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Quantification of heat (**)

Summary - The study of the thermal equilibrium of two bodies (initially at different temperatures) and of the changes of state lies at the base of calorimetry and consequently of heat quantification. Only after a full understanding of these two phenomena, towards the middle of the eighteenth century, did physics of heat take on the connotations of a quantitative science.

Riassunto - Lo studio dell'equilibrio termico di due corpi (inizialmente a diverse temperature) e dei cambiamenti di stato è alla base della calorimetria e quindi della quantificazione del calore. Solo dopo una piena comprensione di questi due fenomeni verso la metà del diciottesimo secolo la fisica dei fenomeni termici ha assunto la connotazione di una scienza quantitativa.

Scientific progress and instrumentation are inextricably intertwined: the discovery of new phenomena can lead to new ways of characterizing or quantifying the systems scientists study, and advances in instrumentation can open up new ways for conducting scientific research.

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As J. Heilbron emphasizes,² the successful quantification of physical theory presupposes the existence of appropriate concepts expressible mathematically and amenable to test by measurements. The quantification of heat theory preliminarily required the concepts of temperature (Θ), capacity (C) and quantity of heat (Q). The notion of temperature emerged in experiments on the dilatation of hot bodies by C. Drebbel, G. Galilei, S. Santorio, et al. in the first half of the XVII century. It was then improved with the realization of the first thermometers by the Accademia del Cimento, the Académie Royale des Sciences, the Royal Society. The notion of capacity (for heat) emerged in experiments on thermal equilibrium by B. Taylor,

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¹ J.I. BRAUMAN, *Editorial*, Science, 242 (1988), n. 4876.

² J.L. HEILBRON, *Elements of Early Modern Physics*, Berkeley 1982, p. 218.

H. Boerhaave, G.D. Fahrenheit, J.T. Desaguliers, et al. in the first half of the XVIII century. By putting two bodies at different temperatures in contact, the equilibrium temperature was measured, and its value was always between the two initial temperatures. Therefore the warmer body cooled down and the colder warmed up and this was explained with a flux of «heat» from one to the other. Generally the warmer body cooled down in a different degree with respect to the warming up of the colder body and this was the birth of the concept of capacity (for heat) of a body. After the 'operative' definition of temperature and capacity, in the second half of the XVIII century the quantity $Q = C \Delta\Theta$ (where $\Delta\Theta$ is the body variation of temperature) was assumed as the measurement of the heat quantity exchanged by a body. Another methodology for measuring heat quantities was developed with the study of the changes of state.

I. Origins

Medieval and Renaissance studies of thermal phenomena were based on the sensory perception of the observer and were dominated by the fundamental conceptual difficulty of the opposites hot and cold of the aristotelian-scholastic philosophy.³ In traditional Arabic alchemy there was the attempt to distinguish between quantities of hot (or cold) and intensity of hot (or cold) in terms of *extensio* or *intensio* of a quality and to a quantification of qualities.⁴ This attempt was taken up and spread in Europe particularly thanks to the work of Arnald of Villanova.⁵

Within this context of concepts was there the problem of establishing a relationship between «intensity of hot» of a mixture and that of its constituents. If, using modern formalism, H is hot, C is cold and I is the intensity of hot of a body, in similar fashion to the laws of motion,⁶ for $H > C$ one has $\Theta = H/C$, where $\Theta = I$ ('classical' law) or $\Theta = 2I$ (Alkindi-Bradwardine's law).⁷ If two bodies m_1 and m_2 in weight, hot intensity I_1 and I_2 , hot and cold H_1, C_1 and H_2, C_2 (for which therefore $\Theta_i = H_i/C_i, i=1,2$) are mixed together, the hot and cold of their «mixture» is given by $H \propto m_1 H_1 + m_2 H_2, C \propto m_1 C_1 + m_2 C_2$,⁸ and thus for the mixture itself one has

³ See: M. CLAGETT, *Giovanni Marliani and late medieval Physics*, New York 1941 (in particular p. 34 and fol.); M. CLAGETT, *The Science of Mechanics in the Middle Ages*, Madison (Wisconsin) 1959 (in particular chap. 6); M. CLAGETT, *Nicole Oresme and the medieval geometry of qualities and motions*, Madison (Wisconsin) 1968 (in particular pp. 50-73); A.C. CROMBIE, *Augustine to Galileo*, «Melbourne», 1957² (in particular p. 263 and fol.); M. GRILLI and F. SEBASTIANI, *Le origini della fisica del calore*, «Physis», 24 (1982), 301 and 25 (1983), 67.

⁴ A.C. CROMBIE, *Quantification in Medieval Physics*, «ISIS», 52 (1961), 143; E. SYLLA, *Medieval Quantification of Qualities...*, «Arch. Hist. Ex. Sc.», 8 (1971), 9. It is almost superfluous to underline the «incommensurability» of the aristotelian-scholastic conceptions and of modern science and thus also the impossibility of establishing an exact correspondence between the terminologies.

⁵ M. MC VAUGH, *Arnald of Villanova and Bradwardine's Law*, «ISIS», 58 (1967), 56.

⁶ As M.B. HESSE emphasizes in *Forces and Fields*, London 1961, p. 63, the term κίνησις, generally translated as «motion», has the more general meaning of «change» (qualitative and quantitative).

⁷ S. DRAKE, *Medieval Ratio Theory vs compund medicines...*, «ISIS», 64 (1973), 67.

⁸ See R. SKABELUND and P. THOMAS, *Walter of Odington's Mathematical Treatment of the Primary Qualities*, «ISIS», 60 (1969), 331.

$$\theta = \frac{H}{C} = \frac{m_1 H_1 + m_2 H_2}{m_1 C_1 + m_2 C_2}.$$

In the medieval work *De graduatione medicinarum compositarum* attributed to Roger Bacon, a law is put forward for the mixture of two portions (m_1, m_2) of the same substance, which using modern formalism may be expressed as $(I_2 - I)$: $(I - I_1) = m_1 : m_2$ ⁹ that is as

$$I = \frac{m_1 I_1 + m_2 I_2}{m_1 + m_2}.$$

A numerical example is also given: if one mixes two pounds of hot water of the sixth degree (of a given 'empirical' scale) with one pound of water of the twelfth degree, the «caliditas» of the mixture is eight degrees, «because the distance between six and eight is half the distance that is between eight and twelve, in the same way as one pound of water is half two pounds of water». This law, which recalls the law of the lever and thus 'statics' while the previous ones go back to 'dynamics', did not have much of a following and was rediscovered *ex novo* only in the eighteenth century.

Certain thermal phenomena as cooling and heating of a body, the thermic behaviour of mixtures (typically of medicines), etc., were observed in the fourteenth, fifteenth and sixteenth centuries with the rudimentary methods available (the only means to determine the «intensity» or the «degree» of hot and of cold of an object was the sensory perception of the observer) and widely discussed.

The aristotelian-scholastic 'theory' of thermal equilibrium of mixtures still had supporters in the seventeenth century; thus J.B. Morin, who thought himself the first to explicitly formulate the law that gives the «degree of hot» of the mixture of two portions of the same substance, in *Astrologia Gallica*,¹⁰ proposed the law

$$\theta = \frac{[m_2 \theta_2] \theta_2 + [m_1 (8 - \theta_1)] \theta_1}{[m_2 \theta_2] + [m_1 (8 - \theta_1)]},$$

that is, the «degree of hot» of the mixture, Θ , is the weighted average of the degrees of hot Θ_2 and Θ_1 ($< \Theta_2$) of the two components, weighed respectively on «calidi virtus totalis», $m_2 \Theta_2$, of the hotter body and on «frigidi virtus totalis», $m_1 (8 - \Theta_1)$, of the colder body. Morin used a widely employed degree of hot scale, the grading of which went from zero to eight and in which the degrees of cold were the complement to eight of those of hot.

⁹ See M. CLAGETT, *Science of Mechanics*, op. cit., chap VI. «When the quantities of two portions to be mixed are different and their *intentiones* are raised to different degrees, [...] whatever the proportion of the quantity of one portion as regards the other, then so much will be the proportion of the difference between the degree of the mixture and the degree of the greater portion of the mixed bodies and the distance that there is between the same degree of the mixture and the degree of the smaller part».

¹⁰ The Hague 1661, pp. 158-159; see D. MC KIE and N.H. HEATHCOTE, *The discovery of specific and latent heat*, London 1935, Appendix.

II. *The thermometer*

G. Galilei suggested moving away from the fundamental conceptual difficulty of the binomials of aristotelian-scholastic physics even in the study of thermic phenomena, also present to some extent as regards these phenomena in atomism that saw heat generating and cold generating atoms. Galilei rejected the hot-cold dualism maintaining that «il freddo non [è] altro che privazione di caldo» («cold [is] none other than the privation of hot».¹¹ The idea of «natura privativa» («privative nature») of cold affirmed itself definitively¹² in the second half of the seventeenth century with the temporary assertion of the kinetic theory of heat.

The second half of the seventeenth century saw the start of considerable experimental laboratory activity regarding the study of thermal phenomena. The emergence of this activity was also linked to the birth of three famous institutions: the Accademia del Cimento, the Académie Royale des Sciences and the Royal Society. There was a deeper study of medieval and renaissance empirical knowledge and research no longer limited to the observing of natural and daily phenomena, but also of processes brought about and controlled in the laboratory. Seventeenth century experimentation, although trying to abolish what A. Koyré calls the world of the more or less, the world of sensory perceptions and qualities, the world of the overestimation of daily experience, still could not overcome a semiquantitative stage in the study of thermal phenomena. This was due to the fact that, even if the construction and study of the first thermometers started at the end of the sixteenth century, the constructing of thermometers able to provide comparable and reproduceable indications only came about at the end of the seventeenth century. This century saw the thermometer more as an object of investigation and discussion than a real measuring instrument. In particular, there was the constructing and study of the air thermoscope¹³ (Drebbel, Galilei, Santorio,... around 1600), the alcohol thermometer (Accademia del Cimento, 1667) and later the linseed oil thermometer (Royal Society, 1701), the air thermometer (Académie des Sciences, G. Amontons, 1702), the mercury thermometer (G.D. Fahrenheit, 1714). Only in the early decades of the eighteenth century were the thermometric scales of two fixed points established (G.D. Fahrenheit, 1714; R.-A. Réaumur, 1734; A. Celsius, 1742). The thermometer then became the basic instrument in the study of thermal phenomena and the temperature became a operatively defined quantity.

In the proposal of the galilean C. Renaldini,¹⁴ member of the Accademia del Cimento, to calibrate the alcohol thermometer by placing it in mixtures of known

¹¹ Fragments of uncertain date; Edizione nazionale delle opere di Galileo, vol. VIII, Firenze 1898, p. 634-636.

¹² There would follow a half-hearted attempt at rediscussing it in the second half of the eighteenth century, with the advent of the theory of two fluids of electric phenomena.

¹³ For the history of the thermometer see: E. MACH, *Principles of the Theory of Heat (Historically and critically elucidated)*, Engl. transl., Dordrecht 1986, chap. 1; W.E.K. MIDDLETON, *A History of the Thermometer and its Use in Meteorology*, Baltimore 1966.

¹⁴ *Philosophia Rationalis atque Moralis...*, Padova 1681.

portions of «ice-cold» water and «boiling-hot» water, it was implicitly assumed that the equilibrium temperature Θ of a mixture of two masses of water m_1 and m_2 respectively at temperatures Θ_1 and Θ_2 was given by

$$\theta = (m_1\theta_1 + m_2\theta_2) / (m_1 + m_2)$$

III. *The mixtures*

The first scientists to experimentally study thermal equilibrium of mixtures in a quantitative fashion were B. Taylor, D.G. Fahrenheit (on a suggestion by H. Boerhaave) and J.T. Desaguliers.

In 1723 Taylor put Renaldini's ideas on the calibration of thermometers into practice.¹⁵ The English scientist in fact mixed different quantities of boiling-hot water and «cold» water so that the total quantity was always the same, and observed that the increase in temperature with respect to the cold water, indicated by a linseed oil thermometer, was «accurately proportional to the quantity of hot water in the mixture».¹⁶

The distinction between heat, seen as the cause of thermal phenomena, and temperature, seen as the indication (on the thermometer) of heat present in bodies, was sufficiently clear, on general lines, at the start of the eighteenth century.¹⁷ It was, however, general opinion that the temperature of a body was directly proportional to the heat possessed by the body and inversely proportional to the volume or mass of the body itself. Naturally, this assumed proportionality between heat of a body and its temperature was, on a practical level, the object of confusion between the two concepts that often ended up mistaken for each other.

Boerhaave¹⁸ maintained that the study of mixtures could lead to the understanding of how heat was distributed between two bodies at thermic equilibrium. On the basis of experiments carried out on his suggestion by Fahrenheit, the great Dutch scientist came to the conclusion that heat was present in the bodies at thermic equilibrium according to their volume. In fact, «mixing» between them a given volume of water V and a volume of mercury equal to $3V/2$, initially at different temperatures, one observed that equilibrium temperature was the same as that seen when mixing equal volumes of water initially at the same temperatures as the previous experiment.¹⁹ Since it was maintained that in equilibrium, heat could be present in bodies

¹⁵ *An Account of an Experiment...*, Phil. Trans. R.S.L. 1723, p. 291.

¹⁶ In fact $\Theta - \Theta_1 = [(m_1 \Theta_1 + m_2 \Theta_2) - \Theta_1] / (m_1 + m_2) = m_2 (\Theta_2 - \Theta_1) / (m_1 + m_2)$, and the term in braces is constant for the way Taylor performed the experiment.

¹⁷ Until the end of the nineteenth century, its nature aside, one talked of heat «contained» in bodies and of heat «exchanged» between bodies, linking the modern concepts of internal energy and heat. A detailed study of the physics of thermal phenomena in the eighteenth century is found in F. SEBASTIANI, *La fisica dei fenomeni termici nel Settecento*, «Physis», 26 (1984), 29 and 27 (1985), 45.

¹⁸ *Elementa Chemiae*, Leida 1732, 2 volumes; I vol., p. 268 and fol.

¹⁹ Because of a misunderstanding with Fahrenheit, Boerhaave enunciated the law of thermal equilibrium of two equal masses or volumes of the same substance in the form $\Theta = (\Theta_2 - \Theta_1)/2$ in-

only according to either volume or mass, Boerhaave concluded that the previous measurement indicated that heat was distributed in equal parts between approximately equal volumes (he considered the factor 3/2 non-significant) of water and mercury (that have different masses for a factor of approx. 14, or around 20 if the factor 3/2 is taken into account).²⁰ Boerhaave was the first scientist to explicitly express heat conservation (which he considers a peculiar substance) in all thermic phenomena and therefore particularly in mixtures.

Desaguliers²¹ instead considered that, «mixing» equal masses of water and mercury at different temperatures, equilibrium temperature was the same as when observing equal masses of water initially at the same temperature as the previous case²² and concluded that heat, of which not surprisingly he had a kinetic view,²³ was distributed between bodies in thermic equilibrium according to their mass.

IV. *The equilibrium temperature of a water-water mixture*

G.W. Krafft,²⁴ considering Morin's formula inadequate, assumed that the more general form for equilibrium temperature Θ of two masses of water m_1 and m_2 initially at temperature Θ_1 and Θ_2 was $\Theta = (a \Theta_1 + b \Theta_2) / (c m_1 + d m_2)$, where a, b, c, d , are coefficients to be determined. In that if the two masses are of the same temperature one has $\Theta = \Theta_1 = \Theta_2$, Krafft placed $a+b = c m_1 + d m_2$; if $m_2 \rightarrow 0$ one has $\Theta = \Theta_1$ (or, if $m_1 \rightarrow 0$ one has $\Theta = \Theta_2$), he also put $c m_1 = a$ and $d m_2 = b$ and definitively $\Theta = (c m_1 \Theta_1 + d m_2 \Theta_2) / (c m_1 + d m_2)$. On the basis of results obtained from some experiments, Krafft found $c/d = 11/8$ and thus (for $\Theta_2 > \Theta_1$) he wrote

$$\theta = \frac{11m_1\theta_1 + 8m_2\theta_2}{11m_1 + 8m_2} .$$

G.W. Richmann²⁵ was the first scientist to explicitly and correctly formulate

stead of in the correct form $\Theta = (\Theta_2 + \Theta_1)/2$ (it is not a printing error!); to this end, see: M.G. IANNIELLO and F. SEBASTIANI, *Il caso Boerhaave*, «Riv. St. Scienza», 1 (1984), 403.

²⁰ Since mercury has a specific heat equal to approx. 1/30 of that of water, 'mixing' equal volumes of water and mercury one obtains $\Theta \cong [\Theta_1 + (\Theta_2/2)] / 1.5$; 'mixing' equal masses one has instead $\Theta' \cong \Theta_1 + (\Theta_2/30)$.

²¹ *A Course of Experimental Philosophy*, 2 volumes, London 1734-44; II vol., p. 296 and fol.

²² It is difficult to explain how Desaguliers, a very able experimenter, could have made such an error.

²³ «The late learned and ingenious Dr. Brook Taylor and myself made some Experiments, whereby it appar'd to us that *actual Heat* was to *sensible Heat* [temperature] as *Motion* [linear momentum] is to *Velocity*». Note that in a completely inelastic collision in one dimension, of two bodies of mass m_1 and m_2 , with initial velocity v_1 and v_2 , the common final velocity v is given by $v = (m_1 v_1 + m_2 v_2) / (m_1 + m_2)$, a similar expression to that of equilibrium temperature of two portions of the same substance $\Theta = (m_1 \Theta_1 + m_2 \Theta_2) / (m_1 + m_2)$.

²⁴ *De Calore ac Frigore Experimenta*, «Comm. Ac. Sc. Petrop. 1744-46», 14 (1748), 218; see also Mc KIE and HEATHCOTE, *op. cit.*, p. 54 and fol.

²⁵ *De Quantitate Caloris, quae post miscelam fluidorum, certo gradu calidorum, oriri debet, Cogitationes*, «Novi. Comm. Ac. Sc. Petrop. 1747-48», 1 (1750), 152; *Formulae pro gradu excessus Caloris mixtiii...*, idem, 168; see also Mc KIE and HEATHCOTE, *op. cit.*, p. 65 and fol.

the law that gives equilibrium temperature of two portions of the same substance. Richmann assumed that heat was distributed uniformly in the mixture of two masses m_1 and m_2 of the same substance initially at temperatures Θ_1 and Θ_2 . Because if the same heat is distributed in a mass 2, 3, 4,... times greater, temperature is reduced to 1/2, 1/3, 1/4,... i.e. temperature is inversely proportional to mass, then if heat relative to mass m_1 is distributed in mass $m_1 + m_2$ a temperature $\Theta' = m_1 \Theta_1 / (m_1 + m_2)$ should result; similarly, heat relative to m_2 should give rise to a temperature $\Theta'' = m_2 \Theta_2 / (m_1 + m_2)$. Since the heat of m_1 and m_2 is distributed in mixture $m_1 + m_2$, final temperature will be given by the sum of the temperatures Θ' and Θ'' calculated above, i.e.

$$\theta = \frac{m_1\theta_1 + m_2\theta_2}{m_1 + m_2}.$$

Richmann compared the previsions of this formula with the results of six experiments relating to water-water mixture noting a good agreement.

Almost at the same time, also abbé Nollet²⁶ stated that when «substances that may be touched, or which may be mixed, are of the same nature, heat moves from the hotter to the less hot according to their volumes [or, as underlined further on, according to their mass, since in the case considered it is the same], that is to say, if two equal quantities of the same liquid, one hot and the other cold, are mixed together, the first shares equally with the second that heat which it has more than the other». He illustrated the statement with the example of two volumes of water the initial temperatures of which were respectively 10 and 40 «degrees of heat», which mixed led to 25 degrees, i.e. $\Theta = (\Theta_1 + \Theta_2)/2$.

In the last edition of the widely read treatise by P. Musschenbroek,²⁷ regarding the equilibrium temperature of mixtures, we read:

«When one mixes together two portions of the same fluid, one of which is hotter than the other, the heat of the former will diminish while that of the other will increase, so that a new degree of heat will result from the mixture.²⁸ To understand this new degree of heat one must resort to the following analogy. Let m_1 be the mass of one of the two portions of liquid, m_2 that of the other; if one designates Θ_1 as the temperature of the first of the two masses and Θ_2 as the temperature of the other mass, the heat of the former will be equal to $m_1 \Theta_1$, that of the second will be equal to $m_2 \Theta_2$. The sum of the heat of the two masses will be $m_1 \Theta_1 + m_2 \Theta_2$ and therefore the temperature of the mixture will equal $(m_1 \Theta_1 + m_2 \Theta_2) / (m_1 + m_2)$ ».

²⁶ *Leçon de physique expérimentale*, 6 volumes, Paris 1743-1748; edizione veneta, 5 volumes, Venezia 1749, vol. IV, pp. 257-258.

²⁷ *Physicae Experimentales et Geometricae*, Leida 1762 (posthuma).

²⁸ This author, like the previous, often used the term *calor* to indicate both temperature and the quantity of heat; in the translation one has tried to adapt the terminology to the modern one.

In these deductions it is taken for granted that the heat «possessed» by one body is equal to the product of its mass times its temperature. Musschenbroek further emphasized that regarding «the mixing of heterogeneous liquids with different temperatures» new experiments needed to be performed.

V. *The capacity for heat*

J. Black is unanimously recognized²⁹ as the founder of the (quantitative) science of heat, having put it on rigorous methodological and metrological foundations with his research started in 1757. Despite the fact that his research was only published in 1803 after his death,³⁰ it had widespread and immediate impact in Britain and on the Continent. This was also due to the publication of: i) an anonymous work (*An Enquiry into the General Effects of Heat; with Observations on the Theories of Mixture*)³¹ gathered from Black's lectures; ii) an anonymous account of a paper on Black's discoveries read by N. Desmarests in 1772 before the Académie Royale des Sciences of Paris;³² iii) *Animal Heat*³³ by A. Crawford, in which Black's discoveries and methods are widely employed; iv) *Essai sur la nouvelle théorie du feu élémentaire, et de la chaleur des corps*³⁴ by J.H. Magellan, in which Black's ideas on heat are widely expounded.

Only with Black did one arrive at clearly and unequivocally distinguishing the concept of temperature (the quantity indicated by the thermometer) from the concept of quantity of heat (the quantity measurable also, but not only, by means of measurements of differences in temperature).

Around 1760 Black experimentally observed that the addition or the subtraction of heat to and from a body could produce both a variation in temperature, a well-known phenomenon which lay at the base of the confusion between temperature of the body and the heat that this «possessed», and a change in its state of aggregation without temperature variation.

Thus in his *Lectures*, Black masterfully emphasized what thermal equilibrium was:

²⁹ On Black see: D. ROLLER, *The early Development of the Concepts of Temperature and Heat*, in «Harvard Case Histories in Experimental Sciences», Harvard (Mass.) 1957, p. 199 and fol.; *Joseph Black 1728-1799*, A commemorative Symposium, Edinburgh 1982 (in particular H. Guerlac's article, J. Black's work on heat, p. 13 and fol.); MC KIE and HEATHCOTE, *op. cit.*, pp. 11-30. Lavoisier, always very low on quotations, on p. 19 of the *Traité élémentaire de chimie* (Paris 1789), declares: «The capacity of bodies to contain [...] heat [is] quite the appropriate expression introduced by the English physicists who had the first correct notions on the subject».

³⁰ *Lectures on the Elements of Chemistry*, edited by J. Robison, 2 volumes, Edinburgh 1803.

³¹ London 1770.

³² *Expériences du docteur Black sur la marche de la chaleur dans certaines circonstances*, «Introduction aux Observations sur la Physique... par l'abbé Rozier», vol. II, 1772; reprint 1777, p. 428.

³³ *Experiments and Observations on Animal Heat, and the Inflammation of Combustible Bodies*, London 1779.

³⁴ London 1780; published later as a whole with the same title in «Observations sur la Physique...», 17 (1781), 375 and 411.

«The heat [has] a tendency to diffuse itself from any hotter body to the cooler around, until it be distributed among them, in such a manner that none of them are disposed to take any more heat 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, acquires the same degree of expansion. Therefore the temperature of them all is the same, and the equilibrium is universal. [...] We must therefore adopt, as one of the most general laws of heat, *that all bodies communicating freely with each other, and exposed to no inequality of external action, acquire the same temperature, as indicated by thermometer.* [...] 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; [...] it is confounded the quantity of heat in different bodies with its general strength or intensity, though it is plain that these are two different things, and should always be distinguished, [particularly] when we are thinking of the distribution of heat».³⁵

And with the same flair he underlines the concept of thermal capacity:

«It was formerly a common supposition, that the quantity of heat required to increase the heat [the temperature] of different bodies by the same number of degrees, were directly in proportion to the quantity of matter in each; and therefore, when the bodies were of equal size, the quantities of heat were in proportion to their density. But very soon after I began to think on this subject (the year 1760), I perceived that this opinion was a mistake, and that the quantities of heat which different kinds of matter must receive, to reduce them to an equilibrium with one another, or to rise their temperature by an equal number of degrees, are not in proportion to the quantity of matter in each, but in proportions widely different from this, and for which no general principle of reason can yet be assigned».³⁶

Black emphasizes that in the mixture, even if «the quantity of heat which [a substance] has gained is the very same as that which [the other] has lost», the two substances undergo a different temperature variation, i.e. they have a different «*capacity* (if [it] may be allowed to use this expression) *for heat*».

Lectures gave no details of Black's method of determining the «capacities for heat», but we have Robison's account in note: «Dr. Black estimated the capacities by mixing the two bodies in equal masses, but of different temperatures; and then stated their capacities as inversely proportional to the changes of temperature of each by the mixture»;³⁷ i.e. $C_2/C_1 = (\Theta - \Theta_1) / (\Theta_2 - \Theta)$ ³⁸ and thus

³⁵ *Lectures*, vol. I, 100.

³⁶ *Lectures*, vol. I, 79.

³⁷ *Lectures*, vol. I, p. 506.

³⁸ Being $m_2 = m_1$ the relation C_2/C_1 is the same as the relation c_2/c_1 of specific heat. The term *specific heat* was introduced by J.H. Magellan in *Essai*, in which was published a table of specific heat measured by R. Kirwan.

$$\theta = \frac{C_1\theta_1 + C_2\theta_2}{C_1 + C_2}.$$

A. Crawford³⁹ attributes to W. Irvine,⁴⁰ Black's pupil and co-researcher, the formula for the calculation of 'specific heat' (capacity of the unitary mass, $c = C/m$) of a body when its mass m_2 is different from m_1 of the water in which it is immersed: $c_2/c_1 = m_1 (\Theta - \Theta_1)/m_2 (\Theta_2 - \Theta)$ and thus

$$\theta = \frac{m_1c_1\theta_1 + m_2c_2\theta_2}{m_1c_1 + m_2c_2}.$$

These formulas are easily derived if one assumes that among the bodies in thermal contact equal and opposite heat quantities

$$Q = m c \Delta\Theta$$

are exchanged (a body gains the heat that the other loses); indeed with the previous notations this involves

$$m_1 c_1 (\Theta - \Theta_1) = - m_2 c_2 (\Theta - \Theta_2),$$

relation from which the preceding ones follow.

It is the general opinion⁴¹ that the study of mixtures, in which heat behaves as a quantity that is conserved, contributed considerably to consolidate substantialistic theories of the nature of heat. The similarity between the formula that gives equilibrium temperature and the one $h = (S_1 h_1 + S_2 h_2) / (S_1 + S_2)$ giving equilibrium level h of a liquid in two communicating vessels with constant sections S_1 and S_2 , initially at levels h_1 and h_2 , is indeed very strict.

VI. *The method of mixtures*

The expressions for the quantity of heat $Q = mc\Delta\Theta$ and for the equilibrium temperature $\Theta = (m_1 c_1 \Theta_1 + m_2 c_2 \Theta_2) / (m_1 c_1 + m_2 c_2)$, in the form that is still found today in physics books, were first published in the famous *Mémoire sur la chaleur*⁴² by P.-S. Laplace and A.-L. Lavoisier.⁴³

³⁹ *Animal Heat*, op. cit., p. 37.

⁴⁰ Like his mentor, Irvine did not publish his own research.

⁴¹ See for example E. MACH, op. cit., p. 173.

⁴² Read at the Académie Royale des Sciences in 1783; included in Mem. Acad. R. Sci., année 1780, Paris 1784, p. 355; published also in a booklet of about eighty pages in Paris in 1783; reprinted in Paris in 1920.

⁴³ For Lavoisier-Laplace cooperation, see the classic essay by H. GUERLAC, *Chemistry as a branch of Physics: Laplace's collaboration with Lavoisier*, «Hist. St. Phys. Sc.», 7 (1976), 193.

«Let us suppose that in general in the mixture [mélange] of more substances that do not chemically react with each other, the quantity of heat always remains the same. On the basis of this assumption [...] one may obtain a general and very simple rule to determine the specific heat of the bodies with the mixtures. In fact, if one denotes the mass of the hotter body as m_2 , expressed in pounds; Θ_2 as the degree on the thermometer that indicates its temperature; c_2 as the heat necessary to raise the temperature of one pound of this substance by one degree; if one terms m_1 , Θ_1 , c_1 the same quantity relating to the less hot body, and finally, Θ the degree on the thermometer that indicates the temperature of the mixture when it has become uniform; it is obvious that the heat lost by the body m_2 is in relation to its mass m_2 and to the number of degrees $\Theta_2 - \Theta$ by which its temperature has decreased, multiplied by quantity c_2 of heat that may raise the temperature of one pound of this substance by one degree; thus, one obtains $m_2 c_2 \cdot (\Theta_2 - \Theta)$ as the expression of this quantity of heat lost. For the same reason, the quantity of heat absorbed by body m_1 is in relation to its mass m_1 and to a number of degrees $\Theta - \Theta_1$ by which its temperature has increased, multiplied by the quantity c_1 , thus giving $m_1 c_1 \cdot (\Theta - \Theta_1)$ as the expression of this quantity of heat. But, since it is assumed that after mixing the quantity of heat is the same as before, one must equate the heat lost by body m_2 to the heat absorbed by body m_1 ; from which is obtained

$$m_2 c_2 (\theta_2 - \theta) = m_1 c_1 (\theta - \theta_1);$$

this expression does not allow knowledge of c_1 or c_2 , but gives their ratio

$$\frac{c_2}{c_1} = \frac{m_1 (\theta - \theta_1)}{m_2 (\theta_2 - \theta)}.$$

Thus one obtains the specific heat ratio of the two bodies m_2 and m_1 , in such a way that if different substances in nature are compared with the same substance, with common water for example, then the specific heat of these substances relative to that of the reference substance may be determined».

Calorimetry based on mixtures may be said at this point to be a methodology gained from the physics of thermal phenomena. J.C. Wilcke, in a paper presented to the Swedish Academy in 1781⁴⁴ and a translation of which was published in France in 1785,⁴⁵ stated that the procedure to be followed to measure the specific heat of a body using the method of mixtures as: i) weighing the body of which one which is to know the specific heat (generally taking a body of unitary mass, i.e. of one pound); ii) immersing the body in «water that is boiling», holding it suspended by

⁴⁴ *Rön om Eldens specifika mychenhet uti fasta kroppar och des afmätande*, «K. Svenska Vet. Akad. Nya. Handl.», 2 (1781), 49.

⁴⁵ *Observations sur la quantité de chaleur spécifique des corps solides, et sur la manière de la mesurer*, «Observations sur la Physique...», 26 (1785), 256 et 381.

a thread, and leaving it for a long while; iii) at the same time, preparing in a thin metal vessel a mass of cold water, «at the temperature of ice», equal to that of the body (the water may be obtained from a vessel containing water and snow, «taking care that there be no snow in the water extracted»); iv) immersing the hot body into this vessel (always holding it by the thread so that it should not touch the sides or the bottom; v) reading the equilibrium temperature of the mixture on a thermometer immersed in the water (taking care that all the mass of the water has reached the same temperature); vi) repeating the measurements times over (about ten times) and arranging the data in a table; vii) calculating the values of specific heat relative to the different measurements and then obtaining the average value.

VII. *Latent heat*

While researching the phenomena that always occur at the same temperature and during which the latter is constant, in order to determine a fixed point in the thermometric scale and the calibration of thermometers, the academics of the Cimento⁴⁶ discovered that water froze «sempre alla medesima tempera di caldo e di freddo» (always at the same degree of hot and cold), and G. Amontons⁴⁷ that «common boiling water cannot gain any greater degree of heat however long it is left on the fire [...] and however intense this fire be». It was then soon realized that all changes of state occur at a welldefined temperature, at a given pressure.⁴⁸ But the constance of temperature itself during the change in state lead to the conclusion that this happened without (or with very little) heat exchange.

Once again, it is Black who discovered that changes in state were accompanied by a considerable exchange of heat. In *Lectures* we read:⁴⁹ «Fluidity was universally considered as produced by a small addition to the quantity of heat which a body contains, when it is once heated up to its melting point; and the return of such a body to a solid state, as depending on a very small diminution of the quantity of its heat, after it is cooled to the same degree». Black is of another opinion: if general opinion were true, snow and ice accumulated over a severe winter should melt rapidly and completely as soon as atmospheric temperature reached the value corresponding to their melting point. Instead, snow and ice melt very slowly and it takes many weeks of hot weather to melt them, to such an extent that they remain on certain mountains over the entire summer. From this Black deduces that a great quantity of heat is necessary to induce melting in ice and it is just because of this that melting happens only slowly.

To prove this hypothesis and to quantify it, Black carried out a series of experi-

⁴⁶ L. MAGALOTTI, *Saggi di naturali esperienze fatte nell'Accademia del Cimento*, Firenze 1667.

⁴⁷ *Discours sur quelques propriétés de l'air et le moyen d'en connoître la température dans tous les climats de la Terre*, «Hist. Ac. Roy. Sc.», année 1702, p. 155.

⁴⁸ See, for example, the articles by M. Grilli and F. Sebastiani quoted in note (1).

⁴⁹ *Lectures*, vol. I, p. 116.

ments.⁵⁰ In particular, mixing different quantities of melting ice with hot water at different temperatures, he observed that equilibrium temperature is considerably less than the one that would have been obtained with two masses of water at the same initial temperature. In fact, while mixing two equal masses of water at the temperature of melting ice ($32^{\circ}\text{F} = 0^{\circ}\text{C}$) and water at 176°F ($= 80^{\circ}\text{C}$), equilibrium temperature resulted to be 104°F ($= 40^{\circ}\text{C}$); instead by mixing two equal masses of melting ice (32°F) and water at 176°F , the ice melted completely and equilibrium temperature was effectively 32°F .⁵¹ Thus, to melt a mass of ice at 32°F the quantity of heat is needed that would produce a rise of 144°F or 80°C in an equal mass of water initially at the same temperature.

Black also dedicated himself to the study of the changing in state from liquid to steam (in particular the boiling of water), demonstrating that also in this case, contrary to general opinion, there was the exchange of a great quantity of heat without for this reason varying the temperature. He thus found that the quantity of heat necessary to evaporate a given mass of water at boiling point ($212^{\circ}\text{F} = 100^{\circ}\text{C}$) was the same as that which would produce a rise in temperature equal to approximately 810°F or 450°C in the same mass of water, if there were no change in state.

Since neither water obtained in the liquid state through the melting of ice, nor steam obtained through the boiling of water are any the hotter despite the great absorption of heat, the heat producing the changes in state was termed «latent heat» by Black. In changes of state, the effect of heat does not involve heating the bodies but changing their state of aggregation: «as ice, united with a certain quantity of heat, is water, so water, united with another quantity of heat, is steam or vapour».

In the mentioned account of the paper presented by Desmarests to the Académie des Sciences in 1772, the pioneer work of Black in the study of thermic phenomena is justly recognized: «The Edinburgh school will leave its mark in the history of physics for having principally dealt with heat [...]; Doctor Black has contributed more than any other to widen knowledge in this field».

VIII. *Equilibrium temperature of a water-ice mixture*

Just in 1772, even J.C. Wilcke presented the results of a series of experiments on equilibrium temperature of a water-ice mixture to the Swedish Academy.⁵² The Swedish physicist, also, observed that by mixing hot water and snow the equilibrium temperature was much less than that foreseen by Richmann's formula. In particular, if water at 72°C ⁵³ was mixed with an equal mass of snow at 0°C , all the snow

⁵⁰ In *Lectures* Black recalls having made public his results on latent heat in 1762, in a conference at the Philosophical Club of Glasgow University, and from then on having presented them in his chemistry lectures in the same university and then in that of Edinburgh.

⁵¹ A. VOLTA in *Memoria intorno al calore* (Pavia 1783) would define this experiment «parlante» (talking).

⁵² *Om Snons kyla vid Smaltningen*, «K. Svenska Vet. Akad. Handl.», 33 (1772), 97; see Mc KIE and HEATHCOTE, *op. cit.*, p. 78 and fol.

⁵³ 72°C , instead of 80°C , because inevitably some water adheres to the snow which is therefore a water-ice mixture.

melted but «all heat was lost» and the resulting water was at a temperature of 0° C. Repeating the experiment with masses of water and snow in different ratios, Wilcke concluded that a considerable quantity of heat was always lost:

«The heat in a mixture of water and snow is not distributed without loss and remaining active, as in the case of a water-water mixture, but a defined and fixed quantity of heat, corresponding to 72 degrees on the thermometer is always lost. This [quantity] melts the snow, that in this regard may be considered in a negative state, it is eliminated or destroyed, without making it any hotter but simply turning it into liquid. So these 72 degrees only serve to produce liquefaction. Successively, the melted snow behaves as cold water and any heat above 72 degrees is uniformly distributed throughout the mass».

Wilcke provided the expression of equilibrium temperature Θ of a mixture of mass m_s of snow at 0° C and a mass m_w of water at temperature Θ_w :

$$\theta = \frac{m_w \theta_w - 72 m_s}{m_w + m_s} = \frac{\frac{m_w}{m_s} \theta_w - 72}{\frac{m_w}{m_s} + 1}$$

With equal Θ_w , Θ only depends on the ratio of masses of water and snow. The equilibrium temperature of the mixture results experimentally greater or equal to zero in cases where $m_w \Theta_w / m_s \geq 72^\circ \text{C}$ (i.e. when all the snow melts) and in agreement with the previous formula. In cases where $m_w \Theta_w / m_s < 72^\circ \text{C}$ (i.e. when not all the snow melts), this formula gives $\Theta < 0$,⁵⁴ in other words, in these cases the mixture should freeze completely, something which is not seen experimentally. To solve this puzzle, at the heart of which lies some confusion between the concepts of temperature and quantity of heat, Wilcke stated that «the lack of heat in snow [at 0°C] is something absolute: it is not, as with cold, something opposite to heat, i.e. the negative of heat, but is really zero».

In the mentioned paper of 1781, Wilcke put forward, without however really putting it into effect, the suggestion of measuring the specific heat of different bodies observing «how much snow must melt to cool each one of the different bodies from a given degree of heat to the point of freezing», because all the heat lost by a body is found in the water obtained through the melting of snow and «its quantity may be known by the quantity of melted snow». In particular, placing the heated bodies at 72° C into a mixture at 0° C of water and snow, so that all the snow melts and the temperature remains at 0° C, the mass of melted snow divided by the mass of the body gives the specific heat of the body.⁵⁵ In this way, Wilcke set the foundations of change of state-calorimetry, in which a quantity of heat Q is measured by

⁵⁴ Ex-post we know that it is not applicable in this case in which not all the snow melts.

⁵⁵ The mass of melted snow is also the mass of water that if initially at 72° C would melt an equal mass of snow; in this way Wilcke assumed as unit of quantity of heat the one melting a unit mass of snow at 0° C.

the mass Δm of substance at the melting point of which it induces the change in state: $Q = \lambda \Delta m$, where λ is the latent heat relative to unit mass. Wilcke also emphasized that, since a substance generally has different specific heat depending on state of aggregation in which it finds itself, the specific heat must never be determined with mixtures of «substances that melt reciprocally».

IX. *The ice-calorimeter*

In the early 1782, during his cooperation with Lavoisier for the study of thermal phenomena, Laplace had the idea of an ice calorimeter,⁵⁶ that was then constructed by the two French scientists in the summer of the same year. Laplace's calorimeter was based on the law: the mass of ice at 0°R ($= 0^\circ \text{C}$) melted by a given quantity of heat is «exactly proportional» to the quantity of the heat itself.⁵⁷

Also in this case the first complete treatment of calorimetric procedure based on changes of state is seen in the mentioned *Mémoire sur la chaleur*.⁵⁸ In it, Laplace and Lavoisier expounded the method for measuring the specific heat of a body using the ice calorimeter, described in detail:

«Wishing to know the specific heat of a solid body, one raises its temperature by any number of degrees, one then places it inside [the calorimeter]; leaves it there until its temperature has decreased to zero, and then collects the water that its cooling will have produced; this quantity of water, divided by the product of the mass of the body and by the number of degrees by which its temperature was above zero, will be proportional to its specific heat. As regards fluids, they will be sealed in vessels of which one has had the foresight to determine the heat capacities, and the operation will be the same as for solids, and to avoid the quantities of water that are due to the cooling of the

⁵⁶ In which i.e. ice is contained in a hollow vessel (thermically insulated by a covering containing other melting ice) and one measures the mass of melted ice that drips into a beaker placed underneath the calorimeter.

⁵⁷ Laplace and Lavoisier measured the constant of proportionality in the following way: «By means of an average taken from many experiments that agree with each other, we have found that the heat necessary to melt one pound of ice [at $0^\circ \text{R} = 0^\circ \text{C} = 32^\circ \text{F}$] may raise the temperature of one pound of water by 60 degrees [R, equal to 75°C or 135°F]; in such a way that if one pound of ice at zero [degrees] is mixed with a pound of water at 60 degrees, two pounds of water at zero [degrees] is obtained. [... I.e.] the heat necessary to melt the ice is the same as three quarters of that which may raise the same weight of water from the temperature of melting ice to that of boiling water». In *Mémoire* Laplace and Lavoisier gave the ice calorimeter the general term «machine»; in *Traité élémentaire* (*op. cit.*, p. 387), Lavoisier would term it for the first time specifically as «calorimeter» (*calorimètre*).

⁵⁸ In a note of which one reads: «After the reading of this article, we have seen, in a very interesting dissertation by Mr Vilke [sic] on heat, that was published in the Stockholm records of 1781, that this gifted physicist had had the idea of employing the melting of snow by bodies for measuring their heat, before us».

fluids, one needs to subtract from the quantities of water collected those that are produced by the vessels». ⁵⁹

One may well assert that by 1783 calorimetry was already a completely established methodology.

⁵⁹ Since in the case of gases and vapours, both the measure specific heat and the heat of condensation, the mass of the substance considered is very small with respect to that of the containers in which it is sealed, Laplace and Lavoisier suggested the following method of measurement: «If inside [the calorimeter] one places a curved snake-like tube, a current [of the gas that one wishes to measure] is established in this tube and by means of two thermometers placed in this current, one at the entrance and the other at the exit [of the calorimeter], one may determine the number of degrees by which [the gas] cools in its change, in this way a considerable mass can be cooled».