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JED Z. BUCHWALD

AND

ROBERT FOX

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CHAPTER 16

THERMAL PHYSICS AND THERMODYNAMICS

HASOK CHANG

16.1 INTRODUCTION

Heat is a subject that has commanded people's attention through the ages, for practical as well as scientific reasons. It is still a major subject in introductory physics textbooks and courses, though the science of heat is now presumed reduced to classical or quantum-mechanical principles through statistical reasoning. This chapter covers the development of the physics of heat while it existed as a truly independent subject, which is to say, up to the mid-nineteenth century. Most attention will be paid to the important yet relatively neglected parts of the history, while well-known areas will be covered briefly with references to existing secondary literature.

The study of heat began to flourish in the late eighteenth century, particularly in the chemical communities of Scotland and France. Intense theoretical and experimental activity continued in this field in the first half of the nineteenth century, mostly in the tradition of the material theories based on the basic assumption that heat was (or at least could be conceptualized as) an all-pervasive, weightless and elastic fluid, most commonly called 'caloric'. Great advances were made in caloric-based theoretical treatments of thermal phenomena, which became more quantitative and systematic. Experimental knowledge developed continually both in extent and precision, often quite independently of theory. Also significant among the nineteenth-century developments was the relocation of the study of heat from chemistry to physics, partly prompted by the increasing interest in heat engines. In this chapter we survey some of the significant themes in the development of thermal physics up to the establishment of classical thermodynamics. Much of the early achievement in this field was lost when the assumptions of the existence and conservation of caloric were rejected

in favour of energy conservation, but many elements survived in interesting forms, and the new thermodynamic theory brought a great deal of lasting insights whose significance reached far beyond the study of heat itself.

16.2 THERMOMETRY AND CALORIMETRY

The scientific study of heat started with the invention of the thermometer. That is a well-worn cliché, but it contains enough truth to serve as our starting point. The thermometer did not simply tell the temperature. It revealed many deeper things, including the distinction between temperature and heat, which became clear through cases of heat gain/loss without temperature change, or *vice versa*. These phenomena were major subjects of research well into the nineteenth century: changes of state (melting, boiling, and so on); temperature changes produced by chemical reactions and mixtures; the heating and cooling of gases by expansion and compression; and the heating of solids by percussion and friction. Once the distinction between temperature and heat was recognized, many important theoretical questions arose regarding latent heat and specific heat, which will be discussed in Section 16.3. There was a good deal of mutual reliance between theory and experiment in this field; some rough methods of thermometry and calorimetry were prerequisites before any serious theorizing could begin, just as some rough concepts of heat and temperature were required for making and using thermometers and calorimeters.

Galileo and his contemporaries were already using thermometers around 1600. By the late seventeenth century thermometers were very fashionable but still notoriously unstandardized. An important pioneer in practical thermometry was Daniel Gabriel Fahrenheit (1686–1736), who was responsible for the use of mercury in thermometers, as well as the curious scale which still carries his name. Fahrenheit's small and reliable thermometers were very popular, especially among physicians. Yet his most renowned customer, the Dutch physician and chemist Herman Boerhaave (1668–1738) noticed that Fahrenheit's own mercury and alcohol thermometers did not agree with each other—which turned out to be a general problem, also noted by the best thermometer-maker of eighteenth-century France, the naturalist R. A. F. de Réaumur (1683–1757). There are many surprising facts in the history of thermometry. For example, Anders Celsius (1701–1744) made the centigrade scale familiar to us today, but in his original thermometer the freezing point of water was marked as 100° , and the boiling point 0° . Generally, up to the late eighteenth century there was no standard method of making thermometers, even in a given country, and the disorder was such that the Royal Society of London in 1776 appointed an illustrious committee chaired by Henry Cavendish (1731–1810) to make definite recommendations about the fixed points of thermometry. (For a comprehensive general history of thermometry, see Middleton 1966). Before the thermodynamic absolute temperature concept came into experimental use (see Section 16.8), practical thermometry

reached a state of near-perfection in the hands of Henri Victor Regnault (1810–1878) at the *Collège de France* in Paris, whose work on thermometry was a foundational part of his government-commissioned study to determine all of the empirical data necessary for the study of the steam engine. Regnault reviewed, criticized, and improved all relevant techniques of thermal physics used by his predecessors, and the description of his procedures and results took up three entire volumes of the *Mémoires* of the Paris Academy, published in 1847, 1862, and 1868–70. Regnault had an immense influence on experimental physics in general, in France and beyond.

There were three major problems in the establishment of thermometry, all of which reflected deep epistemological issues (see Chang 2004 for further details). First of all, which natural phenomena can be used as the ‘fixed points’ of thermometers? The philosophical difficulty here was knowing which phenomena happened at fixed temperatures before one had a reliable thermometer. In fact all manner of phenomena were proposed and used as fixed points: greatest winter cold and summer heat (Accademia del Cimento, c.1640); the melting point of butter (Joachim Dalencé); deep caves (Halley 1693) and the Paris Observatory cellars (de la Hire 1708); ‘blood heat’ (Newton 1701) and the healthy body temperature (Fahrenheit 1720); ‘water hottest to be endured by a hand held still’ (John Fowler, c.1727). By the mid-eighteenth century the freezing and boiling points of water became the most popular fixed points, but questions remained about the fixedness of these points, most of all because of supercooling and superheating phenomena. In the end it was impossible to establish fixed points firmly before making thermometers; rather, thermometers were made on the basis of unjustified fixed points, and such imperfect thermometers helped the development of thermal physics which eventually allowed a better knowledge of fixed points.

Secondly, which thermometric substance expands uniformly with real temperature? Many substances were in use, including air, alcohol (known as the ‘spirit of wine’), and mercury (quicksilver). Initially thermometers were made without much thought as to the exact pattern of the thermal expansion of the fluid used in it; the simple division of the interval between fixed points into equal lengths embodied an implicit assumption of uniform thermal expansion. But it was soon apparent that different fluids had different *patterns* of expansion, so that thermometers made with different fluids disagreed in their readings between (and beyond) the fixed points, even if they were graduated to agree with each other at the fixed points. In the eighteenth century the choice of thermometric fluids became a serious question. Again, the difficulty is an epistemological one: without a trusted method of measuring temperature, how can one ascertain the pattern of the thermal expansion (that is, the relationship between volume and temperature)? Jean-André De Luc (1727–1817), Genevan geologist, meteorologist, mountaineer, and theologian, nearly generated a consensus on this matter by employing the method of mixtures, which had been pioneered by Brook Taylor and Joseph Black. Mix equal amounts of freezing water (at 0° Celsius by definition) and boiling water (at 100°, again by definition) in an insulated vessel; if a thermometer inserted in that mixture reads 50°, it indicates real temperature; such mixtures could be made in various proportions, in order to test

AQ1

AQ2

AQ3

AQ4

thermometers at every point on the scale between two fixed points. De Luc (1772) carried out such tests systematically, and concluded that mercury was the best available liquid. However, the method of mixtures took the specific heat of each thermometric fluid to be constant, and this was a groundless assumption (see Section 16.3). Coming into the nineteenth century, theoretical opinion gravitated to the view that the thermal behaviour of gases was simple and uniform (see Section 16.4). Regnault's work gave partial experimental vindication to this view, but his verdict was a very cautious one: air thermometers were the only ones that had not clearly failed his test of 'comparability': namely, the requirement that two thermometers of the same type should agree with each other in every situation, if that thermometer type is to be trusted.

Thirdly, once a thermometric scale is established, how can it be extended beyond its original domain? This became an important practical question in industrial processes involving temperatures beyond the melting point of mercury and glass, and expeditions to cold places where mercury froze (in particular, Siberia and northern Canada). In fact, the freezing point of mercury was a point of great contention in the late eighteenth century, as that is precisely where mercury thermometers broke down. This pattern was exhibited again and again in low-temperature physics: when a previously unknown degree of cold was achieved, the physical regularity underwriting the best available thermometric method broke down; in this respect, what happened to the mercury thermometer at the freezing point of mercury ($-40^{\circ}\text{C}/-40^{\circ}\text{F}$) was like what happened to an electric-resistance thermometer at the point where the metal in use went superconducting. At the high-temperature end, the most intriguing phase from the early history was the work of Josiah Wedgwood (1730–1795), who founded the porcelain company that is still flourishing. Unhappy that he had no means of ascertaining exactly how hot his furnaces were, he created a clay pyrometer exploiting the fact that clay pieces shrank when exposed to high temperatures. But Wedgwood assumed that the contraction of clay was linear with temperature, and this turned out to be infelicitous. However, it would be wrong to think that Wedgwood did not do better because he was an uneducated artisan; he was dealing with a fundamental philosophical problem: namely, the impossibility of making an assured study of the thermal behaviour of a substance in a temperature range where there was no previously established thermometric method. Wedgwood investigated this problem in a methodical and sagacious way; his high-temperature thermometer was rejected only because it disagreed with various other thermometers, which agreed roughly among themselves.

Unlike thermometry, calorimetry has not yet received a great deal of attention from historians and philosophers of science. However, there are deep philosophical problems here too. There were no direct methods of determining the amount of heat transferred from one body to another, not to mention the total amount of heat contained in a given body. The only way of estimating the amount of heat absorbed or emitted was to observe the intensity of its effect. Two effects usable for this purpose were state-changes and temperature-changes. But inferring the amount of heat from the state change it produces (for example, how much ice is melted) required

a prior knowledge of the relevant latent-heat value, and inferring it from temperature change (how much the temperature of a body of water is raised, for example) required prior knowledge of the relevant specific-heat value. Either way, the measurement of heat relied on the measurement of heat, so calorimetry suffered from a fundamental epistemological circularity.

Calorimetry based on the change of state was developed by Antoine-Laurent Lavoisier (1743–1794) and Pierre-Simon Laplace (1749–1827) in the form of their ‘ice calorimeter’, and it was employed very effectively in the investigations forming the basis of their famous *Mémoire sur la chaleur* (1783). In this instrument a metallic chamber containing a hot body was surrounded by crushed ice; the body was allowed to cool to the melting point of ice, and the amount of ice melted in that process was measured by collecting and weighing the resultant water. With this instrument Lavoisier and Laplace studied various phenomena ranging from the specific heat of solid bodies to the amount of heat produced by animals. The chief theoretical assumptions in this technique were firstly that heat was conserved, and that the latent heat required in melting a unit weight of ice at its melting point was always the same. Although these assumptions would have been difficult to verify actually, there seemed no particular reason to doubt them and no one challenged them. Unfortunately the Laplace–Lavoisier ice calorimeter suffered from practical defects, especially that not all of the water produced by the melting of the ice could be gathered to be weighed, since it tended to become trapped in the small spaces between the pieces of ice.

Since the Laplace–Lavoisier ice calorimetry was the only plausible attempt during this period to use changes of state for heat measurement, its practical failure meant that scientists had to rely on temperature changes in order to measure heat. If a certain amount of heat was given to a reference body of specific heat c resulting in the raising of its temperature by an amount t , it could be deduced that the amount of heat received by the body was ct . This technique, of course, makes calorimetry entirely dependent on thermometry. In addition, the procedure involved two major assumptions: perhaps it was not so problematic to assume the conservation of heat, but more contentious was the assumption that the specific heat of the reference body was constant throughout the range of temperatures involved in the experiment. This assumption was easily and commonly challenged, as we will see below, but in order for calorimetry to get off the ground at all, it had to be upheld at least as an acceptable approximation.

16.3 SPECIFIC AND LATENT HEATS

The notion of latent heat was at the centre of attempts to understand the phenomena in which heat and temperature were seemingly decoupled. When heat became ‘latent’—that is, absorbed into a body without raising the temperature—what exactly

happened to it? Why did it cease to register in thermometers (or be perceivable by our bodies)? The Scottish physician and chemist Joseph Black (1728–1799) was the most famous discoverer of latent heat, although the independent contribution of Johan Carl Wilcke (1732–1796) in Sweden has also been widely recognized. (Generally on the discovery of latent and specific heats, see McKie and Heathcote, 1935, and Roller, 1957, section 2.) Black's notion was that the heat apparently spent in melting ice, for instance, was not destroyed but merely converted into a different state, postulated to lack the power of affecting the thermometer. Although Black himself remained agnostic about the metaphysical nature of heat, his concept of latent heat fitted well into the notion popular among chemists that heat was to be treated as a substance that entered into chemical combinations with ordinary matter. This view was advanced, for instance, by Lavoisier, who went as far as including 'caloric' in the table of chemical elements in his authoritative textbook of the new chemistry, *Traité élémentaire de chimie* (1789). On this chemical view of heat, the latent caloric that entered into combination with particles of matter was the cause of increased fluidity when solids melted into liquids and liquids evaporated into gases; this latent caloric would become sensible again in condensation or congelation. The absorption and emission of heat in ordinary chemical reactions were also explained in the same manner. The notion of the chemical combination of caloric with matter was even incorporated into the terminology, of 'combined' versus 'free' caloric, used alongside the more phenomenological terminology of 'latent' and 'sensible' caloric.

In opposition to the chemical view of heat was that of William Irvine (1743–1787), a pupil and collaborator of Black's in Glasgow, who refused to postulate two different states of caloric. (See Fox, 1971 for a thorough discussion of the origin and development of Irvinist caloric theory.) According to Irvine (1805)¹ there was only one kind of caloric, and the amount of caloric contained in a body was the product of its capacity for caloric and its 'absolute temperature', which would be zero degrees at the total absence of caloric. This idea will be referred to as 'Irvine's hypothesis of heat capacity'. In Irvine's view, latent heat phenomena were consequences of changes in bodies' capacities for caloric, not due to any changes in the state of caloric itself. For instance, the change of state from ice to water involved an increase in heat capacity, which meant that more heat was needed just to keep the body at the same temperature. This was explained by an analogy of a bucket which suddenly widens; the level of water contained in it would go down, and more water would have to be put in just to keep the water level where it was before. The heat of chemical reactions was explained similarly, by pointing to presumed differences between the heat capacities of the reactants and the products. Irvine's hypothesis of heat capacity constituted a great advance on previous theories of heat, since it specified a precise relationship between heat capacity, temperature, and total heat, with theoretical elegance and great explanatory power.

Irvine backed up his theory by measurements which showed, for instance, that water indeed had a higher capacity for caloric than ice. But how did he measure the heat capacities? This was done by identifying the phenomenologically measured

specific heat with the more theoretical notion of *heat capacity*. The standard method of measuring specific heat was the technique of mixtures: typically, a body at a relatively high temperature, say a , would be immersed into a reference body at a lower temperature, b ; the specific heat, c , of the first body would be calculated from the resultant temperature of the mixture, m , as follows:

$$(a - m)c = (m - b)c_o$$

where c_o is the specific heat of the reference body, commonly taken as 1 for the unit amount of water.

Irvine's ideas were highly controversial and never commanded a consensus, but they were adopted and elaborated by a number of influential scientists, especially in Britain. Perhaps the most effective advocate of Irvine's ideas was the Irish physician and chemist Adair Crawford (1748–1795), who was active in London in later life but had attended Irvine's lectures while he was a student in Glasgow. Crawford applied Irvine's ideas in order to arrive at a new solution to the longstanding puzzle on how warm-blooded animals generated heat in their bodies (see Mendelsohn, 1964). Crawford's influential treatise on animal heat (1779, 1788) served as an important conduit of Irvine's ideas to other scholars, including John Dalton (1766–1844), the originator of the chemical atomic theory. Other important Irvinists included Sir John Leslie (1766–1832), Professor of Mathematics and then of Natural Philosophy in Edinburgh, and the Scottish chemist John Murray (*d.*1820), whose textbooks were quite influential in the early decades of the nineteenth century. As it turned out, most of the predictions made on the basis of Irvine's hypothesis were not confirmed, and Irvinism was also theoretically opposed by followers of Lavoisier's chemical caloric theory. Hence Irvine's ideas did not retain much support beyond the first decade of the nineteenth century, but his legacy did have an enormous relevance in the debates that continued. The rejection of Irvinism left a vacuum which needed to be filled in order to restore definiteness to the theoretical treatment of many crucial issues: the relation between latent and specific heat, the total heat content of bodies, the heat content of the vacuum, the adiabatic heating and cooling of gases, the definition of temperature, and so on.

Despite the theoretical controversy surrounding Irvine's hypothesis of heat capacity, the more phenomenological notions of latent heat and specific heat were shared by nearly all investigators. Much effort went into their experimental determination, partly so that the data could be used in testing the rival theories. But long periods had to pass before measurement practices were developed sufficiently to provide precise enough data for most theoretical purposes. The difficulties were not only matters of technical control, but also of theoretical interpretation. Aside from the basic challenges in thermometry and calorimetry discussed in Section 16.2, there were difficulties peculiar to the measurement of the specific heat of gases, so small compared to those of the reference bodies and of the containers used to hold the gases. The first recorded attempt was made by Crawford in the 1780s; as his Irvinist explanation located the origin of animal heat in respiration, it became important to measure the heat capacities of inhaled and exhaled gases. Crawford filled a bladder with various

gases at high temperatures and plunged it into a vat of cold water. His results lacked precision, as the changes in the water temperature were very small and inaccurately measured, and improvements made by others during the next two decades did not go very far.

Moving the state of specific-heat measurements beyond these initial attempts was one of the important goals of the 1812 prize competition sponsored by the First Class (Mathematical and Physical Sciences) of the French Institute, which had replaced the old Paris Academy of Sciences in 1795. The competition was won by François Delaroche (1775–1813) and Jacques Étienne Bérard (1789–1869). They used a constant-flow method, which involved passing a heated gas under a constant pressure through a spiral copper tube immersed in a calorimeter filled with water (Delaroche and Bérard, 1813). From the amount of heat imparted to the water in unit time, and the rate of flow of the gas, Delaroche and Bérard were able to calculate the specific heats (by volume) of various gases under constant pressure. This ingenious method, along with the care they took in eliminating the sources of heat loss, won Delaroche and Bérard wide acclaim, and their results on the specific heat of various gases were considered the best available for several decades. Their work established beyond doubt that the specific heats of various gases were different from each other, the volumetric specific heats ranging from 0.903 for hydrogen to 1.258 for carbon dioxide (taking that of atmospheric air as 1). The work by the other pair of contenders in the competition, Nicolas Clément (1778/9–1841) and Charles-Bernard Desormes (1777–1862), both industrial chemists, was based on less accepted notions and did not receive as much attention. The outcome of the 1812 prize competition had complex and significant theoretical implications, as will be discussed in Section 16.4. Although the basic conceptual difficulties regarding specific and latent heat remained unresolved, improvements continued in laboratory techniques. Some important advances, including the use of the law of cooling, were made by Pierre-Louis Dulong (1785–1838) and Alexis-Thérèse Petit (1791–1820), whose work (1816; 1817) on cooling, thermometry, and specific heats in the late 1810s came to be regarded by many as models of precision experimentation. The experimental work on specific and latent heats, like much else, was nearly perfected by Regnault, who had initially been drawn into thermal physics from organic chemistry through his fascination with the Dulong–Petit law of ‘atomic heat’, which he showed to be only approximately true.

Two significant points of debate illustrate the interesting questions raised by the concepts of specific and latent heat in their interrelationship. One crucial question affecting thermal measurements was whether the specific heat of a given substance depended on its temperature. This is an issue that illustrates very nicely the various ways in which calorists² disagreed sharply with each other on important points of detail. Dalton was one of those who suspected that a change in volume would be cause for a change in specific heat. Dalton thought that there would be a positive correlation between heat capacity and temperature, since the thermal expansion of a body would create more room for caloric to fit in. This seems to have been a common assumption. De Luc (1786–87) had analysed the capacity of bodies for ‘fire’ into ‘geometric’ and ‘physical’ components; the former was an indication of the amount

of ‘pores’ in a body into which fire could fit, and the latter was an indication of the nature of those pores which determined how much fire could fit into a given amount of geometric space. For a given substance in a given state the physical capacity would be constant, but the geometric capacity would increase with the expansion of volume. This sort of consideration raised a serious problem for the method of mixtures for the measurement of specific heat, which was founded on the assumption that the specific heats involved were not temperature-dependent.

A different kind of consideration regarding the temperature dependence of specific heat existed for those who subscribed to the chemical view of heat, and this is a point that came to play a crucial role in later investigations. Since the chemical theorists postulated that caloric could exist in a latent state that did not register in thermometers, they always had to worry about whether the caloric added to a body all remained sensible. Lavoisier and Laplace had given a clear and widely followed opinion on this issue as early as their 1783 memoir: when a body expanded upon heating one part of the absorbed caloric remained free, and was responsible for the raising of temperature; the rest of it, going latent, was responsible for expansion. Then the next question was what proportion of the absorbed heat went latent, and whether that proportion was a function of temperature. If it was, that would be a reason for specific heat to vary with temperature. The increasingly popular opinion on this issue in the first decade of the nineteenth century was that specific heat would *decrease* with increasing temperature. This view was advanced clearly by the abbot–mineralogist René-Just Haüy (1743–1822), in the second edition (1806) of his physics textbook commissioned by Napoleon for the newly established *lycées*. Haüy argued as follows: at lower temperatures the molecules of matter would be closer together and hence exert stronger attractive forces of affinity on each other; therefore a larger portion of the absorbed caloric would have to be spent on expansion, leaving less caloric available for raising the temperature. In other words, at higher temperatures a lower proportion of absorbed heat became latent so that a higher proportion remained available for heating; hence less total heat would be needed for raising the temperature by a unit amount. This conclusion was precisely the opposite of Dalton’s, and there was no clear way of deciding this issue at the time. One of the fundamental problems, again, was that of circularity: in order to reach an experimental conclusion about the temperature dependence of specific heat, a precise thermometer was required; however, testing the correctness of thermometers required the knowledge of the temperature dependence of specific heat.

The other major point of contention involving latent and specific heats in the early nineteenth century was the determination of the absolute zero point of temperature. Although all calorists would have shared a notion of the absolute zero of temperature where a body would become devoid of all caloric, only Irvinism made it possible to attempt the determination of this quantity. Since the product of absolute temperature and heat capacity gave total heat, the measurement of heat capacity and total heat allowed one to deduce the absolute temperature. Even the Irvinists could not measure the total heat of given bodies, but for the present purpose it was sufficient to measure the *change* of total heat in two successive states of a given body. For instance, with the

melting of ice, one could set up an equation for total heat before and after, assuming the conservation of heat:

$$c_i x + L = c_w x$$

where c_i is the heat capacity of ice, c_w is the heat capacity of water, L is the latent heat of fusion, and x is the absolute temperature of ice/water at the melting point. (Since x is 0° in the centigrade scale, the absolute zero of temperature would be x degrees below zero in the centigrade scale.) Similar equations could be set up for any change of state, or for any chemical reaction in which there was an absorption or emission of heat. In each case the absolute temperature could be deduced from measured values of the latent heat (absorbed or emitted) and the heat capacities involved. Measurements were carried out for this purpose by Irvine and Crawford, and other Irvinists, including Dalton and Murray, often cited these measurements and also made their own.

For the chemical calorists, the very basis of these calculations was suspect, since their own notion of specific heat did not support the Irvinist equation for total heat. If total heat were to be given as the simple product of specific heat and absolute temperature, the specific heat would have to be constant throughout the temperature range. This was deemed to be unlikely, or at least unverified, as we have seen above. For the Irvinists, however, the expression for total heat was valid at each given temperature even if the heat capacity varied with temperature, and they could regard the ability to determine absolute temperatures as one of the advantages of their theory. As the theoretical arguments were inconclusive, the debate hinged on an empirical question: were the values of absolute zero obtained from various reactions consistent with each other? Most Irvinists believed that they had obtained consistent results, which served to enhance their belief in the Irvinist caloric theory. Their opponents, starting with Lavoisier and Laplace (1783), thought otherwise. The Irvinists generally responded by blaming the apparent discrepancies on the unreliability of heat capacity measurements. Since the calculated value of the absolute zero was highly sensitive to the heat capacity values ($x = L/(c_w - c_i)$, from the above equation), no clear experimental verdict on this question could be reached until the accuracy in the measurements of specific heat became very high. As it turned out, the better results such as those obtained by Delaroche and Bérard (1813) tended to refute Irvine, which contributed to the eventual demise of Irvinism. The chemical calorists, however, never did find a way of determining the absolute zero, and the topic gradually disappeared from the list of important problems.

16.4 SPECIFIC AND LATENT HEATS

With the firm establishment of the caloric theories of heat in the last decades of the eighteenth century, scientists' ambition grew to develop a general theory of heat by

pinning down the properties of caloric. As Robert Fox (1971) has discussed in great detail, much of this latter phase of caloric physics focused on gases. A clear majority of the calorists in the nineteenth century shared the belief that the nature of caloric was exhibited most clearly in the thermal behaviour of gases, rather than liquids or solids. This view had been anticipated by the German polymath Johann Heinrich Lambert (1728–1777), and earlier by the French physicist Guillaume Amontons (1663–1705). However, the preoccupation with gases came to be widely shared only in the context of caloric theories. One recognized difficulty in that context was the impossibility of isolating caloric in a pure form—a fact usually attributed to its extremely strong affinity for ponderable matter. However, gases (including vapours) were considered to be quite close to a pure form of caloric. Particularly for those who adopted the ‘Newtonian’ picture in which the macroscopic behaviour of matter were to be explained by the attractions and repulsions between microscopic particles, there was assurance that the behaviour of gases would be due mostly to the actions of caloric, since in gases the particles of ordinary matter were separated so far from each other that the forces of affinity between them must be negligible. This assumption of the special status of gases, combined with the belief in the simplicity of nature, set the dominant tone in much of the investigations into thermal phenomena in the first half of the nineteenth century.

The major experimental impetus in this direction came early in the century, in the nearly simultaneous and independent works of Dalton and Joseph-Louis Gay-Lussac (1778–1850) in 1802, showing that all gases expanded by the same proportion when they were heated from one fixed temperature to another. Although this seems like a commonplace observation in retrospect, the experiments actually required considerable improvement in technique, including the drying of gases. Together with the much older Mariotte’s (or Boyle’s) law, Gay-Lussac’s and Dalton’s discovery was largely responsible for the impression that gases in general followed simple laws. It also led many people to assume that the thermal expansion of any type of gas must be equable or uniform, with the consequence that gas thermometers were to be regarded as the true thermometers of nature (see Section 16.1). As both Dalton and Gay-Lussac themselves stated clearly, this additional assumption of uniform expansion was logically groundless, and also empirically unverifiable in the absence of an independently validated thermometric standard, but it was endorsed widely.

The assumption of simplicity was not the only major reason for the early nineteenth-century preoccupation with gases. Part of the attention originated from the greater experimental and theoretical challenges that gases presented in comparison to liquids and solids, due to their great elasticity and compressibility. A whole new arena of investigation was opened up by the recognition that the pattern of thermal expansion could be influenced by varying the external pressure on gases, and the fact that externally enforced compression and decompression of gases resulted in temperature changes. This meant that pressure entered as a crucial variable in the thermal physics of gases, in addition to the others that applied to all bodies (volume, density, temperature and total heat). The considerations arising in this way ended up

yielding tremendous insights applying not only to the behaviour of gases but also to general theories of heat.

One subject of intense dispute was adiabatic heating and cooling: namely, changes of temperature in a body that has no communication of heat with the outside. Assuming the conservation of heat, latent heat provided the only obvious way of explaining these phenomena; consequently, adiabatic phenomena provided an important arena in which competing theories of latent heat could be compared and tested. The modern notion that adiabatic phenomena are clear examples of the inter-conversion of heat and mechanical work does not apply to this period, and caloric theories had no obvious difficulty in explaining these phenomena. The first observations of adiabatic temperature changes occurred in the course of experimenting with the air-pump, in fact, going back to Robert Boyle (1627–1691). The heating of a gas by mechanical compression and cooling by expansion were commonplace observations, as was the heating that occurred when air rushed into a vacuum. Eighteenth-century commentators on these phenomena included many illustrious names: Lambert; the physicist Marc-Auguste Pictet (1752–1825) and the naturalist and meteorologist Horace Bénédict de Saussure (1740–1799), both in Geneva; William Cullen (1710–1790), the teacher and predecessor of Black; and Erasmus Darwin (1731–1802), the grandfather of Charles Darwin. A good deal of motivation for the early discussions came from meteorology, but in France it was the Laplacian work on the speed of sound that created the bulk of interest. Laplace thought that the well-known discrepancy between the observed value of the speed of sound in air and the theoretical value predicted by Isaac Newton (1642–1727) in the *Principia* could be removed by considering adiabatic temperature changes that must take place as the propagation of sound waves compressed and decompressed little pockets of air. Laplace's protégés Jean-Baptiste Biot (1774–1862) and Siméon-Denis Poisson (1781–1840) ably filled out the details (Biot 1802; Poisson 1808). They could not actually calculate the correction factor, but Poisson made the best of that situation by deducing that *if* this correction factor were to resolve the discrepancy between the theoretical and the observational values of the speed of sound, the amount of temperature change in adiabatic compression or expansion would have to be 1° for a change of volume by $1/116$ of the original volume, which served as the standard figure for quite some time.

By the first decade of the nineteenth century, adiabatic phenomena were widely recognized in all major centres of research on heat. However, there was hardly an agreement on their explanation. The Irvinists initially seemed to have an advantage. On the basis of their common assumption that the heat capacity of a body of gas decreased when its volume decreased, it was easy to explain why compression would lead to higher temperatures on the basis of Irvine's hypothesis of heat capacity. Dalton, for example, advanced such an explanation in a paper of 1802. The case of heating by air rushing into a vacuum was more challenging, but Dalton dealt with it by means of another common assumption, that the heat capacity of a given volume of evacuated space was larger than the heat capacity of the same volume of air. The heat capacity of vacuum may seem like a strange idea, and indeed

it makes no sense if we are considering specific heat by weight. However, there is no such problem if the heat capacity is considered by volume, and the notion made eminent sense if one assumed that the vacuum could and did contain some caloric. The latter was a relatively common assumption at the time, at least since Lambert. The filling of the evacuated chamber by air can then be conceptualized as a decrease in the heat capacity of that space, which would raise the temperature unless heat could escape (in fact, if anything, the total quantity of caloric in that space increased, since some additional caloric was brought in by the incoming air). Similar explanations of adiabatic phenomena were given by other Irvinists, including Murray. Leslie gave a somewhat different treatment, on the basis of his belief that perfect vacua were never attained; therefore Leslie conceptualized the phenomenon as that of the compression of the very thin air that was already in the 'evacuated' chamber, and in effect reduced this problem to the more familiar case of heating by compression.

The Irvinist explanations did not go unchallenged. Gay-Lussac led the critique in his 1807 paper with an experimental argument against the assumption that the vacuum contained any caloric. He put a thermometer in a Torricellian vacuum, varied the volume of that empty space, and observed no temperature changes. This attack was followed by Delaroche and Bérard's (1813) more general assault on Irvinism, in the prize-winning memoir on specific heats mentioned in Section 16.3. Delaroche and Bérard determined the specific heat of steam as 0.8470 (taking that of water as 1), by weight; on the other hand, it is a straightforward consequence of the Irvinist explanation of the latent heat of evaporation that the heat capacity of steam should be greater than that of water. Similarly, their values for specific heats of gases refuted Irvinist predictions concerning the heat released or absorbed in chemical reactions. For instance, the formation of water was accompanied by the release of a good deal of heat, so Irvinist principles implied that its heat capacity should be smaller than the weighted average of the specific heats of the reactants, hydrogen and oxygen; Delaroche and Bérard's data indicated just the opposite. In France at least, these results were widely regarded as a decisive refutation of Irvinism.

How did the chemical caloric theory explain adiabatic phenomena? An intuitive picture that had a broad appeal was that gas molecules were like sponges soaked in caloric; as external pressure was applied and the volume of the gas was diminished, some of the caloric would be 'squeezed out'. The Irvinists could understand this by theorizing that the compression reduced the heat capacity of (the molecules of) the gas. The chemical calorists, on the other hand, needed to assume that the caloric squeezed out of molecules by compression existed in a latent state before the squeezing. This, fortunately, squared nicely with the view that thermal expansion was due to latent or combined caloric, discussed in Section 16.3. If the expansion were to be forcibly undone, the caloric that had gone latent in effecting the expansion would have to be returned to the sensible state. The vacuum experiments, however, continued to present theoretical difficulties. Gay-Lussac's experimental argument that the vacuum contained no heat had undermined the basis of the Irvinist explanation but did nothing to pave the way to an alternative explanation.

Clément and Desormes (1819), the unsuccessful contestants for the 1812 prize competition, chose to adhere to the notion that the vacuum contained caloric. Clément and Desormes made considerable progress in the Irvinist analysis of adiabatic phenomena, by treating the vacuum as an entity with a fixed heat capacity, which can mix with gases. Then the compression of a gas can be understood as the destruction of a measure of vacuum, and the absorption, by the air, of the heat previously contained in the destroyed vacuum. In the case of the evacuated-receiver experiment, all of the vacuum is destroyed leaving its heat to the air that enters from the outside. This way of thinking, combined with the standard Irvinist principle of heat capacity, allowed Clément and Desormes to make experimental determinations of many important quantities—by mixing various amounts of air and vacuum of various initial temperatures, recording the resulting temperatures, and measuring the heat capacity of air at various temperatures. Clément and Desormes's results were most interesting. Several determinations made on their principle all indicated values close to 0.4 for the ratio of heat capacities (by volume) of vacuum and air. The agreement between different determinations gave them confidence about the correctness of this result. They also estimated that the total quantity of caloric contained in a vacuum near room temperature (12.5°C) would raise the temperature of an equal volume of air under atmospheric pressure by 114° ; this implied that compressing air adiabatically by $1/114$ of its original volume (which would destroy $1/114$ of the original vacuum) would raise its temperature by 1 degree. Clément and Desormes noted that this value was very close to that calculated by Poisson in 1807, which was $1/116$. In addition, they produced a value for the absolute zero, -267.5°C , which was quite different from most of the earlier values given by Irvinists but uncannily close to -266.66°C , which was the value they obtained following Amontons's idea of extrapolating the thermal expansion curve until the point where the volume of the gas would vanish. As Fox (1971, p. 147) argues, all in all the confidence that Clément and Desormes seem to have felt about the quality of their own work is quite understandable, even if we feel compelled to attribute the pleasing results they obtained to fortunate coincidences or possibly a biased selection of data. However, the Institute's prize committee did not favour their work, and the eventual publication of their memoir in 1819 had little success in reviving the interest in the heat capacity of vacuum and in Irvinist ideas in general.

As the theoretical attention on gases intensified and the measurements of their specific heats improved, the difference between two kinds of specific heats came to be recognized more and more clearly. The distinction made was between (1) specific heat under constant pressure (commonly denoted c_p), that is, the amount of heat required in heating a gas by 1 degree while letting it expand under constant pressure; and (2) specific heat under constant volume (c_v), the amount of heat required in heating a gas by 1 degree while confining it to a fixed volume. The difference between these two specific heats was noted already in Crawford's measurements; however, Crawford did not do much with the distinction, since the numerical difference he detected was very small. Dalton also made a statement that c_p was greater than c_v , but did not elaborate on the distinction extensively. It was probably Häüy (1806) who made the

first clear theoretical argument that there had to be a difference between the two specific heats, as a logical consequence of Lavoisier and Laplace's assumption that when a body is heated different portions of caloric were used in expanding it and in raising its temperature. Then it follows that even an expansion at the same temperature requires an input of heat. If one conceptualizes heating under constant pressure as a two-step process consisting of heating under constant volume and then expansion under constant temperature, it follows that c_p has to be larger than c_v , since $c_p = c_v + c_t$, where c_t is the amount of heat required for the expansion at constant temperature; this was, after all, the 'latent heat of expansion'. This kind of reasoning would become standard in later French caloric theory, as discussed below.

The actual measurement of the difference between the two specific heats presented many difficulties, particularly on the side of measuring c_v (Delaroche and Bérard's constant-flow method, for instance, only gave a measure of c_p). The first credible estimate came in the form of the ratio c_p/c_v (commonly denoted γ), not by direct measurement but through the theoretical discussion concerning the speed of sound. Following on the works of Biot and Poisson discussed previously, Laplace himself came into the scene with a paper published in 1816, in which he asserted that the correction factor on Newton's speed of sound was the square root of γ , and that the value of γ was 1.5 (see the reconstruction of Laplace's argument in Fox, 1971, pp. 161–165); the value required to bring theory and experiment into exact agreement was 1.43, not far from Laplace's theoretical estimate. When Gay-Lussac and Jean-Joseph Welter (1763–1852) finally made a reasonable experimental determination of this quantity and obtained the value of 1.3748, this was close enough to Laplace's value that a good deal of confidence was inspired about the reliability of this whole set of results.

With the gradual demise of Irvinism, the theoretical lead in the understanding of gases was taken in the Lavoisier–Laplace tradition. Soon after the execution of Lavoisier in 1794 during the Revolutionary Terror, Laplace became the clear leader in French thermal physics as well as much else in French science. In association with the chemist Claude-Louis Berthollet (1748–1822), also a former collaborator of Lavoisier's, Laplace dominated the physical sciences in France for quite some time. Both of these leaders subscribed to a broadly Newtonian point of view, in which all phenomena would be explained by the action of central forces operating between point-like particles. The overarching ambition of 'Laplacian physics' (as Fox has termed it) was 'to raise the physics of terrestrial bodies to the state of perfection to which celestial physics has been brought by the discovery of universal gravitation' (quoted in Fox, 1974, p. 95). In the first decade of the nineteenth century Laplace began to make concrete attempts in this direction by creating theories of optical refraction and capillary action based on short-range forces (negligible at macroscopic distances). He could not make much headway in specifying the form of the force laws involved, but he managed to show that the exact form of the laws did not matter.

In the physics of heat, Laplace's strategy was similar. According to Lavoisier, caloric repelled itself (while caloric and ordinary matter had a mutual attraction), but in Newton's tradition such action could be analysed only in terms of action-at-a-distance forces operating between particles. This meant that caloric itself had to

consist of particles (so it was a 'discrete fluid'), and that there had to be a universal repulsive force between caloric particles that was a function of distance between them. Again, there were no clues about what the shape of this force function was, so in Laplace's analyses it was simply written as an unknown function, except that it was assumed to be vanishingly small at macroscopic distances. This force function could not do much work other than giving rise to a host of other symbols which represented its various integrals, to be rendered into a constant (though of unknown value) at a convenient place by the introduction of a definite integral.

Therefore Laplace was forced to take his analyses of heat onto the level of forces between molecules, rather than forces between caloric particles themselves. Laplace's mature view on caloric theory was developed in various papers published in the early 1820s, and summarized in the fifth and last volume of his *Traité de mécanique céleste* (1825), published just two years before his death. The basis of this picture was a molecular construction of matter, and a dynamic equilibrium of caloric radiation between the molecules. The idea of radiative equilibrium was probably adapted from Prévost's work, discussed in Section 16.6, but Laplace was not satisfied until he had provided a microscopic explanation as to why any caloric bound in a molecule would be radiated away from it. In the end, he attributed that to the repulsive force exerted by the caloric contained in neighbouring molecules. But it was difficult to conceive of latent caloric (or combined caloric) to be so easily disengaged from the molecules, so Laplace took the rather extraordinary step of putting *free* caloric into molecules. Latent caloric was postulated to have lost its repulsive force and did not enter this picture of radiative equilibrium at all; free caloric existed within molecules but retained its repulsive force; the radiated caloric existing in the intermolecular spaces was designated as the 'free caloric of space', to be distinguished from free caloric within molecules. By that point he had abandoned the standard Lavoisierian view of latent caloric.

With the ontology thus settled, Laplace proceeded with derivations. A crucial and very useful assumption which Laplace made was that the repulsive force between two adjacent molecules would be proportional to the product of the amounts of caloric contained in them. Thus the basic force equation obtained a semblance to Newtonian gravitation, though it still contained an unknown function of distance. A further constraint was given by the assumption that all molecules in a body of gas in internal equilibrium contained the same amount, c , of free caloric, and that the repulsive force between two molecules would be proportional to c^2 . From such assumptions Laplace managed to derive the familiar gas laws, and also results supporting his long-standing argument that the air thermometer gave the true measure of temperature. However, these achievements seem to have been neglected largely. As Fox (1974) documents, Laplace's influence was waning during the time when he was working out the details of his mature caloric theory. With that context in mind, it is not surprising that his deductions, based on broad speculative assumptions rather than any details about the force function between caloric particles, failed to inspire confidence. Even the faithful Laplacians declined to pursue this line of investigation much further.

16.5 THE MOVEMENT OF HEAT

The main focus of attention in the caloric theories was on the interaction of heat with ordinary matter. In parallel, another tradition of thermal physics grew which paid more attention to the motion of heat and its transfer between bodies. The first half of the nineteenth century witnessed great advances in this area. As a preliminary step, the three different modes of heat transmission recognized to this day—conduction, convection, and radiation—were identified by 1800. Benjamin Thompson (1753–1814), better known as Count Rumford to contemporaries and posterity alike, did much to clarify the distinction between conduction and convection, conceptualizing the former as the transfer of heat between the molecules of a body, and the latter as the transfer of heat effected by the transport of the molecules themselves within a fluid. Although the term ‘convection’ was coined only in 1834 by William Prout (1785–1850) in his *Bridgewater Treatise*, the conceptual distinction between conduction and convection was universally recognized early on as valid, illuminating, and uncontroversial. From this understanding also followed some practical consequences: for instance, the unexceptionable explanation that materials such as eider-down were good insulators of heat, since they obstructed the movement of air molecules trapped in them, retarding the convective propagation of heat.

A topic that caused more excitement and controversy was radiation—the transmission of heat across macroscopic distances that was apparently instantaneous and not reliant on a material medium. The radiation of heat was a phenomenon that had been observed for a long time, in ordinary facts such as the intense and direct heat felt from a fire or hot metallic objects. The more scientific interest in radiant heat seems to have been generated usually by the recognition that it could be reflected by shiny surfaces, even when it was not accompanied by visible light. There is evidence of that observation from as early as the seventeenth century in the works of the Accademia del Cimento in Florence, and later by Saussure and Lambert, but it was probably Pictet (1790) who did more than anyone to draw the attention of physicists to radiant heat. First of all, Pictet’s results were dramatic; in one experiment he demonstrated the radiation of heat between two concave metallic mirrors separated by more than 12 feet. His experiments were also relatively precise and systematic, and linked up with a highly developed theory of heat. Besides, Pictet was a key leader of a thriving and strongly interacting community of natural philosophers in Geneva who also communicated actively with scholars in other major centres of research. Pictet’s lead was followed by a great deal of useful experimental work by Rumford and Leslie on the rates of heat radiation from various types of surfaces.

For explaining the movements of heat more generally, the early decades of the nineteenth century witnessed the development of a tradition of mathematical and phenomenological analyses eschewing physical and metaphysical accounts of the nature of caloric, spearheaded by Joseph Fourier (1768–1830). When Fourier started his work on heat theory around 1805 he was based in Grenoble, serving as the prefect of the department of Isère after accompanying Napoleon on his Egyptian expedition.

In 1807 he presented to the French Institute a memoir containing some important results, including a version of the famous diffusion equation. Not receiving much response to this work, Fourier managed to prompt Laplace to propose an Institute prize-competition on the subject of heat conduction in 1811, which he won handily with a revised version of his 1807 memoir. Publication was delayed (Fourier [1822], 1955), but Fourier's work stimulated a good deal of interest soon enough, and in the end became very influential both in thermal physics and mathematics.

The power of Fourier's work lay not only in a thorough and innovative mathematization of the subject, but even more so in a conscious and explicit narrowing of focus. The narrowing was so extreme that Fourier's analyses dealt with hardly any of the traditional concerns of theories of heat. It is not simply that he refrained from making commitments about the metaphysical nature of heat, which Black, Lavoisier, and numerous other calorists had also done to various degrees. The starting point of his analysis was simply that there be some initial distribution of heat, and some specified temperatures on the boundaries of the body being considered; by what mechanisms these initial and boundary conditions might be produced and maintained were not his concerns. Fourier's notion was that the theory of heat proper should deal only with what is *not* reducible to the laws of mechanics. So the domain of Fourier's theory of heat excluded whatever was treatable by considerations of the forces exerted between particles of matter and caloric; all such mechanical issues Fourier was happy to leave to Laplace and his school for their corpuscularian analysis. Significantly, this meant that the expansive effects of heat, among other things, fell outside Fourier's domain. The only class of thermal phenomena left, then, was the *movement* of heat. It is not clear whether Fourier thought that the flow of heat was not reducible to mechanical actions between caloric particles. What is clear from his published work is that he did not consider such a reduction of heat flow to mechanics to be plausible, at least at that stage.

In sum, Fourier succeeded by defining a very specific class of problems, which he proceeded to solve mathematically. The starting point of a typical problem treated by Fourier was a disturbance in the equilibrium of heat, which causes a flow of heat from places of higher temperatures to places of lower temperatures. In all cases, Fourier noted a dissipation of heat, and the solution of each problem consisted of the temperature distribution as a function of time, and the rate (and direction) at which heat passed through each point in the body. Any effects of heat transfer were not considered, and were perhaps even ignored as inconvenient factors only complicating the analysis. Hence Clifford Truesdell (1980, p. 47) quips that Fourier treated only 'workless dissipation' in his theory.

There were many reasons for the popularity of Fourier's work, one of which was philosophical. Its affinity to positivist philosophy can be seen in Ernst Mach's appraisal ([1896], 1986, p. 113): 'Fourier's theory of the conduction of heat may be characterized as an ideal physical theory . . . The entire theory of Fourier really consists only in a consistent, quantitatively exact, abstract conception of the facts of conduction of heat—in an easily surveyed and systematically arranged *inventory* of facts'. The compatibility with positivist thinking was clear in Fourier's own time

as well. As documented by Fox (1971, pp. 265–266), Fourier attended the lectures of Auguste Comte (1798–1851) on positivism in 1829; Comte for his part admired Fourier's work, so much as to dedicate his *Cours de philosophie positive* to Fourier (and to Henri Marie Ducrotay de Blainville (1777–1850), the anatomist and zoologist). Fox (1974) also identifies Fourier as an intellectual leader of the younger French physicists who staged a silent revolt against Laplacian physics, an important part of which was a positivistic indifference or hostility toward Laplacian hypothesizing about microphysical forces and structures.

Since temperature and quantity of heat were two of the fundamental variables treated in his theory, Fourier did need to have a definite conception of the relation between the two. It was quite a simplified one, based on the working assumption that the specific heat of a given substance was not a function of temperature. It is not clear how much Fourier was aware of the experimental and theoretical arguments for the temperature dependence of specific heat. There is also no apparent worry in Fourier's work about whether any of the heat flowing around in conductors would go into a latent state. These physical assumptions certainly made Fourier's equations simpler than they would have been otherwise. Mach ([1896], 1986, pp. 113–114) made the extraordinary statement that 'in mechanics and in the theory of conduction of heat it is, really, only *one* great fact in each domain which is ascertained'. For mechanics, what he had in mind was universal gravitation; what was the one great fact in the theory of heat conduction? This goes back to the study of the cooling of hot bodies in air by Isaac Newton. Newton's law of cooling stated that the rate of cooling was proportional to the temperature difference between the hot body and the surrounding air. This law held a wide appeal for its intuitive plausibility, though it would be shown to be only approximately true by the works of Biot, Dalton, Dulong, Petit, and others. Fourier allowed that it may not be strictly true, but assumed that it would be true for small temperature differences, and used it as a basis for developing his analyses of the dissipation of heat. As Truesdell (1980, p. 50) emphasizes, it is not exactly Newton's law of cooling that Fourier was using as a basis of their theories. First the law had to be generalized to all heat transfer rather than just the cooling of macroscopic bodies in air, and that generalization is what Mach called the one great fact: 'the velocity of equalization of small differences of temperature is proportional to these differences themselves.' Fourier also had to make a version of this principle that was adapted for continuous media. Making that adaptation gives Fourier's diffusion equation, as follows.

For any point (or an infinitesimal region) within a continuous body, the rate at which heat flows into it would be proportional to how much its temperature deviates from the mean temperature of its immediate surroundings. For the one-dimensional case the latter deviation is expressed as the second-order partial derivative of the temperature function with respect to the spatial coordinate. Intuitively one can see that the second derivative indicates the curvature of the temperature-position curve; positive curvature would correspond to the surroundings on the average being at a higher temperature than the point itself. The rate of heat transfer would also be proportional to the internal heat conductivity of the material. And the change of temperature

would be given by the amount of heat transfer divided by the specific heat of the substance (by weight), and its density. As a result, Fourier ([1822], 1955, p. 112) obtained the following equation:

$$dv/dt = (K/CD)d^2v/dx^2$$

where t and x are the time and space coordinates, v the temperature, K the internal conductivity of the substance, C its specific heat, and D its density; in modern notation we would write the derivatives as partial. For the three-dimensional case we add terms containing the second derivatives in the other spatial coordinates. This basic equation was then modified into various forms suitable for the various shapes of bodies which Fourier considered. There was a predictable reaction from Laplace, who took interest in Fourier's work but considered it incomplete at best, since Fourier's derivation of the diffusion equation did not include any considerations of the micro-physical mechanisms of heat transfer. Already in a paper of 1810 Laplace set himself the task of remedying this defect. As discussed in Section 16.4, Laplace postulated a radiative heat exchange between the molecules within a continuous body. From those considerations Laplace managed to derive Fourier's diffusion equation, and regarded his derivation as supplying the true foundations of Fourier's result.

Regardless of the arguments about the physical basis of the diffusion equation, the difficulty of its solution gave rise to active debates and great advances in mathematics (see Grattan-Guinness, 1990, vol. 2, ch. 9, 12). Fourier found an innovative route to the solutions, drawing on the earlier works of Brook Taylor (1685–1731), Daniel Bernoulli (1700–1782), Leonhard Euler (1707–1783), and Jean le Rond d'Alembert (1717–1783) on the analysis of vibrating cords. These analyses had yielded solutions in the form of sinusoidal standing waves, and Fourier realized that he could find solutions to the diffusion equations in terms of infinite series of sine and cosine functions. This method would eventually develop into what we now call Fourier analysis, with invaluable applications in numerous branches of physics and engineering. Therefore, Fourier's work on heat conduction holds great interest not only for its role in the development of the theory of heat, but also for its place in the history of mathematics and general mathematical physics. Fourier made use of earlier mathematical works and certainly gave back as good as he took. Fourier's work marked a significant step in the development of modern mathematical physics, in which techniques of solving certain definite types of equations are developed without particular regard to physical applications. Then the resultant knowledge of solving a given type of equation can be used for treating various physical situations which bear structural similarities to each other, though they may have hardly anything in common in material terms. Fourier was fond of the structural similarities which allowed the application of the same mathematical techniques to the analyses of apparently diverse physical phenomena, and also saw his work on heat as contributing generally to mathematical analysis. This was to be borne out very nicely when the diffusion equation was later adapted for the analysis of the propagation of electric waves for the purpose of telegraphy.

16.6 DEBATES ON THE NATURE OF HEAT

Despite the positivistic trend in thermal physics fostered by Fourier, debates on the physical and metaphysical nature of heat did not cease. It is well known that Rumford made strenuous arguments in favour of the view that heat consisted in motion, in which he was supported by various others, including Humphry Davy (1778–1829), Thomas Young (1773–1829) and André-Marie Ampère (1775–1836), as well as the little-known John Herapath (1790–1868). Concern about the nature of heat pervaded Rumford's numerous investigations in thermal physics and technical innovations concerning the use of heat (see Brown, 1967, Rumford 1968). When he married the widow of Lavoisier he boasted that her second husband was going to do away with the caloric concept that her first husband had invented, which was probably not helpful for the short-lived marriage. Most famous among Rumford's experiments directed against the caloric theory was the 'cannon-boring experiment', in which he showed that an apparently indefinite amount of heat could be generated by the friction when a solid brass cylinder was hollowed out by a horse-driven drill in the manufacture of cannons; anticipating an Irvinist explanation, Rumford argued that this heat could not be generated by any reduction of heat capacity, as the ground-up metal was shown to have the same heat capacity as the block metal. Rumford also made an experiment demonstrating that heat had no appreciable weight, and considered that an argument against any material theories of heat. (For both of these experiments, and a commentary on them, see Roller, 1957, sections 3 and 4.) The calorists took due notice of these arguments, and Rumford was not an easy man to ignore—either in London, where he founded the Royal Institution, or in Bavaria, where he was made a Count of the Holy Roman Empire, or in his native America, or in Paris, where he spent his last years. But there were sufficient caloric-based explanations of Rumford's experiments, and he failed to persuade the majority of chemists and physicists. It did not come as much of a surprise to most that caloric, a classic imponderable fluid, did not have weight. And the chemical calorists had no trouble arguing that the mechanical agitation in the cannon-boring was liable to shake off some of the combined/latent caloric in the metal to render them free/sensible.

There was, however, more to Rumford's theory of heat than meets the casual retrospective eye. For instance, he made a controversial claim that water, air, and most likely other liquids and gases, were absolute non-conductors of heat, all of the heat transmission in them being due to convection. It may seem that there was no great theoretical issue hinging on this debate, but it was in fact an important part of Rumford's general attack on the caloric theories. He thought that the conduction of heat in solids occurred by the transmission of harmonic vibrations between the molecules. Fluids were unable to sustain such vibrations due to the mobility of their molecules, so heat conduction in them was an impossibility. That reasoning had no force for calorists such as Leslie, since in their view conduction was a flow of caloric between molecules; there was no reason why this intermolecular flow should not happen in liquids. Hence, if Rumford had admitted conduction in fluids, he would have

been pressed to assent to the notion that there was such a thing as caloric flowing through ponderable matter. This theoretical necessity led him to argue that the small amount of apparent conduction observed in fluids was actually due to radiation.

Radiation was a subject dear to Rumford's heart, and he joined in on an interesting controversy arising from Pictet's striking experiments on the reflection and concentration of radiant *cold* (see Chang, 2002). Pictet placed cold objects (an ice cube, for instance) at the focus of one concave mirror, and found that the thermometer placed at the focus of the opposite mirror descended immediately. These experiments impressed his Genevan colleague Pierre Prévost (1751–1839) so much that the latter found himself forced to construct an entirely new framework of understanding the exchange of heat between bodies, which he elaborated over a long period beginning in 1791. Pictet had satisfied himself with the explanation that the apparent radiation of cold was only a consequence of the radiation of heat from the thermometer to the cold object; generally there would always be a radiation of heat from a relatively warm object to a relatively cold object. Prévost generalized this picture further by postulating that *every* object radiated caloric at a certain rate depending on its temperature. A thermal equilibrium would occur when the amount of radiant caloric emitted by a body according to its temperature was balanced out by the amount of caloric received from its surroundings. In other words, there is always caloric radiation coming in and out of every body—when it seems that there is no radiation, that means only that a dynamic equilibrium has been reached.

Pictet's and Prévost's explanations of the radiation of cold satisfied most people, but they failed to convince Rumford, who understood radiant heat as a wave phenomenon, the propagation of the molecular vibrations through an all-pervading ether. Each body would emit rays of a characteristic 'frequency' determined by its temperature, and the rays would have the power to bring the temperature of the receiving body closer toward the temperature of their source. Therefore the exact same rays would act as 'calorific' rays if they are received by a body colder than their source, and as 'frigorific' rays if received by a hotter body. Rumford made an explicit analogy between calorific–frigorific radiation and the propagation and resonance of sound. After successfully repeating Pictet's experiment in 1800, Rumford wrote to Pictet: 'the slow vibrations of ice in the bottle cause the thermometer to sing a lower note' (quoted in Brown, 1967, p. 204). Drawing on his earlier experience in the study of the radiative and reflective power of different surfaces, Rumford performed some experiments to support his view that the radiation of cold was as much a positive phenomenon as the radiation of heat, and that heat and cold were only relative designations. However, his work in this direction does not seem to have been sufficient to overturn the consensus in favour of Prévost.

Among those who subscribed to material theories of heat, the fact that radiant heat was capable of reflection immediately suggested a parallel with light—a parallel that was only to be strengthened when it was discovered that radiant heat was also subject to refraction, and even polarization. These discoveries resonated with the long-standing conjecture that light and heat (and sometimes electricity as well) were different manifestations of the same ultimate entity, which had been advanced, for instance, by

James Hutton (1726–1797), Scottish geologist and intimate friend of Black. The study of radiant heat gave a concrete arena in which speculations about the relation between heat and light could be elaborated. The opening of the nineteenth century witnessed a great revival of debates regarding the relationship between light and heat, due to the announcement of the heating effects beyond the red end of the solar spectrum by the renowned astronomer William Herschel (1738–1822), the discoverer of Uranus. Herschel stumbled upon infrared rays in the course of investigating the differences in the heating powers of different colours in the solar spectrum. Initially he thought that the heating effect observed in the dark space beyond the red indicated the existence of ‘invisible light’. This seemed cogent initially, since the infrared rays from the Sun (and also from terrestrial sources) were shown to obey the same laws of reflection and refraction as light. Further experiments, however, converted Herschel to the belief that what he was observing in the infrared region was not invisible light (which he came to see as a contradiction in terms), but caloric rays. What particularly convinced him in this direction were experiments on transmission, in which some substances were seen to transmit light but absorb heat, or *vice versa*. This he saw as the *separation* of light and heat. Herschel’s considered view was endorsed by many—for instance, in the influential textbooks by John Murray and by Thomas Thomson (1773–1852)—and sometimes infrared heating was even taken as the most convincing experimental proof of the real existence of caloric. However, vexing ontological questions needed to be resolved before any certain conclusions could be reached (see Chang and Leonelli, 2005). This is illustrated nicely by the case of John Leslie, Herschel’s first major critic on infrared rays. In a move that baffled many observers, Leslie denied the existence of infrared rays altogether, blaming the observed heating effects to poor experimental techniques on Herschel’s part. Leslie’s argument was motivated by his view that heat in general was the effect of the combination of light with ordinary matter.

More damaging and lasting criticism of Herschel’s view came from those who accepted his experimental results but disputed his interpretation, on a Rumford-like new ontology which regarded both light and radiant heat as waves. This points to an entire phase of thermal physics, which Stephen Brush (1976) has elucidated and dubbed ‘the wave theory of heat’. The crucial impetus for this development came from the great revival of the wave theory of light in the early nineteenth century, first attempted by Young but achieved more effectively by Augustin Fresnel (1788–1827). For the wave theory of light the phenomena of interference and polarization counted as important evidence, and those who pursued the parallel between light and radiant heat then attempted to demonstrate those phenomena for radiant heat as well. It was Bérard who first claimed to have observed the polarization of radiant heat, in 1813, but a convincing verification of that claim had to wait until the 1834 work of James David Forbes (1809–1868), Scottish geologist and the student and successor of Leslie in Edinburgh. The idea of radiant heat as an ethereal vibration had been advanced by Rumford, and it was easily revived. Now it seemed plausible to treat both light and radiant heat as aspects of one and the same wave phenomenon, which interacted in various manners with substances and sense-organs according to its wavelength. Much experimental and theoretical work in the consolidation of this new view was carried

out by the Italian physicist Macedonio Melloni (1798–1854), who had initially shared Herschel’s view that light and radiant heat were distinct entities (Chang and Leonelli, 2005).

16.7 HEAT AS A STATE FUNCTION

The indisputable major event in thermal physics in the mid-nineteenth century was the emergence of thermodynamics. This is not a whiggish statement: on the one hand, it was already a common view at the time that the arrival of thermodynamics was a major development; on the other hand, the original form of thermodynamics, except in the underlying conceptions that Clausius had (but not shared by others), had very little to do with our modern understanding that heat is only a manifestation of the kinetic energy of the molecules of ordinary matter. (The later developments by which thermodynamics came to be understood in terms of statistical mechanics is discussed in Chapter 25, ‘The Emergence of Statistical Mechanics’.) The arrival of classical thermodynamics continues to raise non-trivial historiographical and philosophical questions: what it was that brought down the dominance of the caloric theory and ushered in the new science of energy and entropy? If the caloric theory was good enough in 1800, why was it no longer adequate in 1850? How did the concept of energy arise, and why did it not come earlier?

It is important to note that there were several different competing theories and traditions active throughout the period, so the story is not simply that of the demise of the caloric theory and the rise of thermodynamics. We have already noted that there were at least two major eighteenth-century calorist traditions (Irvinist and chemical). Early nineteenth-century developments brought in two important new traditions, which were very different from each other and also did not map neatly onto the Irvinist–chemical distinction: the phenomenological tradition of Fourier focused on the movement of heat, and the microphysical tradition of Laplace focused on the forces between particles of caloric and matter. On the anti-calorist side Rumford engendered two different strands of work, though neither found wide acceptance until after his death: the cannon-boring experiment presaged the interconversion of heat and work, and his work on radiation, except for his advocacy of ‘frigoric rays’, fed into the wave theory of heat discussed above.

The line of theoretical development which led directly to classical thermodynamics (and the concomitant demise of the caloric theory) started not from the anti-calorist side, but from within the caloric theory. Nor did it come from the tradition of Fourier, which might seem akin to classical thermodynamics in its macroscopic focus and its attention to the movement of heat. Rather, where we must look is in a curiously macroscopic strand of the latter-day Laplacian tradition. One central ingredient in this type of macroscopic analysis was the assumption that heat was a state function. There can be some confusion or at least ambiguity as to what exactly that means.

Sometimes it is equated with the assumption of heat conservation, but it is more specific than that. From Poisson (1823b, p. 337) we have perhaps the most careful and informative formulation:

It would not be possible to calculate the total quantity of heat contained in a given weight of a gas . . . however, one may consider the excess amount of heat that this gas contains over what it would contain under a certain arbitrarily chosen pressure and temperature. That excess amount, denoted by q , will be a function of p [pressure], r [density], and q [temperature], or simply of p and r because the three variables are related amongst each other by [$p = \alpha r (1 + aq)$; α, a constants]; therefore we have $q = f(p, r)$, where f is a function whose form needs to be determined.

The assumption that q was a state function gave exactly the kind of useful theoretical constraint that Irvine's hypothesis of heat capacity had provided. The rejection of Irvinism deprived the caloric theory of a good deal of empirical content, and the state-function assumption was very helpful in restoring it. Poisson (1823a) put the assumption to effective use in deriving what we now recognize as the adiabatic gas law, $PV^\gamma = \text{constant}$, in the course of furthering Laplace's work on the speed of sound. Poisson imagined a body of gas being heated under constant pressure (hence expanding), absorbing a certain amount of heat, Q . Then he imagined the same gas heating up further by adiabatic compression back to its original volume. Finally, it would be cooled at constant volume back to its original temperature, giving up a certain amount of heat, Q' . If heat is a state function, then the gas must contain exactly the same amount of heat as it started with, when it is restored to its original state. Therefore it follows that Q is equal to Q' , since the second stage in the above process is adiabatic and there is no input or output of heat. The rest of the derivation was completed by noting that Q was proportional to c_p and Q' to c_v (where c_p and c_v are specific heats under constant pressure and constant volume, as discussed in Section 16.3).

The power of the state-function assumption was amply illustrated in Poisson's work, but its most remarkable application came in *Réflexions sur la puissance motrice du feu*, the 1824 monograph by the engineer and army officer Sadi Carnot (1796–1832). Today Carnot is celebrated, with good reason, as a major precursor of thermodynamics whose pioneering work was sadly neglected until after his death. His remarkably original work, achieved in isolation from the most of the scientific establishment of his day, was a synthesis of insights arising from several different contexts. (For much valuable analysis, see Fox's introduction and commentary in Carnot [1824], 1986.) There is little doubt that the primary context of Carnot's work was power engineering rather than theoretical physics. Carnot's ultimate aim was to improve the efficiency of steam engines, efficiency being understood as the amount of mechanical effect extracted from a given amount of fuel. Although Carnot's thinking was very abstract, it was clearly directed by this practical question. The basic theory that Carnot needed in order to answer his question was not in place yet, so he had to do some fundamental thinking on his own; and in doing so he produced ideas whose applicability went far beyond his original problem. When it comes to specific insights Carnot drew from the realm of power engineering, the two of most importance are both traceable to that

renowned improver of steam engines, James Watt (1736–1819). Watt's installation of the separate condenser went back to 1765, but the theoretical lesson Carnot gathered from it was still relatively fresh: it is not merely the presence of heat that produces mechanical work, but the *flow* of heat from a hot place to a cold place. The other insight originating from Watt concerned the 'expansive principle': namely, that the hot steam should be allowed do further work 'on its own' after its introduction into the cylinder, by virtue of its natural tendency to expand. This phase was formally incorporated into Carnot's thinking as the adiabatic-expansion stroke in his famous cycle (see Cardwell, 1971, p. 52). Not restricting himself to steam engines, Carnot also made an explicit analogy to water engines, which went along nicely with his notion that caloric produced mechanical work in the course of 'falling' from a place of higher temperature to a place of lower temperature.

In the realm of heat theory, perhaps the greatest influence on Carnot was the sidelined Clément (now finally settled with a chair at the *Conservatoire des Arts et Métiers* in 1819), rather than any of the luminaries of the *Académie* or the *École Polytechnique*. Carnot followed Clément and Desormes's 1819 work on the steam engine in analyzing the expansive phase after the 'cut-off' of steam as an adiabatic expansion (with cooling), rather than an isothermal one (that is, with constant temperature) to which Boyle's law could be applied. Carnot also believed 'Clément and Desormes' law' (also advanced by Watt, earlier), according to which a given weight of steam at a given temperature contained the same amount of heat, no matter at which pressure (or temperature) it was formed. Finally, no discussion of Carnot would be complete without a mention of the shadow of his father. Lazare Carnot (1753–1823)—one of the most prominent military and political leaders of France in the Revolutionary and Napoleonic periods—was also a keen mathematical physicist, as Charles Gillispie (1971) has described in great detail. It is probably not far-fetched to speculate that Sadi was trying to extend to heat engines Lazare's work on the efficiency of mechanical engines. For instance, Lazare's point that there should be no percussion in machines (in other words, motion should be transferred between parts that maintain the same velocity) is mirrored in Sadi's insight that every time heat is transferred directly across finite temperature differences there will be a waste of potential to generate mechanical work.

Sadi Carnot's approach can be viewed as a happy medium between Fourier's and Laplace's. Like Fourier, he declined to speculate about the nature of heat and the microscopic mechanisms of thermal phenomena, and instead focused on the phenomenological and macroscopic movement of heat. On the other hand, he followed Laplace in investigating the *effects* of heat in altering the states of material bodies mechanically. Carnot ([1824], 1986, pp. 64–66) set this synthesis in stone by adopting an axiom that the production of mechanical effect in a heat engine was always due to a flow of heat (or a restoration of a disturbed thermal equilibrium). It seems that a large part of Carnot's originality arose in the stimulating context of taking a very practical problem and thinking it through in highly abstract and idealized terms. Since he sought to create a general theory of all heat engines rather than only steam engines, he felt compelled to specify his problem without reference to any particular

substances or mechanisms: 'the steam serves simply as a means of transporting the caloric' (Carnot, [1824], 1986, p. 64). At this level of abstraction, the working of a heat engine is divided into two parts: one in which heat is absorbed by the working substance from a hot body, and the other in which the absorbed heat is released into a cold body.

Addressing considerations of maximum efficiency, Carnot was quick to note that the flow of heat does not always produce mechanical effect—as in the cases of 'workless dissipation' that characterized most of Fourier's problems. Carnot ([1824], 1986, p. 70) further noted that any temperature change that was not associated with a volume change involved a wasteful flow of heat, and that all such temperature changes due to a flow of heat between bodies at different temperatures. So, while the working substance in the engine is absorbing heat, its temperature should be equal to that of the heat source (presumed constant), or only infinitesimally lower. When releasing heat, the substance should have the same temperature as the heat sink (or only infinitesimally higher). So an additional stage was needed, to get the substance from the temperature of the heat source to the lower temperature of the heat sink. The only non-chemical way of achieving that without involving a heat transfer was adiabatic expansion. This fitted in nicely with Watt's expansive principle as well, since the practical advice there was that steam should be allowed to expand on its own while cooling. Now just one more innovation was needed. In order to discern purely the mechanical effect of the *passage* of heat through the engine, Carnot needed to consider a situation in which the working substance in the end gave up exactly the amount of heat that it receives. This can be achieved, on the assumption that heat content is a state function, by stipulating that the substance should return exactly to the state in which it began. So Carnot's ideal heat engine operated in cycles, and this is one of the factors that set his analysis apart from most of his contemporary writers on the theory of the steam engine, who merely considered the mechanical effect while the steam was moving the piston and neglected the work one has to supply in order to bring the substance back to its original state.

Carnot's description of his ideal cycle was rather complex, but it did contain the essential elements that we associate with his name: the isothermal communication of heat to and from the working substance; changes in the temperature of the substance by adiabatic compression and expansion; mechanical effect produced in the expansive strokes and spent in the compressive strokes; and a net gain of mechanical effect, due to the expansions taking place at higher temperatures (and pressure) than the compressions. One significant point that Carnot ([1824], 1986, pp. 68–70, 76–77) advanced was that his ideal heat engine would have the same efficiency regardless of the nature of the working substance. This conclusion followed from the mere assumption that the cycle is reversible. According to D. S. L. Cardwell (1971, p. 198), the reverse operation of an engine was not such an unusual concept among engineers at the time; particularly with a water engine it is easy to imagine running it backwards to bring water to a higher place by expending mechanical work. With Carnot's analogy of the fall of caloric, this is quite easy to imagine for heat engines as well. So Carnot says, if one ideal heat engine can produce mechanical effect W by the fall of caloric

Q between two given temperatures, and another engine can operate more efficiently (that is, produce $W' > W$ from the same Q), then we could create mechanical effect from nowhere as follows. Take the more efficient of the two engines, and produce mechanical effect W' by letting Q' fall from the higher to the lower temperature; take a part of the mechanical effect produced that is equal to W , run the other engine backwards with it, bringing Q back up to the higher temperature. Then we have created an amount of mechanical effect equal to $W' - W$ out of nowhere, which is impossible.

Having thus established that there is a unique ideal efficiency for the fall of caloric between two given temperatures, Carnot ([1824], 1986, pp. 91–93) then set out to estimate that efficiency. He conceived the question as one of comparing the amount of heat needed in producing the same amount of motive power in two ideal heat engines operating at different places on the temperature scale. The engine that needs to use less heat would be the more efficient one, so the question was reduced to estimating the amount of heat absorbed in isothermal expansion at different temperatures. Now Carnot imagined heating a sample of air from 1°C to 100°C , allowing it to expand under constant pressure. The end result of that process could also be achieved in two other ways: (a) by increasing the temperature to 100°C under constant volume first, followed by isothermal expansion; (b) by isothermal expansion at 1°C to the desired volume, and then increasing the temperature under constant volume. Either way, the total caloric required would be the same, because the initial and final states of the gas are exactly the same in both cases. Here enters the assumption of heat as a state function. Then Carnot argued that the temperature-increase phase required more caloric in process b than in a (compare b_2 and a_1 in the figure), because the specific heat was higher at higher volume (or, lower density); this latter assumption about specific heats was inferred from the experimental results by Delaroche and Bérard (1813). Finally, since the total heat added in processes a and b were the same, it followed that the isothermal phase a_2 must absorb more heat than that b_1 . That is to say, isothermal expansion required more heat at higher temperatures, and therefore the engine efficiency was lower at higher temperatures.

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Carnot's use of the assumption that heat is a state function was crucial in the above derivation, and in many other parts of the *Réflexions*. In one footnote he stated the assumption explicitly, from which we can see that it was a very similar one to Poisson's version of the general idea, defining the state in terms of the body's 'density, temperature, and mode of aggregation' (Carnot, [1824], 1986, p. 76). For Carnot's modern admirers, this assumption, and the associated belief in the conservation and materiality of heat, are the most unfortunate aspects of his work. Consequently, much has been made of the fact that Carnot's belief in caloric and its conservation was always shaky, and finally renounced very clearly in some unpublished manuscripts composed in his last years. However, it is clear that these 'mistaken' assumptions did very useful work for Carnot. Besides, Carnot's ideas as expressed in the *Réflexions* are what inspired by the originators of classical thermodynamics, while the manuscripts were made public only in 1878 and did not have much scientific impact.

The practical conclusions that Carnot drew regarding engine efficiency did not help the engineers very much, as they either merely affirmed well-known practical

wisdom (such as higher efficiency attainable with higher pressures and with the expansive use of steam), or predicted quite small effects (such as higher efficiency at lower temperatures). However, in the course of this work he also derived, almost as a digression, some very interesting and significant results concerning the physics of ideal gases. For instance, Carnot argued that the amount of heat absorbed in isothermal expansion was independent of the nature of the gas, and that the difference (not ratio) between the two specific heats (c_p and c_v) was the same for all gases and for all densities of a given gas. He also derived a relation between the addition of heat and the increase of volume in isothermal expansion, and a relation between specific heat and volume. These results all followed from the assumption that heat was a state function, and the assumption that the efficiency of all ideal engines was independent of the specific mechanisms involved. So it is not entirely clear why the academic physicists ignored Carnot's work, though it must have had something to do with Carnot's isolation from the academic world.

The revival of Carnot's work was initially due to Emile Clapeyron (1799–1864), civil engineer and graduate of the *École Polytechnique*, whose speciality was the design and construction of steam locomotives. In 1834 Clapeyron published, in the *Journal of the École Polytechnique*, a restatement of Carnot's theory which was both analytically sharper in its mathematical formulations, and intuitively more appealing thanks to the use of Watt's indicator diagram (plotting the state of the working substance by its pressure and volume), which has become the universal mode of representing the Carnot cycle in modern textbooks. Clapeyron did not amend Carnot's basic ideas much at all, but the benefits of the clarification he made in Carnot's ideas were quite clear. To start with, Clapeyron reformulated Carnot's description of the cycle as follows. The substance starts in a certain state, characterized by its volume, pressure, and temperature (T_1). First, it expands isothermally at temperature T_1 , absorbing a certain amount of caloric (Q) from a heat source; during this stroke, mechanical effect (W_1) is produced due to the expansion of the substance. Second, it expands adiabatically, cooling to the temperature of the heat sink (T_2) in the process; during this stroke further mechanical effect (W_2) is produced. Third, the substance is compressed isothermally at T_2 , until it has released to the heat sink the same amount of heat it absorbed in the first stroke; some mechanical effect (W_3) must be expended in this compression. Finally, the substance is compressed adiabatically; this stroke should return the gas to its original volume, and in that case the temperature and pressure of the gas also will be restored to their original values, assuming that the total heat content of the gas will be the same as at the start; further mechanical effect (W_4) is expended in this adiabatic compression. At the end of this closed cycle, the net mechanical effect W , equal to $W_1 + W_2 - W_3 - W_4$, has been produced by the fall of the amount Q of caloric from temperature T_1 to T_2 .

We can see from the above description that Clapeyron not only retained a belief in caloric and its conservation, but gave an even more prominent and explicit place to the assumption of heat as a state function than in Carnot's original formulation. Starting with the characterization of the state of a gas by its volume (v), pressure (p), temperature (t) and quantity of heat (Q), Clapeyron further assumed that knowing

two of those quantities would allow the other two to be determined. This was because there were two relations holding between these variables: the ideal gas law ($pv = R(267 + t)$, in Clapeyron's notation), and also a relation expressing Q as a function of the other variables, as yet unspecified. Deriving and applying that expression for Q was an essential part of Clapeyron's work. On his state-function assumption, Q would be a function of p and v only, if t were fixed; then one can add the assumption that the product pv is a linear function of t , due to the ideal gas law. From those considerations, Clapeyron ([1834] 1837, p. 358) arrived at the following result:

$$Q = R(B - C \log p)$$

where R is a constant and B and C are functions of temperature. This equation was essentially given by Carnot already, but Clapeyron formulated it in a more straightforward way, and used it more effectively as well. The variable C in the equation, later to be known as Carnot's function, was especially important, as Clapeyron was able to show that $(1/C)$ was proportional to the efficiency of the ideal Carnot engine. From this equation for total heat Clapeyron gave new derivations of Carnot's results concerning the amount of heat given off in an adiabatic compression, and the relationship between the two specific heats of gases.

16.8 THE EMERGENCE OF CLASSICAL THERMODYNAMICS

Although the Carnot cycle is a cornerstone of almost any presentation of thermodynamics today, it was not at all an easy transition for physicists to go from Carnot's theory to what we know as classical thermodynamics. *Carnot's* cycle was not the modern *Carnot* cycle, and its transformation into the modern form was an essential part of the emergence of thermodynamics. A striking illustration of the difference between Carnot's theory and thermodynamics is the fact that Carnot's theory lacked the two best-known elements of classical thermodynamics: namely, its first and second laws. It could be argued that Carnot's reasoning already embodied the second law in an implicit form, but the first law was clearly absent. The emergence of thermodynamics and its two laws is a well-known story (for example, Cardwell, 1971; Smith, 1998), so I will not try to tell it in detail. However, a brief summary overall must be given here, and there are also a few lesser-known aspects of the story that will be useful to highlight. The laws of thermodynamics are in fact something of a misnomer, since they have broad roots and consequences reaching far beyond the domain of thermal physics. It is best to acknowledge that these laws are entirely general in their scope and cannot rest on any empirical generalizations concerning heat and its relation to mechanical work. What we can acknowledge, nonetheless, is that the concepts of energy and entropy were first articulated clearly in the context of thermodynamics.

The first law of thermodynamics, otherwise known as the conservation of energy, has very deep roots. The term ‘energy’ is very old, and originally had very vague meanings. The notion of conservation is perhaps even older, appealing to the intuition that nothing real in nature is created out of nothing or disappears into nothing. Various conservation principles had been formulated in science, including Descartes’ conservation of force, Leibniz’s conservation of *vis viva*, and Lavoisier’s conservation of weight in chemical reactions. Heat itself was seen as a conserved quantity in the caloric theories, and the great innovation at the establishment of thermodynamics was the doctrine of the *inter*-conversion of heat and mechanical work, and the consequent *non*-conservation of heat itself. The credit for this innovation goes equally to James Prescott Joule (1818–1889) and Julius Robert Mayer (1814–1878). Travelling as a ship’s physician in the East Indies, Mayer noticed that the venous blood of his patients was redder in the tropics than in cooler climates, which he thought was because in warmer surroundings the body needed to generate less heat, and therefore needed to use less energy, or burn less oxygen (on Mayer, see Caneva, 1993). This chance observation led Mayer to formulate a general doctrine of the interconversion of various forms of energy, though he had some trouble getting his ideas noticed by physicists, and his 1842 paper was published by the chemist Justus Liebig. James Joule’s approach to the subject was more experimental and quantitative than Mayer’s, and he focused on measuring the ‘mechanical value of heat’—namely the ratio between the amount of mechanical work that was destroyed and the amount of heat that was produced as a result—through his famous ‘paddle-wheel’ experiment and other related experiments. With his origin in a provincial brewing family, Joule also had some initial difficulty in being accepted in the academic physics community. However, he did receive opportunities to present his findings to the meetings of the British Association for the Advancement of Science in 1844 and 1845, which gave him visibility and introduction to some better-established scientists.

Later, there was a quite a fraught dispute regarding the priority between Joule and Mayer, especially surrounding John Tyndall’s public championing of Mayer in 1862. Whatever the exact truth of the matter, this priority dispute pales in importance when it is viewed in the context of Thomas Kuhn’s (1977) claim that between 1830 and 1850 as many as twelve different people in various European countries independently arrived at the idea of energy conservation. It is difficult to avoid the impression that a combination of the experiences of power engineering and the long-lasting theme of conservation was bound to yield something like the energy concept. (The concept of energy also had deep cultural resonances, discussed in Chapter 17, ‘Engineering Energy’.) The first general and systematic statement of energy conservation was probably due to Hermann Helmholtz (1821–1894), who presented his classic paper ‘Die Erhaltung der Kraft’ to the Physical Society of Berlin in 1847.

It is even trickier to pinpoint the origin of the second law, although the story involves fewer protagonists. A key figure here is William Thomson (Lord Kelvin) (1824–1907), of Glasgow. Thomson was closely guided by Carnot’s work, even after he was convinced by Joule to renounce the existence of caloric and the conservation of heat. Thomson first encountered Carnot’s work through Clapeyron’s paper

while working as an apprentice in Regnault's laboratory in 1845, and his work in thermodynamics began with an attempt to understand and extend Carnot's ideas. Rudolf Clausius (1822–1888) followed Thomson's rendering of Carnot, and produced his own synthesis of Carnot and Joule. Both Thomson and Clausius focused on the fact that in a Carnot engine mechanical work was produced in the process of heat being transferred from a warmer to a colder place, but modified Carnot's reasoning by noting that not all of the heat arrived at the colder place, the lost portion being turned into mechanical work. In this process the system approached thermal equilibrium, lessening the potential for humans to extract mechanical work even though no energy was destroyed in an absolute sense. Thomson and Clausius agreed that 'heat cannot, of itself, pass from a colder to a hotter body', which was the formulation of the second law of thermodynamics that Clausius gave in 1850. In the terminology introduced by Clausius, we now say that the entropy of a system either increases or at best remains the same; the latter holds if the transfer of heat only takes place across two parts of a system which are at the same temperature. Isothermal heat-transfer also made a condition of reversibility, and Clausius and Thomson agreed that the maximally efficient Carnot engine would be reversible. If there were a heat engine more efficient than a reversible one, then one could use such an engine to run a reversible one backwards, effecting a net transfer of heat from a colder place to a hotter place; but this was deemed impossible, as it violated the second law of thermodynamics.

One notable feature of classical thermodynamic theory is its highly abstract nature. In that vein, a development of great importance was Thomson's establishment of the concept of absolute temperature (see Chang and Yi, 2005). Thomson was certainly appreciative of the achievements of his mentor Regnault in thermometry, but he was unhappy about tying the definition of a fundamental physical quantity to a particular substance (air, in this case). This was Thomson's main concern, rather than counting temperature from an absolute zero. Starting in 1848, he tried out a succession of definitions based on the thermodynamics of ideal heat engines, and by 1854 he had arrived at the notion that the ratio of two absolute temperatures was as the ratio of the quantities of heat taken in and given out at those temperatures in a Carnot cycle. But there were difficulties with using such definitions for experimental work, since it was not possible even to approximate an ideal Carnot engine in reality. More generally, it is not trivial to connect an abstract concept with concrete operations in order to make physical measurements possible. In the end, Thomson argued that an ideal gas thermometer would indicate his absolute temperature, and that the deviation of actual gas thermometers from the ideal could be estimated by means of the Joule–Thomson effect (temperature change in a gas pushed through a small hole or a porous plug). However, the measurement of this effect required measurements of temperature, so there was a problem of circularity. Thomson and Joule forged ahead by measuring the Joule–Thomson effect with an ordinary thermometer. Later investigators, particularly Hugh Longbourne Callendar (1863–1930), refined and justified Thomson's practice as an iterative one: the correction of the gas thermometer based on the Joule–Thomson effect is itself subject to an error; however, after the first-order correction is made to the thermometer, the Joule–Thomson effect measurements can be corrected,

resulting in second-order corrections; and so on. The first-order corrections were already small enough, and Callendar trusted that higher-order corrections would be negligible. With the operationalization of the absolute-temperature concept, thermal physics had reached a notable point of maturity and synthesis. Ironically, however, a whole other set of transformations had just got seriously under way, with a new microscopic energy-based understanding of heat and temperature and the rendition of the entropy concept in statistical terms (see Chapter 25).

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NOTES

1. Irvine did not publish his views, but they spread through his teaching and personal contacts. Some of his essays on heat were published posthumously by his son (also named William), but only in 1805.
2. I follow Robert Fox's usage of this term to designate those who did their thermal physics on the basis of caloric.