete differential, in other words, that the entropy S exists as a quantity of state (RANKINE 1865, BOLTZMANN 1866, CLAUSIUS 1871).

Their starting point was the principle of least action in a somewhat more general form; but to reach the desired goal, in the beginning the movement of individual particles had to be restricted in extremely unnatural ways, for example, with each particle having to move in a closed path with identical periods. Although these restrictions could be moderated later, by the beginning of the 1870s it had become clear that particularly in the case of irreversible processes, an interpretation of the second law using solely mechanical principles was not possible.

The trains of thought followed by CLAUSIUS and BOLTZMANN can be summarized as follows [Spassky 1977]: We write the action function of an individual particle:

$$\int_{t_1}^{t_2} (\mathfrak{E} - U)\,\mathrm{d}t = \int_{t_1}^{t_2} [\mathfrak{E} - (E_0 - \mathfrak{E})]\,\mathrm{d}t = \int_{t_1}^{t_2} 2\mathfrak{E}\,\mathrm{d}t - \int_{t_1}^{t_2} E_0\,\mathrm{d}t.$$

Here $\mathfrak{E}$ is kinetic energy, U is potential energy, and E_0 is total energy. For the variation, the constant E_0 is irrelevant, and so the last term may be omitted. We therefore have

$$\int_{t_1}^{t_2} 2\mathfrak{E}\,\mathrm{d}t = \int_{t_1}^{t_2} mv^2\,\mathrm{d}t = \int_{t_1}^{t_2} mvv\,\mathrm{d}t = \int_{P_1}^{P_2} mv\,\mathrm{d}s.$$

Suppose our system consists of n particles each with three degrees of freedom. And suppose that the state

▲ **Figure 4.134** RUDOLF CLAUSIUS (1822–1888): After studies at the University of Berlin, taught at a number of German universities as well as the Swiss Federal Institute of Technology, in Zurich. 1865: formulation of the second law of thermodynamics and introduction of the notion of entropy. His work on the kinetic gas theory, which began in 1857, is also of significance.

of the system is characterized by specifying the $3n$ positional coordinates in $3n$-dimensional space:

$$x^{(1)}, y^{(1)}, z^{(1)}; x^{(2)}, y^{(2)}, z^{(2)}; \ldots; x^{(n)}, y^{(n)}, z^{(n)}.$$

Suppose that at time t_1, the system is at the point

$$P_1\left(x_1^{(1)}, y_1^{(1)}, z_1^{(1)}; x_1^{(2)}, y_1^{(2)}, z_1^{(2)}; \ldots; x_1^{(n)}, y_1^{(n)}, z_1^{(n)}\right)$$

in configuration space and is moving along a curved path in this space, arriving at time t_2 at the space point

$$P_2\left(x_2^{(1)}, y_2^{(1)}, z_2^{(1)}; x_2^{(2)}, y_2^{(2)}, z_2^{(2)}; \ldots; x_2^{(n)}, y_2^{(n)}, z_2^{(n)}\right).$$

If we supply the system with heat δQ, then the system describes a different, neighboring path between P_1 and P_2. The variation in the action function for the entire system is given, after some not very complicated intermediate calculations, by

$$\delta \int_{t_1}^{t_2} 2\mathfrak{E}\, dt = \int_{t_1}^{t_2} (\delta \mathfrak{E} + \delta U + \delta L)\, dt + \sum_i m^{(i)}\left(\dot{x}^{(i)}\delta x^{(i)} + \dot{y}^{(i)}\delta y^{(i)} + \dot{z}^{(i)}\delta z^{(i)}\right)\Big|_{t_1}^{t_2}.$$

Here $\mathfrak{E}$ is now the sum of the kinetic energies of all the particles, U is the potential energy, L is the work of the system against external forces, and $\mathfrak{E} + U = E$ is the total energy of the system. If we now take the average values for all the quantities that appear, for example, in the equation

$$\overline{\mathfrak{E}} = \frac{1}{\tau}\int_{t_1}^{t_2} \mathfrak{E}\, dt, \quad \tau = t_2 - t_1,$$

for the kinetic energy, we obtain the equation

$$2\delta\left(\tau \overline{\mathfrak{E}}\right) = \tau\left(\delta \overline{E} + \delta \overline{L}\right) + \sum_i m^{(i)}\left(\dot{x}^{(i)}\delta x^{(i)} + \dot{y}^{(i)}\delta yy^{(i)} + \dot{z}^{(i)}\delta z^{(i)}\right)\Big|_{t_1}^{t_2}.$$

However, the heat added to the system serves, on the one hand, to increase the internal energy and, on the other hand, to perform work against the external forces; therefore, we have

$$\delta E + \delta L = \delta Q.$$

We thereby obtain

$$2\delta\left(\tau \overline{\mathfrak{E}}\right) = \tau\delta Q + \sum_i m^{(i)}\left(\dot{x}^{(i)}\delta x^{(i)} + \dot{y}^{(i)}\delta yy^{(i)} + \dot{z}^{(i)}\delta z^{(i)}\right)\Big|_{t_1}^{t_2}.$$

To make the last term disappear, we require the above-mentioned overdetermined conditions. If the particles move over closed paths with a common period $\tau = t_2 - t_1$, then each individual term will be zero in the sum: the state of each particle is the same for times t_1 and t_2. A weaker condition would be to require the entire sum to be equal to zero. In this case, we obtain

$$2\delta\left(\tau \overline{\mathfrak{E}}\right) = \tau\delta Q.$$

However, the average kinetic energy is proportional to the temperature:

$$\overline{\mathfrak{E}} = KT,$$

that is,

$$\frac{\delta Q}{T} = \frac{2K\delta(\tau T)}{\tau T} = 2K\delta \ln \tau T.$$

This proves that—under the given condition—$\delta Q/T$ is a complete differential, that is, its integral depends only on the final state of the system and not on the manner in which this state was achieved. Here we are considering the initial state as fixed.

BOLTZMANN clearly understood in 1872 that "the problems of the mechanical theory of heat are also problems of probability theory." He presented his famous kinetic equation for the change in the general

distribution function $f(x, y, z; \dot{x}, \dot{y}, \dot{z}, t)$ in the following form:

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial x}\dot{x} + \frac{\partial f}{\partial y}\dot{y} + \frac{\partial f}{\partial z}\dot{z} + \frac{X}{m}\frac{\partial f}{\partial \dot{x}} + \frac{Y}{m}\frac{\partial f}{\partial \dot{y}} + \frac{Z}{m}\frac{\partial f}{\partial \dot{z}} = \left[\frac{\partial f}{\partial t}\right]_{\text{collision}},$$

where X, Y, Z denote the components of the external force acting on the particles; the term on the right-hand side gives the change in the distribution function per unit time due to the collisions. This quantity depends in a rather complicated way on the form of the distribution function itself. It is at once clear that the collisions change nothing in the Maxwell–Boltzmann distribution; indeed, they ensure that a gas with such a complicated distribution function at a given point in time will enter into a state of equilibrium with the Maxwell–Boltzmann distribution if no external effects on the gas are permitted. However, that is but one of the consequences of the theorem presented by Boltzmann in 1872 and later called the H theorem, which states that if the distribution function $f(x, y, z; \dot{x}, \dot{y}, \dot{z}, t)$ satisfies the kinetic equation, then as a function of time, the quantity

$$E = \iiiint\!\!\int\!\int f \ln f \, \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}\dot{x}\,\mathrm{d}\dot{y}\,\mathrm{d}\dot{z}$$

can only decrease (or remain constant at a minimal value), that is,

$$\frac{\partial E}{\partial t} \leq 0.$$

The integration extends over all possible values of the six variables. The thought immediately arises that E must be closely related to the entropy. A simple calculation shows that in the equilibrium state, E is proportional to the negative entropy.

As a curiosity, we should mention that, according to tradition and not completely verified, the name "H theorem" is based on a misunderstanding: The letter E had long been reserved to denote energy, and so the uppercase letter eta (H) was taken from the Greek alphabet.

Below, we sketch Boltzmann's ideas published in 1877 in a somewhat modernized form.

We consider a system consisting of N molecules, where the structure of the molecules can be arbitrarily complex. We therefore need more information in order to be able to characterize the state of the molecules.

The position of a molecule with f degrees of freedom can be uniquely specified by the f coordinates $q_1, q_2, \ldots, q_f$. To describe the state of such a molecule, the spatial coordinates x, y, z generally do not suffice; rather, one must introduce an f-dimensional space with coordinates $q_1, q_2, \ldots, q_f$ in which the molecule's position is represented by this point.

For a complete specification of the state of a molecule, we need in addition to the information about its location, information about its motion. The most useful approach is to use "canonically conjugate" momenta $p_1, p_2, \ldots, p_f$, associated with the spatial coordinates. The canonically conjugate quantities q and p also play a role, as we have seen (Section 4.2.7) in the Hamiltonian equations of motion in mechanics.

The position and motion of a molecule, or, more generally, its state of motion, are described by the set of $2f$ generalized coordinates $q_1, q_2, \ldots, q_f; p_1, p_2, \ldots, p_f$. We now use these as ordinary Cartesian coordinates in a $2f$-dimensional space. To this end, we place q_1 on the first axis, q_2 on the second, and finally p_f on the $2f$th. It should not cause any difficulty that we are only able to visualize up through coordinate q_3. We call the space thus obtained the *phase space* of the molecule. We can now say that the state of a molecule corresponds to a particular point in phase space because each point specifies both the spatial and momentum coordinates. We now divide the phase space into volume elements with volume $\mathrm{d}q_1 \cdots \mathrm{d}q_f \cdots \mathrm{d}p_f$ and number the resulting "cells" consecutively. Using this enumeration, we can identify individual locations in the phase space. We now know the state of a gas if at a given point in time we know, for each marked "individual" distinguishable molecule, the cell in phase space in which it is located. We call this state, which is determined by specifying all coordinates of the molecules that we consider to be
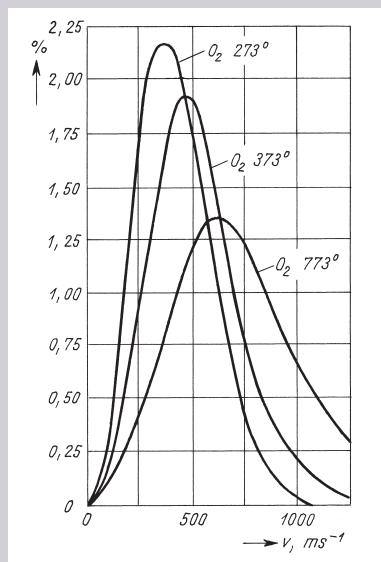
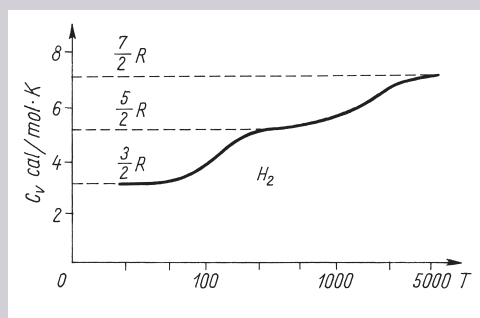▲ **Figure 4.137** The Maxwell velocity distribution.

▲ **Figure 4.138** Temperature dependence of the specific heat of hydrogen gas measured at constant volume. As the temperature increases, it appears that the number of degrees of freedom increases. This phenomenon will be explained later only by quantum theory.

distinguishable, the *microstate*. We now proceed from the assumption that *each microstate of a gas thus defined appears with equal probability*.

The measurable macroscopic state of a gas is given by the number of molecules in the various phase-space cells, or, in other words, by the density of the molecules in phase space.

If there are N_1, N_2, …, N_n, molecules in the N cells of phase space numbered 1, 2, …, N, then we are dealing with the macroscopic state characterized by the numbers N_1, N_2, …, N_n. The number of possible microstates associated with this macroscopic state is

$$P_{td} = \frac{N!}{N_1! N_2! \cdots N_n!}. \qquad (2)$$

This number is called the thermodynamic probability of the associated macroscopic state.

A gas left to itself progresses in a brief period of time from a given initial state to a state with maximal thermodynamic probability. For example, consider two parts of a container separated by a partition that contain gas at different pressures; for the volume of the entire container, the probability of this distribution is much less than the probability of a uniform distribution. Hence, if we remove the partition, then the pressures will equalize. A further example: If a jet of gas enters a gas-filled container at a uniform speed, then the velocities of the molecules in the jet will rapidly change: the molecules will scatter uniformly in every direction and the absolute values of their velocities will satisfy the Maxwell distribution because this state is much more probable than the initial state.

Expression (2) for the thermodynamic probability has its maximum at $N_1 = N_2 = \cdots = N_i = \cdots$, that is, at constant density, assuming that each element of phase space is assigned the same energy. However, if we associate energy E_i with the element that contains N_i particles and if the total energy E is a specified constant, then a different result is obtained. Expressed mathematically, we are now seeking a maximum for the thermodynamic probability P_{td} with the constraint that $\sum_i N_i E_i = E_0$; in addition, there is the natural (at least in classical problems) constraint $\sum_i N_i = N$ that the number of particles is constant. The solution with the greatest probability is the following "Boltzmann distribution":

$$N_i = A e^{-E_i / kT}.$$

In the derivation, N and all the N_i are taken to be large; it is therefore possible to calculate with continuously variable values of P_{td}, and one can also use Stirling's asymptotic formula for $N!$:

$$N! \sim \sqrt{2\pi N} \left(\frac{N}{e} \right)^N.$$

We have found in the thermodynamic probability a quantity that says something about the direction of processes. In nature, processes run in such a way that the total thermodynamic probability for all bodies involved in the process increases. This statement seems familiar to us because in thermodynamics, the same is said about the entropy: Entropy is the quantity that in macroscopic thermodynamics determines the direction of processes. We recall that according to the second law of thermodynamics, the entropy in a closed system can only increase. Therefore, there must be a close connection between the thermodynamic probability of the macroscopic state of a gas and the entropy. That is, the entropy should be a function of the thermodynamic probability.

This function can easily be determined. According to the laws of thermodynamics, the total entropy of two gases confined in containers isolated from each other

is equal to the sum of the individual entropies of the two gases: $S = S_1 + S_2$. The probability W that at a given time the entire system will be in a particular state is given by $W = W_1 \times W_2$, where W_1 and W_2 are the thermodynamic probabilities of the two gases. We know that the probability for the simultaneous occurrence of two independent processes is equal to the product of the probabilities of the individual processes, so from what we have said, it follows that $S = f(W)$ must be chosen such that $S = S_1 + S_2$ can be satisfied with $f(W_1 \times W_2) = f(W_1) + f(W_2)$. This requirement determines the function $f(W)$ as

$$S = k \ln W,$$

since the logarithm of a product is equal to the sum of the logarithms of the factors. Here k is the well-known universal Boltzmann constant. This relationship was first formulated by BOLTZMANN in 1877 and generalized in 1879 by MAXWELL.

Having succeeded in establishing a relationship between entropy and the probability of the state of a gas, we may state that the second law of thermodynamics, with its statement about the growth in entropy, is no longer to be seen as absolute and valid under all circumstances. Namely, if every microstate of a gas is realized with equal probability, then over a sufficiently long period of time, the gas will take on every possible state. We know, however, that the maximal entropy is associated with the majority of these states; nevertheless, other states with a smaller entropy must occur, even if only very seldom.

One formulation of the second law—the one closest to our common sense—is that heat does not of its own accord pass from a colder body to a warmer body. By the above, this is not strictly true. It is not out of the question that when two bodies of different temperatures touch, the result will be that the colder one becomes colder and the warmer one becomes warmer. Within the kinetic theory of heat, this means that spheres moving at an average low velocity collide with the faster ones in such a way that the velocities of the faster spheres increase, while those of the slower ones correspondingly decrease. According to the laws of mechanics, this is possible: possible yes, but by the above, highly unlikely. To understand the order of magnitude involved, let us calculate the probability that the very small heat quantity of 1 erg flows by itself from one body at temperature 14° C to a body at 15° C: As the measure of change in entropy, $\Delta S / k$ is given by

$$\frac{1}{k}\Delta S = \frac{1}{k}\left(\frac{dQ}{T_1} - \frac{dQ}{T_2}\right) = \left(\frac{1}{288} - \frac{1}{289}\right)\frac{1}{1.38 \times 10^{-16}} \approx 10^{11},$$

from which we obtain the value

$$\frac{W_1}{W_2} = e^{-\Delta S/k} = e^{-10^{11}} = \frac{1}{e^{10^{11}}}.$$

Now, $e^{10^{11}}$ is an unimaginably large number, and we must execute correspondingly many experiments if we expect to observe the result indicated above. We may therefore be certain that we will never observe energy flowing from a colder body to a warmer body.

We can now state the second law of thermodynamics more precisely: If a gas is in a state whose entropy is significantly smaller than the maximum possible value, then the probability is very great that at a later time, a larger value for its entropy will be measured.
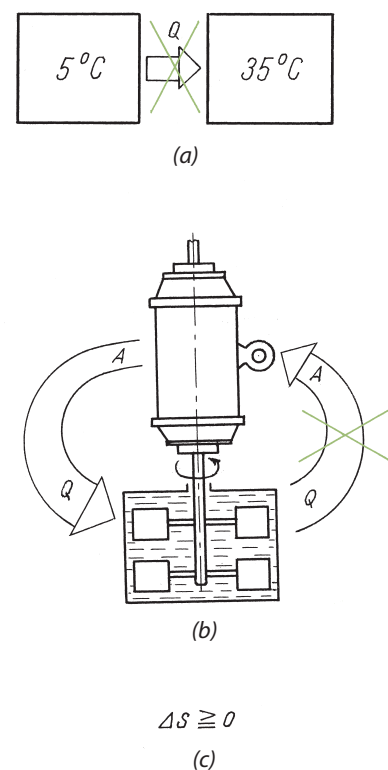

▲ **Figure 4.139** Various formulations of the second law of thermodynamics.

(a) Heat cannot *of itself* pass from one body to a hotter body without additional processes participating in the system. The possibility of other processes must be emphasized, because in a refrigeration system, a body can have heat extracted from it and passed to the warmer environment; however, there complex processes are involved.

(b) A quantity of heat cannot be transformed into mechanical work with 100% efficiency. The work done by the motor here is transformed completely into heat, but this heat cannot be completely turned back into work. Hence, the arrangement shown will not work, even though it does not contravene the law of conservation of energy.

(c) The entropy of a closed system cannot decrease. Closed systems move on their own only into states of greater entropy, that is, states that are more probable or more disordered. Because entropy is a state quantity, this formulation is the best for deciding which end states in complex processes can be reached from given initial states. Thus, for example, recently the question was discussed whether the efficiency of fuel cells can be greater than 100%. Fuel cells are galvanic cells in which the chemical energy of fuels is transformed directly into electric energy using chemical reactions that may take place even at room temperature. At first glance we may think that an efficiency of more than 100% would be in violation of the first law of thermodynamics, the conservation of energy, because we would get more energy out of the system than we put in. However, we must consider that the

Figure 4.139 *continued*

environment belongs to the total system, and the apparatus could "pump" heat out of the environment. But what does the second law say about the possibility of such a process? By itself it cannot occur. However, if the entropy in the reaction products is greater than the entropy of the initial fuel, then this increase of entropy can compensate for the decrease of entropy due to the "pump" and the entropy of the entire system can increase. Consequently, the efficiency of certain fuel cells can—theoretically—be greater than 100%. In practice, however, such efficiencies are yet to be demonstrated.
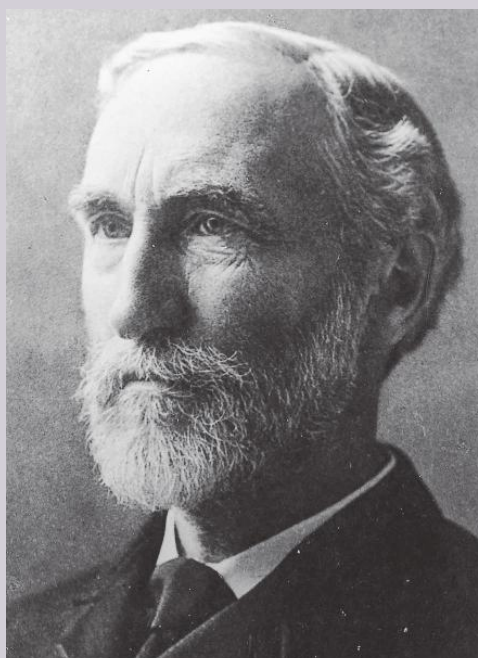
▲ **Figure 4.140** JOSIAH WILLARD GIBBS (1839–1903): Studied at Yale University. First doctor of engineering in the United States (1862) with a dissertation titled *On the Form of the Teeth of Wheels in Spur Gearing*. After a three-year study of mathematics and physics at various European universities, from 1871 professor of theoretical physics at Yale. One of his most significant works is *A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces* (1873), in which the connections between volume, entropy, and energy are studied. MAXWELL was so impressed by this method that he built a model and sent it to GIBBS. In 1876, GIBBS's best-known work, *On the Equilibrium of Heterogeneous Substances*, appeared, in which he introduces the thermodynamic potentials, presents the most general conditions for equilibrium, and discusses the thermodynamics of surface phenomena and of electrochemical processes. In 1902, his book on the fundamental principles of statistical mechanics was published. The *Great Soviet Encyclopedia* offers the following evaluation:

> In GIBBS's work, not a single error has thus far been discovered, and every one of his ideas is still valid in today's science.

BOLTZMANN's statistical interpretation of entropy, as presented above, made it possible to provide a convincing answer to all objections to the interpretation of thermodynamic phenomena within the framework of mechanics. These were the two most important objections:

1. Let the particles of the gas move as a mechanical system, which is to say that the gas assumes a series of states. According to the laws of mechanics, the opposite movement, where the gas traverses the same states in the opposite direction, is also possible. However, the laws of thermodynamics allow only changes in state in the direction in which entropy increases (LOSCHMIDT, 1876).

2. Every closed mechanical system in its movement will repeat any of its states arbitrarily closely after sufficient time, so that every intermediate increase in entropy must be compensated for by a loss in entropy at some other time (ZERMELO's objection, 1896, based on POINCARÉ's inversion theorem).

Yet another objection should be mentioned. We again start from the point of view that a gas can be seen as a mechanical system whose course of motion is determined by the laws of mechanics, and we also assume that every microstate of a gas is realized with equal probability. However, given the laws of mechanics, the specification of the initial state determines all future states of the gas over the course of time, so that the gas passes through *deterministic*, not *probabilistic*, states. But if we assume that the microstate is measured at stochastically chosen points in time, then it is reasonable to ask about the frequency with which we find that the gas obeys the deterministic laws of motion, in any given state. The question is whether we can then also show, using the equations of mechanics, that under such conditions every microstate of a gas will be found with the same frequency. Indeed, using Hamilton's equations of motion, JOHN VON NEUMANN was able to show that a system with a great many degrees of freedom runs through all the energetically allowed microstates (ergodic hypothesis) or at least approaches such states arbitrarily closely (quasiergodic hypothesis). With this it has been proven that, if we make our observations at random times, we will encounter a gas in every microstate with equal frequency, meaning that every microstate occurs with equal probability.

Yet before the fundamental problem of classical statistical mechanics could finally be explained in this way, it had lost its significance. It turned out that the phenomena of microphysics do not satisfy the equations of classical mechanics but must be described in terms of the probabilistic laws of quantum mechanics, which make possible a much simpler justification for the assertion that all microstates occur with the same frequency. The most important result for our further consideration is therefore not the complete reduction of the laws of thermodynamics to the laws of mechanics, but instead the derivation of strictly valid, apparently causal laws of macroscopic physics from probabilistic statements about elementary events, such as the occurrence of microstates.

The statistical treatment of thermodynamic processes in the framework of classical physics reached its zenith with the work of GIBBS (Figure 4.140) in the first years of the twentieth century. GIBBS envisioned a macroscopic system under investigation as a single object with a large number of degrees of freedom. Thus, a gas consisting of n pointlike particles has $N = 3n$ degrees of freedom.

The state of the entire system can therefore be characterized at any moment in time by specifying N generalized spatial coordinates $q_1, q_2, \ldots, q_N$ and the N generalized momentum coordinates $p_1, p_2, \ldots, p_N$. In the $2N$-dimensional phase space of the system, a single point therefore corresponds to the associated state. The movement of this point is prescribed by the Hamiltonian equations. The result is an extensive domain of validity for GIBBS's method applicable to every system whose laws can be given in Hamiltonian canonical form. This method can, for example, be extended even to electromagnetic fields.

Let us now picture our system as existing in a large number of instances with identical physical structure except for the initial state. Suppose that the corresponding point in $2N$-dimensional phase space is specified for each instance. We thus have before us a GIBBS ensemble that can be characterized by a distribution function $f(q_i, p_i, t)$ of these points. It then turns out that the various distribution functions correspond to various physical situations. The most important role is played by the Gibbs canonical ensemble (1901), whose distribution function has the form

$$f(q_i, p_i) = A\mathrm{e}^{-\frac{H(p_i, q_i)}{kT}}.$$

This function describes the behavior of a system in thermal equilibrium with its environment; $H(p_i, q_i)$ is the well-known Hamiltonian function: the total energy expressed in terms of the conjugate spatial and momentum coordinates.

4.6 The Structure of Matter and Electricity: The Classical Atom

### 4.6.1 *Chemistry Hinting at the Atomic Structure of Matter*

Earlier in this book, we became acquainted in some detail with the beginnings of atomic theory. We went back as far as PARMENIDES and his world model of a static homogeneous sphere that represented the denial of all change, but whose broken-up fragments we tried to link to the atomic ideas of DEMOCRITUS. While for 2000 years, atomism was only able to explain qualitative, or philosophical, questions, we saw the first signs of a quantitative theory advanced by DANIEL BERNOULLI in the middle of the eighteenth century, which was subsequently expanded by WATERSTON and JOULE, and then, above all, by CLAUSIUS, MAXWELL, and BOLTZMANN in the completed form of the kinetic theory that is more or less valid today. To be

Figure 4.140 *continued*

The *Encyclopaedia Britannica* explains somewhat more concretely that GIBBS's principles have been formulated so generally and abstractly that the possibilities for their application were fully recognized only decades after the fact and that even quantum statistics can be built on this sturdy foundation. As an additional example of progress in this area, one might mention the thermodynamics of irreversible processes, or nonequilibrium thermodynamics, which developed only recently.

Thermodynamic potentials are, in general, functions of the state variables: volume (V), pressure (p), temperature (T), entropy (S), and internal energy (U). They make possible or simplify the calculation of characteristic quantities of a given system such as specific heat capacity or heat of reaction. Specifying the conditions for the equilibrium state is also simplified with their help:

1. The "free energy" introduced in 1882 by HELMHOLTZ: $F = U - TS$, $dF = -SdT - pdV$. It yields, under constant temperature ($dT = 0$), the "freely transformable energy of the system." If $dT = 0$ and $dV = 0$, then $dF = 0$; that is, in constant-temperature, constant-volume systems, the free energy approaches an extreme (minimal) value.

2. The Gibbs heat function $H = U + pV$ (HEIKE KAMERLINGH ONNES gave it the name enthalpy): For $dp = 0$, a change in enthalpy yields the heat of reaction of the chemical processes taking place.

3. The free enthalpy or Gibbs function: $G = H - TS = F + pV$ plays the same role for $dT = 0$, $dp = 0$—that is, for constant-temperature, constant-pressure processes—as free energy plays for constant-temperature, constant-volume systems; its value reaches a minimum at equilibrium.
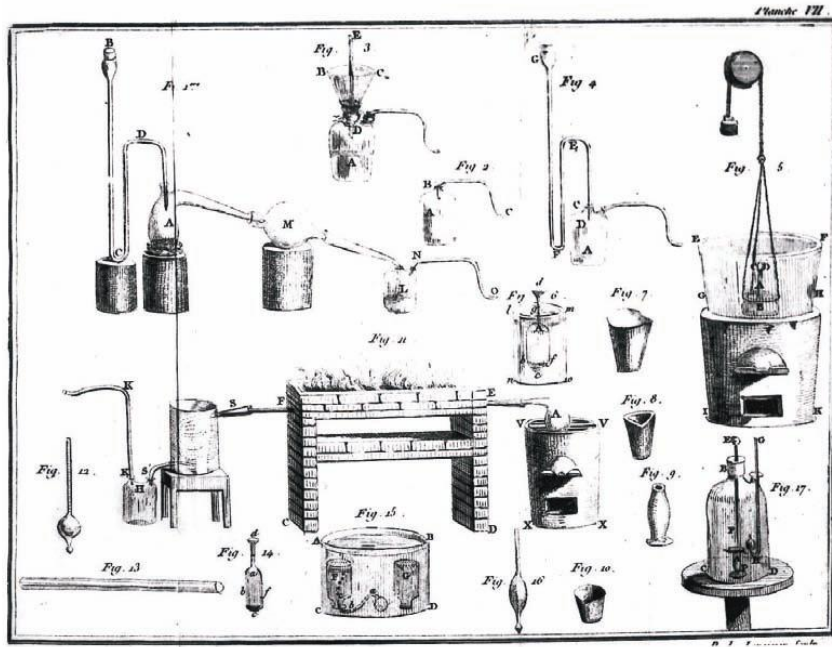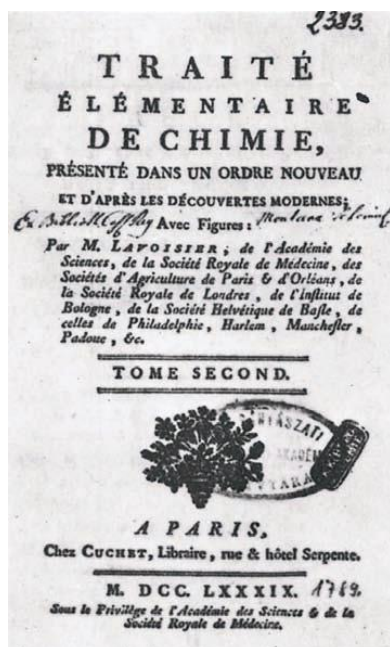
▲ ▶ **Figure 4.141** Title page of LAVOISIER's epoch-making book on chemistry with a double page of figures. (Library of the University for Heavy Industry, Miskolc.)