

was subjected to experimental tests by Count Rumford and by Davy, and make clear the role of their experiments in weakening the foundations of that theory.

The final downfall of the caloric theory and the subsequent correlation of the sciences of heat and mechanics did not occur until near the middle of the nineteenth century and is not treated in detail here. But the reader will be able to see how, from thermometry through heat measurements to early speculations about what heat is, the thread of scientific history here followed finally led to the development of the modern theory of heat as a mode of motion. It also led to the enunciation of one of the great generalizations of physical science—the principle of conservation of energy.

1. EVOLUTION OF THE THERMOMETER

The earliest forms of the thermometer appear to have been suggested by a sixteenth-century revival of interest in various mechanical devices and toys invented during the Hellenic period, particularly by Philo of Byzantium and Hero of Alexandria. Certain of these ancient devices depended for their operation upon the expansion of air when heated. But the idea of adapting them to the purpose of indicating “degrees of hotness,” or temperature, seemingly occurred to no one in ancient or medieval times.

Galileo's barothermoscope, ca. 1592-1603. Although it is not known with certainty who first conceived the idea of trying to measure temperatures, the adaptation of the ancient devices to this purpose is generally attributed to Galileo Galilei. He seems not to have appreciated the invention, for his own writings, so far as they have survived, contain only one incidental reference to the principle of the instrument. However, records left by several of his friends and students indicate that he devised and used it shortly after 1592.

The instrument was merely a glass bulb containing air and having a long stem which extended downward into a vessel of water. As the temperature changed, the air in the bulb expanded or contracted and the water in the stem fell or rose. Thus air was the *temperature-indicating substance*, and its expansion served as the *temperature-indicating property*. Galileo appears also to have added to the device a scale, which probably consisted of a long narrow strip of paper attached to the stem and marked off in degrees “at pleasure.” One such scale was divided into eight large spaces, and each of these into 60 smaller ones, a scheme possibly suggested by the graduation of astronomical instruments into degrees and minutes.

Since there was no thought of basing these scales on standard, reproducible temperatures, the temperature indications were at best only semiquantitative. Thus Galileo's instrument is usually referred to as a *thermoscope*, a term that first came into use in 1617, rather than as a *thermometer*, a term that was not coined until 1624. More accurately speaking, his instrument was a "barothermoscope," for it indicated changes in atmospheric pressure as well as temperature; but this fact apparently was not clearly recognized until some time after the invention of the barometer (1643).

One of Galileo's colleagues, Sanctorius, who was professor of medicine at the University of Padua, applied Galileo's barothermoscope to the detection of fevers and other physiologic studies. Recognizing that fiducial points are needed for a satisfactory measuring device, Sanctorius made marks on his scale to indicate the two readings obtained when the bulb of the instrument was exposed, first to snow, and then to the flame of a candle.

First liquid-expansion thermoscopes, 1632-1641. The expansion of a liquid was probably first employed for estimating temperatures by Jean Rey, a French physician, in 1631. His instrument, which he used for taking the temperature of patients, was a glass bulb and stem similar to Galileo's, except that it was inverted and partly filled with water. The upper end of the stem was left open, so the readings were influenced by evaporation of the water, although not to an appreciable extent by changes in atmospheric pressure.

The first thermoscope with the end of the stem sealed, and also utilizing the expansion of alcohol instead of water (Plate I, 1, 2), was developed in 1641 by the Grand Duke Ferdinand II of Tuscany, who was soon to become one of the founders of the Florentine Accademia del Cimento (Academy of Experiment). Ferdinand used this instrument for meteorologic purposes and in experiments on the artificial hatching of eggs. He also invented an entirely new type of thermoscope (Plate I, 5), consisting of a number of blown glass bubbles suspended in alcohol, their weights being adjusted so that first one and then another would sink as the temperature rose and the density of the alcohol decreased.

The Accademia del Cimento, during its brief existence from 1657 to 1667, manufactured many temperature-measuring devices, mainly of the alcohol-in-glass expansion type. They were marvels of glass blowing (Plate I, 4) and were long used for meteorologic and other purposes in different parts of the world. The divisions on the scale were marked by minute glass beads of different colors attached to the stem, and the scale on the stem was constructed by dividing into a number of equal parts the space between the two marks indicating "the most severe winter cold" and "the greatest summer heat." Since these two extreme

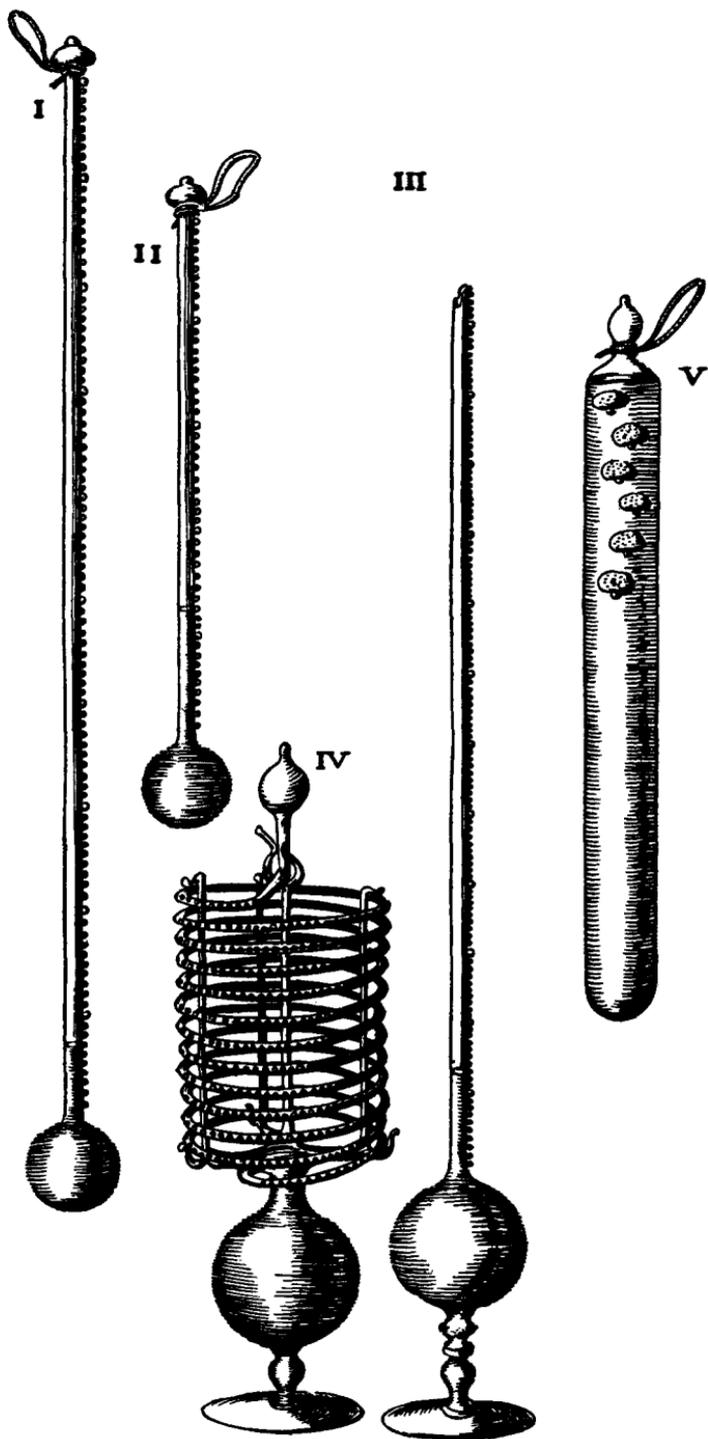


PLATE I. Thermometers of the Accademia del Cimento.

temperatures could not be determined with any precision, no standard thermometric system was established by their use. However, this Florentine scheme for constructing a scale eventually made possible a universally comparable measure of temperature. The main problem, it turned out, was to find temperatures for determining the fixed marks that could be reproduced experimentally with precision.

The one-fixed-point method of calibration, 1665. Another method of calibration affording a universally comparable measure of temperature was independently proposed in 1665 by Robert Boyle, Robert Hooke, and Christiaan Huygens. This is to mark on the thermometer stem a *single* fixed point, which is to be determined experimentally and is to serve as a starting point; and then to place "degree" marks on the stem, each of them corresponding to an expansion or contraction of a certain fraction — say $1/1000$, or $1/10,000$ — of the volume of the thermometric substance when at the temperature corresponding to the fixed point. For the temperature to be used in establishing the single fixed point, Boyle suggested the freezing temperature of oil of aniseed; Hooke, the freezing temperature of water; and Huygens, either the freezing or the boiling temperature of water.

The two-fixed-point method of calibration, 1669-1694. The method used on Florentine thermometers, in which the space between *two* fixed marks is divided into a number of equal parts, or "degrees," is called the *two-fixed-point method*. In 1669, Honoré Fabri, a Jesuit who had been a corresponding member of the Accademia del Cimento, adopted the temperature of melting snow to determine the lower fixed point; but for the upper fixed point he retained the indefinite "greatest summer heat."

Dalencé, in 1688, suggested that the temperature for the upper fixed point be changed to the melting temperature of butter, thus affording greater precision and more nearly comparable readings. He assigned the respective values -10° and $+10^{\circ}$ to his two fixed points, and divided the interval between them into 20 equal parts.

In 1694, the freezing and the boiling temperatures of water were proposed as the two fixed-point temperatures by Carlo Renaldini, a professor at Padua and a former member of the Accademia del Cimento. He divided the interval between these fixed points into 12 equal parts, possibly because the number 12 is easily subdivided or because there are 12 inches to the foot.

Eventually it became clear that both the melting temperature of ice and the boiling temperature of water are influenced by changes in the atmospheric pressure. So it was agreed that these two temperatures when the pressure is one standard atmosphere shall be used to establish the

fixed points; these points are referred to as the *ice point* and the *steam point*.

First air thermometer, 1699–1702. The first air thermometer that was not at the same time a barometer was developed by Guillaume Amontons, a French physicist. In one form of this instrument, the pressure of the air is kept constant, and temperatures are measured by observing changes in the volume of the air. In another form — the one first developed by Amontons — the volume of the air is kept constant, and temperatures are measured by observing changes in the pressure of this air, instead of in its volume. In other words, air is here the thermometric substance, and either its volume or its pressure is the thermometric property.

Origin of the Fahrenheit system, 1702–1717. Ole Roemer (Rømer), the Danish astronomer, proposed in 1702 that the temperature of a certain mixture of ice and salt be made the lower fixed point and assigned the value 0° , and that the steam point be made the upper fixed point and assigned the value 60° . Thus this was a sexagesimal system. G. D. Fahrenheit, who was a celebrated maker of meteorologic instruments, visited Roemer in Copenhagen in 1708 and subsequently undertook the calibration of thermometers along similar lines. In 1717 he proposed a scheme essentially like the one that is today called the "Fahrenheit system," in which the values 32°F and 212°F are assigned to the ice and steam points, respectively.

Fahrenheit was the first to use a cylindrical rather than a spherical bulb in thermometers, and contributed in other important ways to the art of thermometry by his improved methods of making reliable alcohol-in-glass and mercury-in-glass thermometers. Mercury had previously been used in barometers and, to some extent, as a thermometric substance, but no one before Fahrenheit seems to have thoroughly appreciated its advantages over other liquids for this purpose.

Origin of the centigrade system, 1710–1743. What today is known as the "centigrade system," in which the values 0°C and 100°C are assigned to the ice and steam points, is believed to have been first suggested as early as 1710 by Elvius, a Swede. It was later proposed, seemingly independently, by the eminent Swedish botanist, Linnaeus, in 1740, and by Christian of Lyons in 1743. This system is often credited to Anders Celsius, a Swedish astronomer, possibly because of a casual association suggested by the "C" for centigrade, coupled with the fact that Celsius used a centesimal system as early as 1742. However, Celsius' system was inverted with respect to the centigrade in that he assigned the values 100° and 0° to the ice and steam points.

Some recent developments. It eventually became clear that the properties of different substances are not generally the same functions of

temperature and, therefore, that thermometers constructed from different substances do not agree exactly with one another at temperatures other than the fixed points. So it was desirable that a particular thermometric substance, together with some particular property of this substance, be chosen to serve as the ultimate standard in practical thermometry. In the nineteenth century, H. V. Regnault showed that the constant-volume hydrogen thermometer was highly suitable for this purpose; it was adopted as the practical standard and was so used until 1927.

Because of experimental difficulties in the use of any gas thermometer, the Seventh General Conference on Weights and Measures, with a representation of 31 nations, adopted in 1927 a standard working scale designated as the *international temperature scale*. This scale is defined by a series of fixed points, which have been determined by gas-thermometer measurements, and by the specification of suitable thermometers for interpolating between the fixed points and extrapolating to higher temperatures. For example, the platinum electrical-resistance thermometer is used in the range -190° to 660°C , and for higher temperatures thermoelectric and optical thermometers are employed.

Among liquids, mercury is found to agree fairly closely with the gas scale, and mercury-in-glass thermometers are still used in cases where facility of observation is more important than the highest attainable degree of precision.

2. JOSEPH BLACK'S DISCOVERIES OF SPECIFIC AND LATENT HEATS

The invention of the thermometer provided the means for developing not only thermometric measurements but an entirely new science — that of *heat measurements*; and the pioneer in the latter development was Joseph Black (1728–1799). Black, as a young man, studied medicine, first at the University of Glasgow, and then at the University of Edinburgh, where he received the M.D. degree in 1754. It was during these years that he started his researches in chemistry and probably also began to form his new ideas about heat.

In 1756 Black returned to Glasgow as a professor. It was here, during the three years between 1759 and 1762, that he made his main discoveries in heat. In 1766 he returned to Edinburgh, where he occupied the chair of medicine and chemistry until his death. During all these years he also engaged extensively in the private practice of medicine.

Until Black made his discoveries, there was no clear distinction in people's minds between the concepts of "quantity of heat" and "degree

of hotness," or "temperature." The qualitative idea of "heat" as a "something" concerned with thermal phenomena had long existed, of course. The simple fact that an object close to a fire warms up, which surely was known from the time when man discovered fire, must have suggested that something passes from the fire to the object. But to these early people, this something that passes might well have been thought to be temperature, or degree of hotness, itself; or, again, it might be a separate something, called "heat," this heat and the resulting increase in hotness of the object seeming to play the respective roles of cause and effect.

To have clarified these ideas would have been almost impossible as long as people had to depend mainly on their thermal sense organs for a knowledge of thermal phenomena. The thermal sense organs, as is now known, generally afford us judgments that depend not on temperature alone but on a blend of several thermal properties of a body. For instance, if we touch metal and wood in cold weather, the metal will "feel" colder than the wood, even though a thermometer applied to these objects will show them to be at the same temperature.

The clarification started only after the invention of the thermometer, near the beginning of the seventeenth century. Thus Francis Bacon (1620) and, after the middle of the seventeenth century, the members of the Florentine Academy, showed evidence of distinguishing between temperature and heat. But it was Black who, in the middle of the eighteenth century, made the distinction sharp and who, moreover, was the first to conceive clearly of heat as a *measurable* physical quantity, distinct from, although related to, the quantity indicated by a thermometer and called *temperature*.

Black never published his great discoveries on heat, although he taught them in his academic lectures. These lectures, which also incorporated his chemical researches, were published in 1803, after his death, being written out by John Robison from Black's notes and those taken by some of his students. "Black's heavy duties, ill health, lack of initiative, and almost morbid horror of generalization prevented him from going further than forming a plan" for a book.

Robison dedicated the *Lectures* to James Watt (1736-1819) in a letter, printed at the beginning of volume I, of which the following is a part:

Dear Sir:

By placing your name in the front of this edition of the Lectures of our excellent Master, I think that I pay my best respects to his memory, and also do a service to the Public. By thus turning the Reader's attention to Dr. Black's most illustrious Pupil, I remind him of the important services derived from his discoveries: for surely nothing in modern times

has made such an addition to the power of man as you have done by your improvements on the steam engine, which you profess to owe to the instructions and information you received from Dr. Black. . . .

I show the Reader, in your example, that there is no preëminence in scientific attainment which he may not hope to reach by rigidly adhering to the sober plan of experimental inquiry, so constantly inculcated by Dr. Black; and turning a deaf ear to all the fascinating promises of splendid theories. The spark, which I thus throw out, may chance to light among suitable materials—some *felices animæ, quibus hæc cognoscere curæ est*—minds perhaps unconscious of their own powers. Even yours might have lain dormant, had not Dr. Black discovered its latent fire. . . .

Early in his lectures, Black mentions the various theories that had been devised to explain the nature of heat—what heat “really is.” But he warns his listeners that one cannot properly understand these theories, or how they are applied, until one has become acquainted with the effects of heat and with some discoveries that preceded the theories and gave occasion to them:

Our first business must, therefore, necessarily be to study the facts belonging to our subject, and to attend to the manner in which heat enters various bodies, or is communicated from one to another, together with the consequences of its entrance, that is, the effects that it produces on bodies. These particulars, when considered with attention, will lead us to some more adequate knowledge and information upon the subject—which again will enable you to examine and understand the attempts that have been made to explain it, and put you in the way to form a judgment of their validity.

The part of the *Lectures* devoted to the subject of heat covers some 225 printed pages. Thus the excerpts that appear in the present document represent only a very small fraction of the whole. However, they have been selected so as to bring out Black’s main discoveries.

[Excerpts from Volume I of]

LECTURES ON THE ELEMENTS OF CHEMISTRY

Delivered in the University of Edinburgh

by the late

JOSEPH BLACK, M.D.

Professor of Chemistry in that University

Physician to His Majesty for Scotland; Member
of the Royal Society of Edinburgh, of the
Royal Academy of Sciences at Paris,

and the Imperial Academy of
Sciences at St. Petersburg

Now published from his Manuscripts

by

John Robison, LL.D.

Professor of Natural Philosophy in the University
of Edinburgh

1803

Of the Distribution of Heat

An improvement in our knowledge of heat, which has been attained by the use of thermometers, is the more distinct notion we have now than formerly of the *distribution* of heat among different bodies. Even without the help of thermometers, we can perceive a tendency of heat to diffuse itself from any hotter body to the cooler ones around it, until the heat is distributed among them in such a manner that none of them is disposed to take any more from the rest. The heat is thus brought into a state of equilibrium.

This equilibrium is somewhat curious. We find that, when all mutual action is ended, a thermometer applied to any one of the bodies undergoes the same degree of expansion. Therefore the temperature of them all is the same. No previous acquaintance with the peculiar relation of each body to heat could have assured us of this, and we owe the discovery entirely to the thermometer. We must therefore adopt, as one of the most general laws of heat, the principle that *all bodies communicating freely with one another, and exposed to no inequality of external action, acquire the same temperature, as indicated by a thermometer*. All acquire the temperature of the surrounding medium.

By the use of thermometers we have learned that, if we take a thousand, or more, different kinds of matter — such as metals, stones, salts, woods, cork, feathers, wool, water and a variety of other fluids — although they be all at first of different temperatures, and if we put them together in a room without a fire, and into which the sun does not shine, the heat will be communicated from the hotter of these bodies to the colder, during some hours perhaps, or the course of a day, at the end of which time, if we apply a thermometer to them all in succession, it will give precisely the same reading. The heat, therefore, distributes itself upon this occasion until none of these bodies has a greater demand or attraction for heat than every other of them has; in consequence, when we apply a thermometer to them all in succession, after the first to which it is applied has reduced the instrument to its own temperature, none of the rest is disposed to increase or diminish the quantity of heat which that first one left in it. This is what has been commonly called an “equal heat,” or “the

equality of heat among different bodies"; I call it the *equilibrium of heat*.

The nature of this equilibrium was not well understood until I pointed out a method of investigating it. Dr. Boerhaave imagined that when it obtains, there is an equal quantity of heat in every equal volume of space, however filled up with different bodies; and Professor Musschenbroeck, in his *Physica*, expressed his opinion to the same purpose: "Est enim ignis æqualiter per omnia, non admodum magna, distributus, ita ut in pede cubico auri et aëris et plumarum, par ignis sit quantitas." ["For the heat is distributed through all (the bodies), not in proportion to their (weight), so that in a cubic foot of gold and of air and of feathers, there will be an equal quantity of heat.] The reason they give for this opinion is that, to whichever of those bodies the thermometer be applied, it gives the same reading.

But this is taking a very hasty view of the subject. It is confounding the quantity of heat in different bodies with its intensity [temperature], though it is plain that these are two different things, and should always be distinguished, when we are thinking of the distribution of heat. . . .

Hermann Boerhaave (1668–1738) was a great teacher of medicine at the University of Leiden who performed a useful service by collecting and classifying the scientific knowledge of his period and publishing it in textbooks on medicine (1708) and on chemistry (1732). Pieter van Musschenbroeck (1692–1761) went to Leiden in 1740 as professor of philosophy; he also wrote extensively on physical science.

As Black says, Boerhaave and Musschenbroeck thought that, if a number of different objects were placed in, say, a room and allowed to remain there until all had acquired the same temperature, as indicated by a thermometer, then this meant that heat was also distributed uniformly throughout the room and its contents—that every cubic inch of space in the room, whether it be occupied by wood, metal, air, or anything else, contained the same quantity of heat. On the contrary, asserts Black, when the various objects have come to the same temperature, there exists, not an equal distribution of heat throughout the room, but what he calls an "equilibrium of heat," meaning that there is no longer any flow of heat among the objects. Notice that *temperatures* are *observed* with a thermometer, whereas Black's notion that a something called *heat* passes from bodies of higher temperature to those of lower temperature is of the character of a hypothesis.

In the section that follows, on "Capacities for Heat," Black investigates the question of the quantities of heat needed to increase the temperatures of different bodies by the same amount. He says that it was formerly supposed that these required quantities of heat were directly proportional to the "quantities of matter" in the bodies; or, since the "quantities of matter" in different bodies can be compared by compar-