



Elementary Concepts and Fundamental Laws of the Theory of Heat

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Abstract

The elementary concepts and fundamental laws concerning the science of heat are examined from the point of view of its development with special attention to its theoretical structure. The development is divided into four periods, each one characterized by the concept that was attributed to heat. The transition from one to the next period was marked by the emergence of new concepts and new laws, and by singular events. We point out that thermodynamics, as it emerged, is founded on the elementary concepts of temperature and adiabatic wall, and on the fundamental laws: Mayer-Joule principle, or law of conservation of energy; Carnot principle, which leads to the definition of entropy; and the Clausius principle, or law of increase in entropy.

Keywords Thermodynamics · Fundameantal laws of thermodynamics · Fundamental concepts of thermodynamics

1 Introduction

The theory of heat that emerged around the middle of the nineteenth century became known as thermodynamics. This theory regards heat as work that can be interconverted into other types of works, such as mechanical work. The process involving heat and mechanical work was called a thermodynamic process by Kelvin and the entire discipline was then called thermodynamics by Rankine in 1859. However, the investigation on heat did not started with the appearance of thermodynamics. Before that, a theory prevailed that considered heat as a material fluid, denominated caloric by a group of french scientists in 1787. Major steps in the development of the investigation on heat also occurred previously, such as the discovery of the specific and latent heats around the middle of the eighteenth century and the invention of the thermometer around the middle of the seventeenth century. This last event marks the transformation of the concept of heat as a sensation to the concept of heat as a quality of bodies.

The purpose of this paper is the analysis of the main events, such as those just mentioned, as well as the emergence and development of the main concepts and laws

related to the investigation on heat, with special attention to the their theoretical aspects. Our analysis starts at the beginning of the seventeenth century and distinguishes four periods according to the concept that was attributed to heat, that is, according to the viewpoint about the nature of heat. In the first period, that ended around the middle of the seventeenth century, heat was understood as just a sensation that could be measured. In the second period, there was one sole concept related to heat, which was the one measured by the instrument called thermometer. This period ended around the middle of the eighteenth century when there appeared a second concept related to heat in addition to the one measured by the thermometer. The latter became known as intensity of heat, or temperature, and the new one became known as quantity of heat, later associated to material heat. The next period corresponds to thermodynamics.

Thermodynamics regards heat as a type of work. All types of work, including the thermal work, are assumed to be generated by conservative forces¹ so that their interconversion obey the law of conservation of energy. The conservative forces responsible for the thermal work are nothing else but those forces acting at the microscopic level. However, the law of conservation of energy as formulated when thermodynamics emerged was not derived from a microscopic law but came from the macroscopic law advanced independently by Mayer and Joule concerning the interconversion of heat and mechanical work. A

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¹A conservative force allows us to define potential energy and to demonstrate the law conservation of energy.

conservation law also existed in the caloric theory, but it was associated to caloric. It was taken for granted by Lavoisier and Laplace in their investigation on heat with the use of an ice calorimeter, and by Carnot to explain the production of work by a heat machine. According to Carnot, when caloric passes from a high to a low temperature, it generates mechanical work as happens to a body when it descends from a high to a low level.

The set of concepts and laws associated with each period is analyzed with the purpose of revealing its theoretical structure from the perspective of what is meant to be a scientific theory. A scientific theory consists of a set of elementary concepts and fundamental laws from which we may derive other concepts and laws, which describe and explain the real phenomena related to the subject of the theory. In this sense, past theories may be regarded as scientific theories [1].

2 Scientific Theory

Science is an enterprise that provides us with a rational understanding of objective reality, known as scientific knowledge. Such an understanding affords the explanation of natural phenomena, and the prediction of phenomena in nature or in the laboratory. Scientific knowledge, as can be noted, is not a unity, but has a fragmented structure. Each fragment is a science in itself and is related to a certain section of objective reality. The existence of several sections reflects the division of knowledge into areas and sub-areas. The unification of sciences and the reduction of one science to another are questions raised by some scientists and philosophers but cannot be regarded as a necessity.

What we call scientific laws constitutes the essence of scientific knowledge. However, a set of laws concerning an area of knowledge does not properly constitute a science. The laws should be connected directly or indirectly so as to form an organic whole. An example is Kepler's laws, originally disconnected, but which were connected by Newton by means of his gravitational law. We can say, therefore, that a science, in addition to be associated with a section of the objective reality, is also constituted by a set of laws that form a logically connected set, that we call scientific theory.

A scientific theory [1–8] consists of an abstract mathematical structure endowed with an interpretation, a correspondence rule between abstract terms and real concepts. The mathematical framework, with its logical connections, in association with interpretation, guarantees the rational description and explanation of the real object. The mathematical structure consists of a set of primitive terms and derived terms, and a set of postulates (or axioms) and theorems. The primitive terms are those considered undefined, that is to say, devoid of definition. Derived terms

are those defined from the primitive terms. Postulates are statements or relationships taken to be true without the requirement of demonstration. Theorems are propositions or relations obtained from the postulates by means of deductive argumentation.

In scientific language, primitive terms are called elementary concepts while derived terms are called derived concepts. In Newton's mechanics, "time" and "space" are elementary concepts but "velocity" and "acceleration" are derived concepts. Postulates (or axioms) are known as fundamental principles or fundamental laws, and theorems are known simply as laws. In Newton's formulation of mechanics, the second law, which says that force is proportional to acceleration, is a fundamental law.

In this paper, we will be concerned with the elementary concepts of the theory of heat and their interpretations. As an example drawn from Newton's mechanics, let us consider the concept of time. Although abstract time is undefined, real time, which is its interpretation, can be grasped when we measure it experimentally, for example by means of a pendulum. However, this does not mean that we are giving a definition of time. What the pendulum marks should not be regarded as the definition of time. The interpretation of a primitive term cannot be understood as its definition [8].

In the theory of heat, there are basically two thermal concepts that should be considered as elementary. One is temperature, established with the invention of the thermometer, and interpreted as the physical quantity measured by the thermometer. The other is heat, which was established within the caloric theory and interpreted as the physical quantity measured by the calorimeter such as the ice calorimeter, described by Lavoisier and Laplace in their memoir on heat. Within thermodynamics, on the other hand, heat is identified as work and in this sense, it cannot be regarded as an elementary concept anymore. However, heat should be distinguished from other types of work. One way to do this is to introduce the concept of adiabatic wall understood as a second elementary concept of the theory.

3 Degrees of Heat

Our body is naturally endowed with several senses that allow us to perceive the environment. One of these is the sense of hotness and coldness. This sense is not as accurate as the other senses but is capable of distinguishing some degrees of hotness and coldness, as long as we are not exposed to extreme heat or extreme cold. The sensation of heat and cold may sometimes be very subjective, resulting in an imperfect perception, an observation that may have stimulated the development of an instrument to measure the degrees of heat and cold. Whatever was the motivation, such

an instrument began to be developed, in modern times, in the beginning of the seventeenth century [9, 10].

According to Castelli [11], an instrument to measure the degrees of heat and cold was developed by Galileo before 1603. The instrument was made up of a glass bottle with a small spherical body and a very long and narrow neck. It is set up upside down, with the mouth immersed in a small recipient with water. In contact with a colder or hotter body, the water in the neck goes up or down, and a measure of the degrees of heat and coldness is given by the level of water in the neck. A similar instrument was used by Santorio for meteorological and medical purposes at least from 1612 and it was described by Biancani in 1617, who called the instrument “thermoscope” (*thermoscopium*), and by Santorio himself in 1625 [10]. An instrument of the type of those associated with the names of Galileo and Santorio was described by Leurechon in a book published in 1626 together with another type in which the long tube had a “J” shape [12]. In this book, he coined the french word “thermomètre” (which passed into English as “thermometer”) to mean the instrument for measuring the degrees of heat or coldness.

The instruments of Galileo and Santorio, and those described by Leurechon, which we call “air thermoscopes,” were sensible to variations in atmospheric pressure because one end of the glass tube of the instruments was open.² However, this fact could not have been appreciated because the atmospheric pressure had not yet been discovered [13]. In 1654, Ferdinando II, one of Galileo’s patrons, built a thermometer, which was free from variations of atmospheric pressure, by sealing a glass tube containing alcohol [10]. The Ferdinando’s liquid-in-glass thermometer received further improvements from members of the Accademia del Cimento, founded in 1657 and dissolved 10 years later [10].

Whether the motivation for sealing the glass tube was to correct the problems caused by variations of the atmospheric pressure or just to prevent evaporation, it is hard to say. However, the first motivation is plausible because, at the time Ferdinando built his thermometer, the atmospheric pressure had already been discovered and Torricelli had already invented, in 1644, an apparatus to measure it [10]. The variability of the pressure and its influence on the air thermoscope was mentioned explicitly by Pascal in 1648 [10].

By the middle of the seventeenth century, the air thermoscope may be said to be separated into two distinct instruments, that measured two distinct quantities, corresponding to two distinct physical concepts. The first was the barometer, which measures the atmospheric pressure, and the other, the thermometer, which measures the degrees of heat.

²Nowadays, the word “thermoscope” names a thermometer without a scale [10]. Tisza calls the air thermoscope a “barothermoscope” [13].

The thermometer received the attention of other scientists who tried to improve the instrument by testing other thermometric substances and by setting a scale for the degrees of heat. In the scale used by Newton [14] in his linseed oil thermometer, the freezing point of water was taken as zero degree, the blood heat as 12 degrees, and the boiling point of water as 34 degrees. Fahrenheit, who invented the mercury thermometer, describes his scale in 1724. He marks 32 degrees for the freezing point of water and 96 degrees when the thermometer is held in the mouth, or under the armpit [15].

4 Quantity of Heat

Around the middle of the eighteenth century, investigations concerning heat led to the emergence of the concept of quantity of heat. This new concept arose mainly in connection with the study of mixtures of liquids [16, 17]. In 1732, Boerhaave addressed the problem of explaining why the degree of heat of a mixture of water and mercury, initially at different degrees of heat, is closer to that of the water. To this end, he proposed that the material “fire is distributed in the bodies in proportion to their bulk, or extension” [18]. Between the years 1759 and 1763, Black developed his ideas about heat [17] leading him to an explanation that differs from that of Boerhaave. Black explained that mercury requires a smaller quantity of heat than water to raise the same number of degrees of heat, that is, the same quantity of heat will change the degrees of heat of the mercury by an amount greater than that of the water. With this explanation, Black was introducing a new concept related to heat, that of quantity of heat, distinct from the intensity of heat [17], which is measured by the thermometer.

In an anonymous account of 1770 concerning Black’s studies on heat [19, 20], the intensity of heat is also called “temperature.” The meaning of this term, as the quantity measured by the thermometer, is a reduction of the more general meaning, now obsolete, of “temperature,” which is the condition of the air and bodies as to heat and cold, moist and dry, and other qualities, as exemplified by the following sentences in a publication of 1725 concerning Boyle’s works: “this liquor perpetually varies its temperature, as to cold and heat” and “the temperature of the air is neither considerably moist, nor considerably dry” [21]. Thus, until the eighteenth century, “temperature” meant the tempering of the qualities in a substance, and only after that, it acquired the present precise physical meaning [9], restricted to the qualities of “cold and heat” only.

The emergence of a second concept related to heat, namely that of quantity of heat, seems natural to us, but it was not to someone at the beginning of the eighteenth

century. To clarify this point, we use an example presented by McKie and Heathcote [17]. Let us think about the concept of a color, considered as a quality as much as heat. Although "intensity of blue" is meaningful to us, it is very hard to assign a meaning to "quantity of blue." Therefore, around the middle of the eighteenth century, the concept of heat as a quality, understood as being measured by the thermometer, changed to mean material heat, later on known as caloric. The old meaning of heat as quality was transferred to "temperature."

5 Heat Capacity and Latent Heat

The explanation given by Black concerning the mixtures of liquids resulted in the concept of heat capacity, which is the quantity of heat necessary to raise the temperature of a body by a certain amount. The determination of heat capacity by Black was based on the following rule to be used when two bodies of equal masses at different temperatures are mixed [20]. The heat capacity of one body is proportional to the inverse of the variation of its temperature. Denoting by c_1 and c_2 the heat capacities, and by θ_1 and θ_2 the temperatures of the hotter and colder bodies before the mixing, this rule may be written in the form

$$\frac{c_1}{c_2} = \frac{\theta - \theta_2}{\theta_1 - \theta}, \quad (1)$$

where θ is the final temperature. Using this rule, the heat capacity of the substances could be determined in relation to that of the water. In addition to the heat capacity, another fundamental concept discovered by Black was that of latent heat [20]. Black argued that the total mass of ice did not melt at once as the temperature of the air reaches that of the melting point. The entire process of melting takes some time because a certain quantity of heat is needed to be transferred to the ice while the temperature remains the same. This reasoning applies also to the boiling of a mass of water. Since in both processes the temperature remains invariant, heat could not be perceived and for this reason Black called it latent heat. The melting and boiling phenomena showed unambiguously the distinction between temperature and quantity of heat.

The idea of latent heat was used by Lavoisier and Laplace in their study of specific heats of solids and liquids by means of an ice calorimeter, carried out in 1783 [17], and reported on their memoir on heat [22]. The measure of heat developed inside the calorimeter was determined by the weight of ice melted. In their memoir on heat, Lavoisier and Laplace discussed two theories regarding the nature of heat. One of them is the material theory of heat which assumes that heat is a fluid, a few years later called caloric, which diffuses and penetrates the bodies by reason of their

temperatures, and their particular disposition to retain it. The other regards heat as the result of insensible movement of the molecules of matter. Lavoisier and Laplace did not decide which hypothesis to use and for this reason they assumed only principles that were common to both, as is the case of the conservation law [22]: "the amount of free heat always remains the same in the simple mixture of bodies" (*la quantité de chaleur libre reste toujours la même dans le simple mélange de corps*). From this conservation law, Lavoisier and Laplace immediately derived the rule expressed by formula (1) [22]. Employing the same notation used in this formula, the quantity of heat lost by the hotter body is $q_1 = c_1(\theta_1 - \theta)$ and that gained by the colder one is $q_2 = c_2(\theta - \theta_2)$. But, by the conservation law, $q_1 = q_2$, which leads us to formula (1).

The french word "calorique," which originated the term "caloric," was coined by the authors of *Méthode de Nomenclature Chimique* in 1787 [23] to replace "material heat", and the french term "calorimètre," origin of "calorimeter," was coined by Lavoisier in 1789 [24].

The heat capacity of gases was first determined experimentally by Crawford in 1777 [25]. He believed that a variation in the volume of a gas would change the heat capacity but his experiments showed no appreciable difference in the heat capacity measured when the gas is allowed to expand and when it is not [25]. A clear distinction between the two types of specific heat, that measured at constant pressure and that at constant volume, was made by Haüy in 1806 [26]. He also explained why the former is greater than the latter by using Laplace separation of caloric into two types: the sensible caloric, which affects the thermometer, and the latent caloric, which does not. According to Haüy, the difference in the heat capacities comes from the latent caloric which causes expansion but does not change the temperature [25].

6 Expansion and Contraction

The use of air pumps in the study of the pneumatic properties of gases led to the observation that the temperature of the receiver decreased during exhaustion and increased during the refilling. The discovery of this phenomenon is attributed to Cullen, who described it in 1755 [25], but the phenomenon was also observed independently by Darwin, who described it in 1788, about 13 years after his observation [27]. According to him, the mechanical expansion of air attracts the matter of heat from the neighborhood, that is, the mechanical expansion of air results in its cooling. He explained the cold air at high altitudes by saying that a mass of air expands as it rises, resulting in its cooling [27].

When air is mechanically compressed, explained Biot in 1802, one part of the latent heat becomes sensible

heat, perceived by an increase in the temperature. In the expansion, a part of the sensible heat becomes latent, resulting in a decrease in the temperature. This explanation appears in a report of Biot concerning the velocity of sound in the air [28], motivated by Laplace’s opinion in this matter. Laplace believed, at least by 1802, that the propagation of sound in air was not a process in which the temperature remains constant, as was implicit in a calculation due to Newton of the speed of sound, but could vary due to compressions and rarefactions [29]. In his explanation, he assumes that the quantity of heat during the dilatations and rarefactions remains the same. The process without the intervention of heat was later on called “adiabatic” by Rankine in a publication of 1859 [30].

Haüy in 1806 explained more clearly the mechanical expansion in terms of the caloric [26]. There are two kinds of caloric: the free caloric, which affects the thermometer, and the latent caloric, which does not. In an expansion, a gas absorbs latent heat by transforming free caloric into latent. The free caloric may come from inside or outside the body. If the whole free caloric comes from inside, there is no exchange of heat with the environment and a cooling occurs. If it comes from outside, there might be no change in temperature. Haüy’s reasoning became a common explanation of the adiabatic expansion [25].

7 Caloric Theory

Around the first decade of the nineteenth century, doubts about the concept of a material heat have decreased and the material theory of heat, also known as caloric theory, was widely accepted [17, 25]. The phenomena related to heat are due to an imponderable material called caloric, or merely heat, which is contained in every part of a body and that can pass from one part to the another part of a body or from one to another body [31]. Caloric is an elementary concept of the theory and its quantity is measured by the calorimeter. The fundamental law of the theory is that caloric is a conserved quantity [22]. Temperature is another elementary concept of the theory and is measured by the thermometer. The temperature θ of a body and the heat q per unit mass contained in a body are considered as being determined by the state of the body. In the case of a liquid or a gas, they are functions of the pressure p and the volume v per unit mass of the gas, that is, $\theta(v, p)$ and $q(v, p)$.

The elastic properties of gases involve not only the pressure and volume but also the temperature. Boyle had established that the pressure of air enclosed in a recipient is inversely proportional to its volume [32]. From the Gay-Lussac study of dilatation of several gases at constant pressure, it follows that the proportionality constant is linear in the temperature [33]. Boyle law combined with Gay-Lussac

results allow us to write the relation between the pressure p , the volume v per unit mass, and temperature θ in the form

$$pv = R(\theta_0 + \theta), \tag{2}$$

which we call Boyle-Gay-Lussac equation, where R and θ_0 are constants. In an expansion at constant pressure, the fraction $\alpha_p = (1/v)(\partial v/\partial\theta)_p$ of the volume increased per unit of temperature is $\alpha_p = 1/(\theta_0 + \theta)$. Gay-Lussac measured this quantity at zero degree of the centigrade scale for several gases and found the same value 1/266.66 per degree centigrade. But at $\theta = 0$, $\alpha_p = 1/\theta_0$ which yields $\theta_0 = 266.66$ degrees centigrade [33].

The specific heat is the heat necessary to increase the temperature of a unit of mass by one degree. If the volume remains constant during the heating, one defines the specific heat at constant volume $c_v = (\partial q/\partial\theta)_v$. If the pressure is kept constant, implying a variation in the volume, one defines the specific heat at constant pressure, $c_p = (\partial q/\partial\theta)_p$. Measurement of specific heats of gases at constant pressures were conducted by Delaroche and Bérard in 1812 for several gases [34]. The specific heat by weight for the air was found to be $c_p = 0.2669$ in units where that of water is equal to 1. Due to the experimental difficulties in the measurements of the specific heats at constant volume, only much later, the direct value of c_v was obtained experimentally [25]. Dulong and Petit carried out measurement of the specific heat of solids and found that the product of the specific heat by weight multiplied by the atomic weight was a constant [35]. From this general result they conclude the following law: “the atoms of all simple substances have exactly the same capacity for heat” (*Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur*).

Let us consider now the process with no exchange of heat which became relevant in the explanation of the propagation of sound in gases. The velocity of sound is the square root of $\partial p/\partial\rho$, the variation of the pressure p with the density ρ . If the variation is isothermal one finds $(\partial p/\partial\rho)_\theta = p/\rho$ for a gas obeying Boyle-Gay-Lussac equation and recalling that $v = 1/\rho$. This gives $(p/\rho)^{1/2}$ for the velocity of sound in a gas, which corresponds to the result obtained by Newton [29]. According to Laplace, the variations should be considered adiabatic and not isothermal so that the appropriate quantity is $(\partial p/\partial\rho)_q$. Using the usual rules for calculating derivatives, we may write this quantity as

$$\left(\frac{\partial p}{\partial\rho}\right)_q = \left(\frac{\partial p}{\partial\rho}\right)_\theta + \left(\frac{\partial p}{\partial\theta}\right)_\rho \left(\frac{\partial\theta}{\partial\rho}\right)_q = \left(\frac{\partial p}{\partial\rho}\right)_\theta \left(1 + \frac{\alpha_p}{\alpha_q}\right), \tag{3}$$

where α_p is the fraction of the volume increased per unit of temperature at constant pressure, defined above, and $\alpha_q = -(1/v)(\partial v/\partial\theta)_q$ is the fraction of the volume

increased adiabatically per unit of temperature. Using the Boyle-Gay-Lussac equation, one finds

$$\left(\frac{\partial p}{\partial \rho}\right)_q = \frac{p}{\rho}(1+k), \quad (4)$$

where $k = 1/(\theta_0 + \theta)\alpha_q$. From (4), one writes the velocity of sound in a gas as $[p(1+k)/\rho]^{1/2}$. This relation between the velocity of sound and k and that of k with α_q were obtained by Poisson in 1808 [36] and they correct Newton's calculation by a factor $(1+k)^{1/2}$. Poisson did not measure α_p but obtained its value indirectly from experimental values of the speed of sound. He obtained [36] the following results $k = 0.4254$ and $\alpha_q = 1/116$ per degree centigrade at the temperature of six degrees centigrade and by the use of Gay-Lussac result for θ_0 .

Next, we show another relationship involving $(\partial p/\partial \rho)_q$. Using again the usual rules for calculating derivatives, we may write

$$\left(\frac{\partial p}{\partial \rho}\right)_q = -\frac{(\partial q/\partial \rho)_p}{(\partial q/\partial p)_\rho} = -\gamma \frac{(\partial \theta/\partial \rho)_p}{(\partial \theta/\partial p)_\rho} = \gamma \left(\frac{\partial p}{\partial \rho}\right)_\theta, \quad (5)$$

where $\gamma = c_p/c_v$ is the ratio between the specific heat at constant pressure and constant volume. Using the Boyle-Gay-Lussac equation, we find

$$\left(\frac{\partial p}{\partial \rho}\right)_q = \gamma \frac{p}{\rho}, \quad (6)$$

which leads to the result that the velocity of sound in a gas is $(\gamma p/\rho)^{1/2}$, a result announced by Laplace in 1816 [37] and derived explicitly by him in a publication of 1822 [38]. Laplace's result corrects Newton's calculation by a factor $\gamma^{1/2}$. Gay-Lussac and Welter obtained experimentally the value $\gamma = 1.3748$ for the air, a result reported by Laplace in a note on the velocity of sound [39]. In 1829, Dulong reported his experimental values of γ for several gases including the atmospheric air for which he found $\gamma = 1.421$ [40].

If the ratio γ of the specific heats can be considered constant along a certain range of ρ , (6) can be integrated, with the solution $p \sim \rho^\gamma$, equivalent to $p \sim v^{-\gamma}$, a result found by Poisson [41] and valid along the adiabatic curve. Using the relation $p \sim v^{-\gamma}$, we immediately obtain a relationship between α_q and γ , namely, $\alpha_q = 1/(\theta_0 + \theta)(\gamma - 1)$, where we used Boyle-Gay-Lussac equation. Carnot used this result in combination with Gay-Lussac result $1/\theta_0 = 1/267$ per degree centigrade and Poisson result $\alpha_q = 1/116$ per degree centigrade to find $\gamma = (267 + 116)/267 = 1.44$ [42]. It also follows from the relation between α_q and γ that the quantity k that appears in (4) is related to the ratio of the specific heats by $\gamma = 1+k$.

Motivated to understand how the heat machines produce motive power (*puissance motrice*), that is, mechanical work, Carnot carried out investigations on heat that were published

in 1824 [42]. Ten years later, in 1834, Clapeyron published a memoir [43] in which he presented Carnot results and propositions in an analytical form. He also made use of a pressure versus volume diagram, which revealed to be most convenient because mechanical work is represented as an area in this diagram. Clapeyron used the terms "quantity of mechanical action" (*quantité d'action mécanique*) to mean "mechanical work," although Coriolis had already introduced the term "work" (*travail*) in 1829 [44]. In his paper, Clapeyron introduces also the relation which was later called Clausius-Clapeyron equation. Both publications received little attention but were eventually acknowledged by Kelvin in 1848 [45] and by Clausius in 1850 [46] in their papers on heat.

The studies carried out by Carnot led him to a remarkable law that links work to heat. After saying that a heat engine operates in a cycle, Carnot introduces the cycle, that now bears his name, composed by two isothermal and two adiabatic processes. A body that undergoes this cycle receives a quantity of heat at higher temperatures and gives the *same* quantity of heat at lower temperature. To obtain a relation between work and heat, Carnot uses an analogy with a mechanical system. When a body descends from a certain height to another height, it performs a work proportional to the product of the mass of the body and the difference of heights, and the work does not depend on the substance of the body. Thus, Carnot assumes that the heat machine undergoing his cycle, performs a work w proportional to $q\Delta\theta$, where $\Delta\theta$ is the difference in the temperatures of the isotherms and q is the heat that "descends" from the higher to the lower temperature. This assumption is written as

$$\frac{w}{q} = \frac{\Delta\theta}{C}. \quad (7)$$

A second and most important assumption of Carnot is that the work does not depend of the substance of the body undergoing the cycle and depends only on the temperatures of the isotherms. This means to say that C depends only on θ_1 and θ_2 , the temperatures of the two isotherms. Setting $\theta_1 = \theta + \Delta\theta$ and $\theta_2 = \theta$, then for small difference in temperatures, $C(\theta)$ will depend only on θ [43]. Following Clapeyron [43], we consider a small cycle. Since the work is the area of the cycle in the plane p - v , then $w = \Delta p \Delta v$ because Δp and Δv are small. For small heat absorbed, we may replace q by dq in (7) to get

$$\frac{1}{C} dq d\theta = dp dv. \quad (8)$$

From (8), it follows that the Jacobian $\partial(\theta, q)/\partial(p, v) = C$, that is,

$$\frac{\partial \theta}{\partial p} \frac{\partial q}{\partial v} - \frac{\partial q}{\partial p} \frac{\partial \theta}{\partial v} = C. \quad (9)$$

Once the function $C(\theta)$ is known, (9) gives a relation between temperature and heat. In the case of a gas obeying the Boyle-Gay-Lussac equation, it follows from (9) that

$$v \frac{\partial q}{\partial v} - p \frac{\partial q}{\partial p} = RC. \quad (10)$$

The solution of this equation is $q = RC \ln v + A$ where A is a function of the product pv . From this equation, it is possible to determine c_p and c_v and to show that $c_p - c_v \geq 0$.

Let us now consider the boiling of a liquid. If the pressure is kept constant, the temperature remains invariant as long as there is liquid to be boiled. In this case, $\partial\theta/\partial v$ vanishes. But $\partial q/\partial v$ equals the ratio $\ell/\Delta v$, where ℓ is the latent heat per unit mass, and Δv is the difference between the volume per unit mass of the vapor and the liquid, so that (9) becomes

$$\frac{\partial p}{\partial \theta} = \frac{\ell}{C \Delta v}, \quad (11)$$

which is the equation that relates the slope of the transition from the liquid to vapor in the p - θ plane with the latent heat, and known as Clausius-Clapeyron equation.

As we have seen, the caloric theory considers two types of caloric: the sensible, which affects the thermometer, and the latent, which does not. The existence of latent caloric explained melting and boiling of a substance and also the compression of gases. In this case, the decrease in volume induces the conversion of part of latent caloric into sensible caloric causing an increase in temperature. This conversion is manifest, for example, in hammering a piece of metal, which causes an increase of temperature. However, the existence of two types of caloric and the conversion of one into another was criticized by Dulong and Petit, due to the lack of evidence, and by Berzelius, due to absence of decrease in volume in certain exothermic reactions [25]. In spite of the criticisms, the caloric theory survived until around 1850, as is apparent in the work of Kelvin of 1849, who calls the conservation of caloric as Carnot's fundamental principle [47].

8 Mayer-Joule Principle

In an account of his theory concerning heat, published in 1842 [48], Mayer makes a connection between heat, work (*Fallkraft*) and motion. However, according to Mayer, heat is not motion nor work but they can be transformed into each other. Thus, heat can be generated from the disappearance of motion, for example, by friction, and heat can be transformed into motion, for instance, in a steam engine. Mayer believed in the materiality of heat [25], but not in its conservation as happens to caloric. He further assumes that there is a fixed relation between work and heat production and found that the amount of heat necessary to warm a certain quantity of water by one degree centigrade

is equivalent to the fall of the same quantity of water by a height of 365 meters [48].

Three years later, in a publication of 1845 [49], Mayer explains his method by considering a gas enclosed in a vessel of volume V and pressure p . The work w performed by heating the gas at constant pressure starting at 0°C is $w = p\Delta V = pV\Delta\theta/\theta_0$. During the heating at constant pressure the gas absorbs a quantity of heat equal to $mc_p\Delta\theta$ where m is the mass of the gas. If the gas were heated at constant volume, the heat absorbed would be $mc_v\Delta\theta$. Mayer argues that the difference $q = m(c_p - c_v)\Delta\theta$ is the heat that is transformed into work. The mechanical equivalence of heat is given by the ratio $w/q = p/[\rho(c_p - c_v)\theta_0]$, where ρ is the density of the gas. Mayer applies this result for the atmospheric air by using the value of the specific heat c_p obtained experimentally by Delaroche and Bérard and the experimental value of γ obtained by Dulong and Petit to find $c_v = c_p/\gamma$.

In 1843, Joule published a paper on production of heat by magneto-electric devices [50]. If heat is not a substance, writes Joule in this paper, but is understood as a state of vibration, there is no reason why it could not be produced by mechanical or magneto-electric means. He begins to doubt whether the heat was indeed generated in these processes and not simply transferred. However, his experimental work led him to assert that heat is indeed generated and is not a conserved quantity like caloric. Joule went on further by asserting that heat produced is proportional to the work consumed in the operation. To increase by one degree Fahrenheit one pound of water, he finds it is necessary to raise a body of 838 pounds by one foot [50]. Later in 1850 [51], by using a paddle-wheel apparatus, he finds the value of 772 pounds raised by one foot.

In spite of the distinct viewpoints concerning the nature of heat, Mayer and Joule had the same idea about the conversion of work into heat, that is, the heat generated q in a certain process is proportional to the work dissipated w , that is $q = aw$, and the proportionality constant a is universal. This is to be understood as a fundamental law and for brevity, we call it Mayer-Joule law or Mayer-Joule principle. This law should also be understood as embracing the conversion of heat into work as occurs in a heat machine.

9 Carnot Principle

The Mayer-Joule law was manifestly in conflict with the conservation of caloric, a principle that was used by Carnot to explain the production of work by a heat machine. This was the viewpoint of Joule who suggests the abandoning of Carnot's fundamental principle [52]. Kelvin, on the other hand, held the opinion that the renunciation of Carnot's principle would produce enormous difficulties that could

only be overcome by further experimental investigations and an entire reconstruction of the theory of heat [47]. This conflict was finally resolved by Clausius, who reported his solution in a publication of 1850 [46].

Clausius reasoning was as follows. Carnot, in his book on the relation between work and heat, introduces his cycle and a fundamental principle, which we split into two parts. (1) The work performed by the substance undergoing the cycle is proportional to the heat absorbed at the higher temperature and depends only on the two temperatures of the cycle, and not on the nature of the substance. (2) The heat delivered at the lower temperature is equal to the heat absorbed, in accordance with the conservation of caloric. Clausius perceived that this second part could be removed and replaced by the Mayer-Joule law without affecting the first part. Thus, according to Clausius, the heat delivered is smaller than the heat absorbed and the difference is converted into a certain quantity of work, in accordance with Mayer-Joule law. Denoting by q_1 and q_2 the heats absorbed and delivered, respectively, the heat consumed, $q_1 - q_2$, will be proportional to the work w , that is,

$$q_1 - q_2 = aw. \quad (12)$$

The first part of the Carnot's fundamental principle amounts to say that w/q_1 depends only on the two temperatures θ_1 and θ_2 of the two isotherms of the Carnot cycle, which can be represented by (7), with q_1 replacing q . This part is not in contradiction with Mayer-Joule law but there is an overlap with Mayer-Joule law because it also deals with the conversion of heat into work. However, it is possible to get rid of the overlap to reach an independent proposition. Writing (12) in the form $q_2/q_1 = 1 - aw/q_1$, we see that the ratio q_2/q_1 must have the same properties as w/q_1 , that is, it depends only on the two temperatures θ_1 and θ_2 , which allows to write

$$\frac{q_2}{q_1} = \frac{T(\theta_2)}{T(\theta_1)}, \quad (13)$$

where $T(\theta)$ is a yet unknown function of temperature θ , which does not depend on the nature of the substance undergoing the cycle. This proposition is to be understood as a fundamental law, which for brevity we call Carnot law or Carnot principle, and to be understood as independent of the Mayer-Joule law.

10 Clausius Theory

To develop his theory of heat, Clausius used the Mayer-Joule law, which relates heat to work, and the Carnot law, which relates heat to temperature. The main results of his theory are contained in two papers published in 1850 [46] and 1854[53]. In this section, we derive from the two

laws the main results found in these two papers but we follow a mathematical approach slightly distinct from that of Clausius, but similar to that of Clapeyron which we used in Section 7.

Setting $\theta_1 = \theta + \Delta\theta$ and $\theta_2 = \theta$, then for small values of the difference in temperatures, expression (13) of the Carnot law can be written as

$$\frac{q_1 - q_2}{q_1} = \frac{T'(\theta)}{T(\theta)} \Delta\theta. \quad (14)$$

To determine the unknown function $T(\theta)$, Clausius uses the Boyle-Gay-Lussac equation and the subsidiary condition that, in an isothermal expansion of a gas, all the heat absorbed is converted into work, which according to Clausius is experimentally verified as much as the Boyle-Gay-Lussac equation [46]. If q is the heat absorbed at constant θ , then for small values of volume increment Δv , this subsidiary condition gives $q = ap\Delta v = aR(\theta_0 + \theta)\Delta v/v$ where we have used the Boyle-Gay-Lussac equation. Since q_1 and q_2 are the heats absorbed at constant temperatures $\theta_1 = \theta + \Delta\theta$ and $\theta_2 = \theta$, then

$$\frac{q_1 - q_2}{q_1} = \frac{\Delta\theta}{\theta_0 + \theta}, \quad (15)$$

valid for small values of $\Delta\theta$. Comparing with (14), one reaches the result

$$T = \theta_0 + \theta. \quad (16)$$

We may call T temperature because it differs from θ just by a constant. A scale for T was devised by Kelvin [54] based on the relation (13), that is,

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}, \quad (17)$$

valid for a Carnot cycle.

In the paper of 1854 [53], Clausius undertakes a major step in the development of the theory by showing that dq/T is an exact differential. To reach this result, Clausius writes relation (17) in the form $q_1/T_1 + q_2/T_2 = 0$ where, here, he uses the convention that heat absorbed is positive and heat delivered is negative. From the generalization of this equation to several Carnot cycles, he finds that in any cyclic process

$$\oint \frac{dq}{T} = 0, \quad (18)$$

which means that dq/T is an exact differential. From this result, it follows that there exists a state function s whose differential ds is this exact differential, that is,

$$ds = \frac{1}{T}dq. \quad (19)$$

Using the result $T = \theta_0 + \theta$ into (14), it can be written as $(q_1 - q_2)/q_1 = \Delta T/T$, or yet as $aw/q_1 = \Delta T/T$ if we use the Mayer-Joule law, given by (12). Since we are

considering a small Carnot cycle, we may replace q_1 by dq and use pdv for the work w , to find

$$\frac{1}{T}dqdT = a dpdv, \tag{20}$$

which becomes identical to (8), if we set $C = aT$. But, contrary to what happens in the caloric theory, used by Clapeyron, here, dq is not an exact differential. Using (19), we find

$$ds dT = adp dv. \tag{21}$$

Taking into account that s and T may be considered functions of p and v , because both ds and dT are exact differentials, it follows immediately that the Jacobian $\partial(T, s)/\partial(p, v) = a$, that is

$$\left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial s}{\partial v}\right)_p - \left(\frac{\partial s}{\partial p}\right)_v \left(\frac{\partial T}{\partial v}\right)_p = a. \tag{22}$$

From (22), the following relation can be derived

$$\left(\frac{\partial T}{\partial v}\right)_s = -a \left(\frac{\partial p}{\partial s}\right)_v. \tag{23}$$

The derivation uses by the following identities

$$\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_s &= \left(\frac{\partial T}{\partial v}\right)_p + \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_s \\ &= \left(\frac{\partial T}{\partial v}\right)_p - \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial s}{\partial v}\right)_p \left(\frac{\partial p}{\partial s}\right)_v. \end{aligned} \tag{24}$$

Replacing (22) in this equation, one gets relation (23). If we now define the differential du by

$$du = Tds - a pdv, \tag{25}$$

then, relation (23) says that du is an exact differential, which was obtained by Clausius in 1850 [46]. As we shall see, only later on, in 1854 [53], that Clausius realized that (25) could be understood as the equation for conservation of energy and that u could be identified as the energy of a body.

By the use of the equations just obtained, some results can be found. For instance, using (22) for the case of a gas obeying the Boyle-Gay-Lussac equation, which we may write as $pv = RT$, we get

$$v \frac{\partial s}{\partial v} - p \frac{\partial s}{\partial p} = aR, \tag{26}$$

whose solution is $s = aR \ln v + B$ where B is a function of pv and thus a function of T only. From the solution, we may determine c_p and c_v and show that they depend on temperature only and that their difference $c_p - c_v = aR$ is a constant.

Some results obtained from the caloric theory are found to be in accordance with the heat theory of Clausius. In adiabatic processes, for instance, there is no exchange of heat so that the process looks like there is a conservation of heat. Equation (5) and those that follow from it in

connection to the Boyle-Gay-Lussac equation, for instance, remain valid. Also, (11), related to the process of boiling of a liquid, remains valid because in the course of deriving this equation we have considered a Carnot cycle such that the difference in the heat absorbed and the heat delivered become negligible, and again, this process works like one in which heat is conserved. Since in the process of boiling the pressure and temperature remain invariant while the volume varies, it follows that $(\partial T/\partial v) = 0$ and (22) becomes $(\partial T/\partial p)(\partial s/\partial v) = a$. But $(\partial s/\partial v)$ equals $\ell/T \Delta v$, where ℓ is the latent heat per unit mass and Δv is the difference between the volume per unit mass of the vapor and the liquid, so that

$$\frac{\partial p}{\partial T} = \frac{\ell}{aT \Delta v}, \tag{27}$$

which is the Clausius-Clapeyron equation. It becomes identical to (11), obtained by Clapeyron, if we set $C = aT$.

The elementary concepts and fundamental principles of Clausius theory of heat are as follows. Heat and temperature are considered to be elementary concepts. Temperature is measured by the thermometer and heat by the calorimeter. The theory is based in two fundamental principles that Clausius calls the first and second fundamental theorems. The first we have called Mayer-Joule principle, and the second, Carnot principle. From these two principles, it follows that the differentials ds and du given by (19) and (25) are exact differentials, which means to say that s and u are state functions just as T , but not as q , which is not. In the case of a gas, they may be considered as functions of pressure p and volume v .

11 Conservation of Energy

The view that heat is a mode of motion was a speculation raised by some authors, even during the period dominated by the caloric theory, in particular from those who criticized the materiality of heat, such as Davy and Dulong [25]. Lavoisier and Laplace, in their memoir on heat [22], mentioned that some authors treat heat as being the result of insensible motion of molecules. What type of motion was it was not clear and what laws could be drawn from it were not given. The situation began to change with the works of Mayer and Joule because the law that they discovered independently could be interpreted as the conservation of energy. Between 1842 and 1847, this law was also announced by Colding and Helmholtz [55].

In his studies concerning the conservation of energy (*Kraft*), reported in a publication of 1847 [56], Helmholtz considers a system of material points that move under the action of their mutual forces, which are assumed to be central forces. For such a system, Helmholtz shows that the

sum of the potential energy (*Spannkraft*) and the kinetic energy (*lebendige Kraft*) is constant, which constitutes the principle of conservation of energy. Considering that, according to Joule, mechanical work can be converted into heat, Helmholtz raised the possibility that the quantity of heat would be the expression of the kinetic energy and the potential energy of the atoms. The former would correspond to the free heat and the latter to the latent heat. It should be remarked that, by considering central forces, Helmholtz was in fact assuming that at the microscopic level the forces are conservative, from which follows the conservation of energy. The general conservation of energy at microscopic level laid down by Helmholtz supported the Mayer-Joule law, but no one at that time had derived the latter from the former.³

In his first paper on heat of 1850, Clausius assumed, independently of Helmholtz, that heat consists in the motion of particles that is supposed to exist within a body and that the quantity of heat is a measure of their kinetic energy (*lebendige Kraft*), so that the general mechanical principle of equivalence between kinetic energy and work could be applied to heat [46]. In the paper of 1854 [53], he writes the expression of the conservation of energy in the form

$$\Delta U = Q - W, \quad (28)$$

where Q is the quantity of heat imparted to a body during the passage from one state to another, W is the external work performed by the body, and ΔU is the variation of the quantity U . Later on, Clausius adopts the terminology employed by Kelvin [57] and calls U the energy of the body. Equation (28) is an expression of conservation of energy only if ΔU does not depend on the path used to go from one to the other state, which is equivalent to say that U is a state function. Equation (28) can be written in the differential form

$$dU = dQ - dW, \quad (29)$$

which together with the understanding that dU is an exact differential, which means that U is a state function, is the expression of the conservation of energy in differential form. Notice that the differentials dQ and dW are not exact, and for a fluid $dW = pdV$ where p is the pressure and V the volume.

In his paper of 1850 [46], based on the Mayer-Joule and Carnot laws, Clausius demonstrated that dU in (29) is indeed an exact differential. In Section 10, we presented this demonstration, which ended in (25), following a path slightly distinct from that of Clausius. The demonstration

presented two crucial steps. The first is to show from the Carnot law that

$$dS = \frac{dQ}{T} \quad (30)$$

is an exact differential, where T is the temperature. The second step is to show from the Mayer-Joule and Carnot laws that

$$dTdS = dpdV. \quad (31)$$

However, further developments of the theory were carried out in a way in which the conservation of energy in the form given by (29) was assumed to be a fundamental law and not as a derived law. Thus, according to this scheme, (31) becomes an equation derived from (29) and (30) as can be readily verified.

12 Clausius Principle

In the development of the theory, it became clear to Clausius that the ratio Q/T between heat and temperature plays a relevant role. As we have seen, this ratio has the same value for the two isothermal processes of the Carnot cycle, a result that led Clausius to show that $dS = dQ/T$ is an exact differential as we have demonstrated above. Clausius called the ratio Q/T the value of a transformation, and thus, the quantity S could be called the transformation content (*Verwandlungsinhalt*) but in 1865 Clausius proposed to call S the "entropy" from the Greek words η τροπή meaning "the transformation" [58].

The next major step in the development of the theory was the establishment by Clausius, in 1865, of the following equality concerning the variation of entropy of a system in contact with the environment [58],

$$S - S_0 = \int \frac{dQ}{T} + N, \quad (32)$$

where S and S_0 are the entropy of the final and initial states of the system. The temperature T on the right-hand side of this equation is to be understood as the temperature of the environment and dQ the infinitesimal heat exchanged with the environment, being positive when heat is absorbed by the system. The quantity N , which was called by Clausius the uncompensated transformation (*unkompensierte Verwandlung*) [58], is never negative so that we may write

$$S - S_0 \geq \int \frac{dQ}{T}. \quad (33)$$

This inequality, established by Clausius, is a direct consequence of a fundamental principle which in the simplest form is stated by Clausius as follows [59]: "heat cannot by itself pass from a colder to a hotter body" (*die Wärme nicht von selbst aus einem kälteren in einem*

³In fact, the derivation of macroscopic laws from microscopic laws was the aim of the kinetic theory advanced by Clausius, Maxwell, and others.

wärmeren Körper übergehen kann). Here, we derive the inequality from this principle, which we call Clausius principle, by the use of a reasoning slightly different from that of Clausius.

We consider two bodies A and B that suffer a process such that the heat delivered by one body is absorbed by the other. This restriction is written as $Q + Q' = 0$, where the unprimed and primed quantities refer to A and B, respectively. In addition, the total energy and the total volume are invariant, restrictions that we write as $\Delta U + \Delta U' = 0$ and $\Delta V + \Delta V' = 0$. In this case, according to the fundamental principle, heat passes from the hotter body to the colder body because the restriction "by itself," which means that no other effect should occur, is fulfilled because there is no work or heat exchanged with the environment.

Let us imagine that bodies A and B undergo isothermal process at temperature T and T' , respectively, and that the body A absorbs a certain quantity of heat $Q > 0$ from B. In this case, the only possibility allowed by the fundamental principle is that $T \leq T'$, which can be translated into the inequality $Q [f(T) - f(T')] \geq 0$ for any monotonic decreasing function $f(T)$ of the temperature. The same inequality holds true if the body A gives heat to the body B because in this case $Q < 0$ and, in accordance with the fundamental principle, $T \geq T'$.

Next, we let the body A undergo a process in which the temperature T may vary. The inequality now reads

$$\int dQ [f(T) - f(T')] \geq 0, \tag{34}$$

where the integral is performed along the process undergone by the body A and T' is assumed to be a known function of the state of the body A. This equation can be written in the form

$$\int dQ f(T) + \int dQ' f(T') \geq 0, \tag{35}$$

where the second integral is performed along a process which is connect with the process undergone by the body A, in such a way that the heat absorbed by A equals the heat delivered by B, that is, $dQ + dQ' = 0$.

If we choose $f(T) = 1/T$, (35) reads

$$\int \frac{dQ}{T} + \int \frac{dQ'}{T'} \geq 0. \tag{36}$$

In this form, each of the integrals equals the variation in entropy and thus, we may interpret the inequality as also valid when the integrals are performed for any process, without the need of any connection between the process undergone by A and the process undergone by B, and without the restriction $Q + Q' = 0$. Within this new interpretation, only the restrictions $\Delta U + \Delta U' = 0$ and $\Delta V + \Delta V' = 0$ must be enforced. If we set one the integrals as $S - S_0$, we reach the Clausius inequality (33).

Combining (29) and (30), we may write for a mechanical system

$$dU = TdS - pdV, \tag{37}$$

where dU , dS , and dV are exact differentials. This equation was interpreted geometrically by Gibbs as describing a thermodynamic surface in the space (U, S, V) [60]. Temperature and pressure were interpreted geometrically as being related to the inclination of the tangent plane at any point of the thermodynamic surface. The coexistence of two thermodynamic phases is represented by a straight line segment whereas the coexistence of three phases is represented by a plane triangle. The invariance of the temperature when the pressure is kept constant at coexistence of two phases becomes a direct consequence of the geometric property that all points of a straight line segment correspond to the same temperature and pressure.

According to Gibbs, the stability of thermodynamic equilibrium is represented by the following property of the thermodynamic surface. Let us consider a tangent plane to a given point of the thermodynamic surface. Any other point of the surface will lie above the tangent plane considering that the axis of energy is the vertical one. This property is translated by the inequality

$$(U - U_0) - T_0(S - S_0) + p_0(V - V_0) \geq 0, \tag{38}$$

where (U_0, S_0, V_0) is a given point of the surface and T_0 and p_0 are the temperature and pressure at that point. This property is equivalent to say that thermodynamic surface has the property of convexity.

The convexity property of the Gibbs thermodynamic surface, given by (38), is a consequence of the Clausius inequality. To show this result, we start by writing (36) in the form

$$S_0 - S + \frac{Q'}{T_0} \geq 0, \tag{39}$$

where we assuming that the body B undergoes a process at a constant temperature T_0 and constant pressure p_0 and that the body A undergoes a processes such that the final temperatures is T_0 . But $Q' = \Delta U' + p_0 \Delta V' = -\Delta U - p_0 \Delta V$, which replaced in (39) gives

$$(S - S_0) - \frac{1}{T_0}(U - U_0) - \frac{p_0}{T_0}(V - V_0) \leq 0, \tag{40}$$

which is equivalent to inequality (38).

13 Thermodynamics

The theory of heat was called by Clausius the "mechanical heat theory" (*mechanischen Wärmetheorie*) [53]. Kelvin, in his first papers on the subject, used the terms "dynamical theory of heat" to name the theory of heat

and called the process involving heat and mechanical work a thermo-dynamic process [54]. In 1859, Rankine named "thermodynamics" the theory describing the conversion of heat into mechanical energy and conversely [61].

13.1 Elementary Concepts

In the Clausius theory of heat, analyzed in Section 10, temperature and heat were regarded as elementary concepts. But, taking into account the connection between heat and energy and that energy is a derived concept, heat may also be understood as a derived concept. Indeed, it is possible to define heat by the use of the concept of adiabatic wall, and this is the scheme adopted by many authors [62–68]. In this case, of course, adiabatic wall could not be defined as wall impermeable to heat because we would be facing a circular reasoning. Some authors avoid the circularity by assuming a definition of adiabatic walls that does not refer to heat. We avoid the circularity by adopting the concept of adiabatic wall as being an elementary concept of the theory. Thus, we adopt two elementary thermal concepts:

- 1 *Temperature*, which is measured by a thermometer, whose scale can be built according to a method devised by Kelvin, which uses (13).
- 2 *Adiabatic wall*.

Using adiabatic walls, we may determine the quantity of heat that is exchanged with the system in a certain thermodynamic process. To this end, we define an adiabatic process as the one for which the walls enclosing the system are adiabatic. By moving the adiabatic walls, an *adiabatic work* is performed on the system. We also define a thermal process as the one for which the walls are kept immobile. A *thermal work* is performed on the system by the use of a paddle-wheel apparatus, or similar, while the system is enclosed by adiabatic walls. Let us consider a thermodynamic process from an initial state to a final state and let us approximate the process by a succession of pairs of small adiabatic and thermal processes. The work performed W in the process is the sum of the adiabatic works of each small adiabatic process. The heat exchanged Q in the process is the sum of the thermal works performed in each one of the small thermal processes. According to this definition of heat, an adiabatic wall does not allow the passage of heat.

It should be noticed that the adiabatic work is independent of the path and depends only on the initial and final states. This result allows a distinct but equivalent way of introducing the concept of adiabatic wall as did Fermi. According to him, "there exists certain substances called thermal insulators [adiabatic walls] having the following properties: when a system is completely enclosed in a thermal insulator" the work depends only on the initial and final

states [64]. Born introduces adiabatic wall as follows [63]. The equilibrium of a system enclosed by rigid adiabatic walls cannot be disturbed by any external process. According yet to Born, this form of introducing adiabatic wall does not use the notion of heat. According to the proposal of adiabatic wall being an elementary concept, the existing definitions of adiabatic wall should in fact be understood as real interpretation of the theoretical elementary concept of adiabatic wall.

13.2 Fundamental Laws

The theory developed by Clausius [46, 53, 58], as we have described above, can be understood as based on the following fundamental laws:

- 1 *Conservation of energy*, expressed by (29). More precisely, by saying that dU given by (29) is an exact differential. It is a consequence of the Mayer-Joule principle.
- 2.1 *Heat and temperature relation* expressed by (30), or more precisely, by saying that dS given by (30) is an exact differential. This law allows the definition of entropy and is a consequence of the Carnot principle.
- 2.2 *Increase of entropy*, expressed by the inequality (33). It is a consequence of the Clausius principle.

Treatises on thermodynamics usually ground the theory on two fundamental principles called *first law* and *second law* of thermodynamics [64, 65, 69–72]. The first law is the principle of conservation of energy, which is the law 1. The second law is stated in several different forms, *supposedly* leading to both the laws 2.1 and 2.2. Sommerfeld calls the laws 2.1 and 2.2, respectively, the first and second part of the second law [72] whereas for Pauli the law 2.1 is the mathematical statement of the second law [71]. Some statements of the second law, such that of Planck [69], are declarations about the increase of entropy in isolated systems and, in this sense, they are equivalent to law 2.2 alone.

The statement of the second law by Carathéodory [62], which was supported by Born [63], is explicitly based on the concept of adiabatic walls as an elementary concept. According to Carathéodory, given two states, it is not always possible to connect them by an adiabatic process. From this axiom, Carathéodory shows the existence of integrating factor for the differential $dU + dW$, which allows the definition of entropy. Thus, Carathéodory statement leads to the law 2.1, with the integrating factor understood as the inverse of temperature, but it does not seem to lead to a law of increase in entropy in the sense of law 2.2.

Next, we analyze the original statement of the second law by Clausius, considered to be equivalent to other statements, such as that of Kelvin about the impossibility of producing work by cooling a body below the coldest of the surrounding objects [54]. The laws 2.1 and 2.2 are supposed to be

logical consequences of these statements. The law 2.2 can indeed be derived from the Clausius statement with the help of the law 2.1, as we have shown above. However, law 2.1 does not seem to be necessarily a logical consequence of the second law. Usually, the reasoning [72] leading to law 2.1 from Clausius statement is based on the use of two Carnot cycles, one being driven clockwise and the other anticlockwise, from which one obtains (13) and consequently the law 2.1. However, by a similar reasoning, it is possible to draw the same conclusion if we use a statement that contradicts that of Clausius. The paradox is solved if we recognize that the derivation is based on some premises that might not be contained in the second law. For instance, the derivation implicitly assumes that the heat absorbed during the isothermal expansion equals the heat released along the isothermal contraction. Thus, the law expressed by (13), which leads to the law 2.1, might not be a logical consequence of Clausius statement but could stand as an independent fundamental law.

13.3 Irreversibility

Our account of the theory of heat up to this point does not seem to involve time. However, this is not so. Our presentation of the laws is usually made in terms of processes, which are *time* evolutions of states. When we say that heat spontaneously passes from a hotter to a colder body, it means that the process of heat transfer begins at a certain instant of time t and ends at a later time t' , where $t' > t$ due to the tacit convention that time increases as time goes by. This is an irreversible process because the inverse process does not occur, that is, spontaneously heat does not pass from a colder to a hot body.

Let us consider the law 2.2. If both sides of Clausius inequality (33) is divided by the increase in time $\Delta t > 0$, and after taking the limit $\Delta t \rightarrow 0$, we find

$$\frac{dS}{dt} \geq \frac{\Phi}{T'} \tag{41}$$

where $\Phi = -dQ'/dt$ is the flux of heat to the system, that is, the heat transferred to the system per unit of time, and T' is the temperature of the environment. The following restrictions should be fulfilled: $dU + dU' = 0$ and $dV + dV' = 0$ where the prime and unprimed quantities refer to the environment and system, respectively. If the system is isolated, $dU = 0$, $dV = 0$, the heat flux vanishes and $dS/dt \geq 0$, that is, the entropy of an isolated systems does not decrease.

Let us suppose that the environment is a heat reservoir, whose temperature is kept constant. In this case, $dV = 0$ and $dU = -dU' = dQ'$ and inequality becomes

$$\frac{dU}{dt} - T' \frac{dS}{dt} \leq 0 \tag{42}$$

and $F = U - T'S$ decreases with time. For long times, that is, in thermodynamic equilibrium, $dU - T'dS = 0$ and T' equals the temperature of the system.

With the purpose of involving time, explicitly, we rewrite law 2.2 as

2.2 *Increase of entropy*, expressed by the inequality (41).

14 Discussion and Conclusion

We have analyzed the historical development of the investigation on heat with the purpose of pointing out the main concepts and laws, with emphasis on the elementary concepts and fundamental laws. Our analysis shows that the development passed through four periods, each one characterized by the concept that was attributed to heat. The transition from one period to the next is marked by the emergence of new concepts and new laws, which formed a new conceptual framework. The causes for the emergence of a new conceptual framework may be related to the desire to solve the problem raised by conflicting situations or may just be a singular event that triggered new ways of perceiving and studying the real phenomena. The transition from the first to the second period may be attributed to the invention of the thermometer. From the second to the third, it may be caused by the discovery of specific and latent heats. From the third to the fourth, the transition may be caused by the contradiction between the law of conservation of caloric and the equivalence of heat and work discovered by Mayer and Joule.

Our analysis has shown that thermodynamics is based on two elementary thermal concepts: temperature and adiabatic wall. The use of adiabatic wall allows the introduction of adiabatic process from which we may distinguish work and heat. According to our analysis, thermodynamics is founded on the three laws: (1) law of conservation of energy, which is the first law of thermodynamics, (2.1) the Carnot law, and (2.2) law of increase of entropy. In many treatises on thermodynamics, these two last laws are understood as a logical consequence of a single law, the second law of thermodynamics. However, we believe that it is conceptually more appropriate that law 2.1 and 2.2 be considered as two independent fundamental laws. This conceptualization is in accordance with the point of view advanced by Ehrenfest-Afanassjewa [73] according to which we might say that laws 2.1 and 2.2 should be understood as logically independent axioms, one referring to reversible processes or to bodies in equilibrium or near equilibrium, and the other associated to irreversibility. The misleading derivation of law 2.1 from the the second law, presented in most textbooks, gives the impression that law 2.1 comes from irreversibility. In fact, for irreversible

processes, law 2.1 does not apply although law 2.2 together with law 1 remain valid.

Some treatises on equilibrium thermodynamics such as those of Gibbs [60, 74], Callen [66], and Tisza [75] are based on the laws 1 and 2.2 as fundamental laws, and entropy is considered to be an elementary concept, but not temperature. In this case, law 2.1 becomes a definition of temperature. An important feature of these approaches is that they are centered on equilibrium states rather than processes [13]. In Gibbs thermodynamics, law 2.2 is identified as the condition for stability of a thermodynamic system which is translated into the property of convexity of the equilibrium surface in the space spanned by energy, entropy and volume. Gibbs' approach based on convexity was praised by Maxwell to the point that he wrote several new sections about it in the fourth edition of his book on the theory of heat [76]. The same can be said about Gibbs in relation to Clausius. In his paper on the equilibrium of heterogeneous substances, Gibbs [74] quoted the two final sentences of Clausius' paper of 1865 [58]: "Die Energie der Welt ist constant. Die Entropie der Welt strebt einem Maximum zu."

Our historic account ends with Gibbs equilibrium thermodynamics but the theory of heat continued to be developed in several directions, accompanied by the emergence of new concepts, such as the thermodynamic potentials and Legendre transformation, as well as the development of thermodynamics of phase equilibria and the concept of chemical potential by Gibbs [74]. A major step in the development of thermodynamics occurred during the first decade of the twentieth century with the emergence of the Nernst principle on the existence of lower bound for the entropy [77]. We should finally mention also the development of a thermodynamics for nonequilibrium systems and the emergence of the concept of entropy production, incorporated in the approaches of Onsager [78] and Prigogine [79].

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