Revista Brasileira de Ensino de Física, vol. 44, e20220008 (2022)
www.scielo.br/rbef
DOI: https://doi.org/10.1590/1806-9126-RBEF-2022-0008

Structure of the analytical theories of heat

Mário J. de Oliveira*[1]

[1]Universidade de São Paulo, Instituto de Física, Rua do Matão, 1371, 05508-090 São Paulo, SP, Brasil.

Received on January 09, 2022. Accepted on February 11, 2022.

We examine the analytical theories of heat developed by Laplace, Poisson and Carnot, and the thermodynamic theories based on the energy conservation and the principle of the increase of entropy formulated by Clausius. We present an analysis of the approaches developed by Maxwell, Gibbs, Planck, Duhem, Nernst, and De Donder as well as the irreversible thermodynamics of Prigogine, and the theory of liquid gas transition of van der Waals. We show that the thermodynamic potentials dominated the development of the theory of thermodynamics since Gibbs. They were introduced by Massieu under the name of characteristic functions and were demonstrated by Gibbs to have the suitable properties to characterize equilibrium of systems with variable composition, and to hold the convexity properties. We also show that the thermodynamic potentials were the relevant quantity in the Duhem approach to thermodynamics and to thermochemistry.

Keywords: Analytical theories, theories of heat, thermodynamics, thermochemistry.

1. Introduction

In 1850, Clausius published a paper where he introduced the fundamental principles of the mechanical theory of heat which a few years later was called thermodynamics. This accomplishment was carried out by Clausius by the reconciliation between the principle of Carnot and the principle of equivalence between heat and work established by Mayer and Joule. The principle of Carnot contains two parts one of which concerns the efficiency of the Carnot cycle. This part was retained by Clausius whereas the second part, which was based on the conservation of heat, was dismissed by Clausius. In another paper, Clausius introduced the second law of thermodynamics in the form of the increase of a quantity that he introduced and called entropy.

The Carnot theory preceded that of Clausius and was based on the caloric, a concept that emerged in the second half of the eighteenth century, and was employed by Laplace and Lavoisier in the explanation of their experiment on the specific heat of substances. Other theories of heat that appeared after Clausius, the thermodynamic theories, were based on the two fundamental laws laid down by Clausius. All these theories of heat, which we call analytical theories, are examined here, starting from the caloric theories of Lavoisier and Poisson, going through theories the of Gibbs and Duhem founded on the thermodynamic potentials, and ending with the irreversible thermodynamics of Prigogine.

Our analysis is based on the idea that a scientific theory consists of laws and concepts which are derived by means of a deductive reasoning from other laws and concepts [1, 2]. The derivation starts from one or more laws that are the fundamental laws or postulates of the theory, and from some concepts that are the primitive concepts understood as undefinable concepts. In addition to this abstract framework, a scientific theory is supplied with a real interpretation which include the measurements of the physical quantities.

The analytical theories of heat analyzed here are understood as having the temperature and heat as primitive concepts, that is, these two concepts are understood as theoretically undefinable, although this is not explicitly stated by the authors of the theories. Some authors seem to give definitions of these concepts but in fact they are referring to the way the concepts are measured or to the units of measurement. This happens when it is said that temperature is the quantity measured by a thermometer or that heat is the quantity measured by the calorimeter. These are not theoretical definitions but real interpretation of the concepts.

Within thermodynamics, we might think at first sight that heat could be considered to be a derived concept because heat is understood as work, and work is a derived concept. However a distinction must be made between heat, sometimes called internal work, and the external work, usually called simply work. The distinction between the two types of works is attained by the use of adiabatic walls. But an adiabatic wall is understood as a wall that prevents the passage of heat and we fall in a circular reasoning. To circumvent this problem we could reconsider heat as a primitive concept or consider the adiabatic wall as a primitive concept, as solution that we find more appropriate [3].

The concepts of thermal equilibrium and reversible process are key concepts in the analytical theories of heat analyzed here. A reversible process is defined as a change of states that connects equilibrium states.

---

* Correspondence email address: oliveira@if.usp.br

However, this statement seems to be a contradiction in terms as once in equilibrium, the system never changes its state. A reversible process should thus be understood as a sufficiently slow process such that any state along the process is an equilibrium state. An equilibrium state should not be confused with stationary states where fluxes of various types maintain the system in an invariant state. An equilibrium state is characterized by the absence any type of fluxes, particularly heat flux.

Although it is usual in thermodynamic reasonings to refer to processes, and thus to the time evolution of the state of a system, a characteristic of the exposition of thermodynamics is the lack of an explicit reference to time. This is particularly true in the case of reversible processes that are the central subject of equilibrium thermodynamics. For instance, it is usual to write the thermodynamic equations in terms of differentials such as the fundamental equation $dU = TdS - pdV$ instead of

$$\frac{dU}{dt} = T\frac{dS}{dt} - p\frac{dV}{dt} \tag{1}$$

To avoid misunderstanding, it suffices to keep in mind that usually the differentials correspond to or are a consequence of a positive increment in time, $dt > 0$. With this proviso, if the differential dS refers to a variation with time, then $dS > 0$ means that S increases with time.

For a better understanding of the second law of thermodynamics when stated in terms of the entropy, it is necessary to keep in mind that in fact it encloses two parts [3]. One of them is related to the definition of entropy, written as $dQ/T = dS$, and the other is the increase of entropy proper. Sometimes, the second law of thermodynamics is regarded as the first part only. However, the essential of the second law is contained in the second part.

In addition to the fundamental laws, the theories of heat include other specific laws that are not derived from the fundamental laws, but are consistent with them. Examples are the equation of state of an ideal gas and the Avogadro law, which also refers to an ideal gas. Other examples include the van der Waals equation and the Gibbs phase rule.

The development of the subject whose theoretical aspect concern us here can be found in papers and books related to thermodynamics [3–11] and to thermochemistry [12–16].

2. Laplace and Poisson

The measurement of the heat capacity of several substance was the subject of a memoir on heat jointly written by Lavoisier and Laplace, and presented to the Academy of Sciences in 1783 [17]. The measurements were accomplished by the use of an ice calorimeter that they invented for that purpose. Concerning the nature of heat, they stated that the physicists were divided in this matter. Some regard it as a fluid that expands over all the bodies, penetrating them as a result of their temperature, and may combine with them, in which case it ceases to affect a thermometer. Others regard heat as the result of the insensible movement of the molecules of matter. Under this hypothesis, heat is understood as the sum of the living forces of the molecules, which are the product of the mass of each molecule by its speed squared.

Lavoisier and Laplace did not make a decision on which hypothesis to choose. They simply adopted the principles that are common to both, one of them being the principle of conservation of free heat, which is the heat that is communicated from one body to another when in contact. When bodies are placed in contact among themselves the free heat remains the same. If in a combination or in a change of states of substances, the free heat decreases, then it will appear when the original state is reestablished. For example, when ice is transformed into water, a certain quantity of heat is consumed but it reappears when water becomes ice.

In his Elements of Chemistry [18, 19], published in 1789, Lavoisier presented a table of simple substances which included caloric along with light, oxygen, azote, hydrogen, and others. In accordance with the reformulation of chemical terminology, the term caloric replaced the old terms heat, principle or element of heat, fire, igneous fluid, and matter of fire. The new term caloric also reflected the new explanation of chemical reactions involving heat given by the chemistry of Lavoisier. Another reason for the introduction of the new term is the desire of Lavoisier to denominate cause and effect by distinct terms. Thus, caloric is the cause of heat. Lavoisier admits the cause of heat, the caloric, to be *a real and material substance, or very subtle fluid, which insinuates itself between the molecules of all bodies* [18, 19]. We see that caloric corresponds to the first of the two hypothesis mentioned above which were raised by Lavoisier and Laplace in their memoir on heat [17].

A theory of heat based on the concept of caloric emerged in the last quarter of the eighteenth century, which Maxwell in 1871 referred to as the *caloric theory* of heat [20]. A theory of gases based on the caloric was developed by Laplace and also by Poisson. The papers that they published on this subjected, published in 1822 [21] and in 1823 [22], respectively, will be now examined.

The basis of the theory of Poisson on the heat of gases and vapors is the assumption that the heat contained in a body such as a gas or a vapor is a function of the state of the body. This assumption is understood as a direct consequence of the conservation of the free heat. In accordance with this assumption, the heat per unit mass q is taken as being a function of the pressure p and the density ρ,

$$q = f(p, \rho). \tag{2}$$

A second equation is the one involving the pressure, the density and the temperature θ. Poisson assumes that they are related by

$$p = a\rho(1+\alpha\theta), \tag{3}$$

where α is equal 0.00375 and the coefficient a is a characteristic of each gas.

The specific heat is defined by $dq/d\theta$, but one should consider which quantity, the pressure or the volume, should be kept constant. Denoting by c the specific heat at constant pressure, then

$$c = \frac{dq}{d\rho}\frac{d\rho}{d\theta} = -\frac{dq}{d\rho}\frac{\alpha\rho}{1+\alpha\theta}, \tag{4}$$

and denoting by c' the specific heat at constant volume, then

$$c' = \frac{dq}{dp}\frac{dp}{d\theta} = \frac{dq}{dp}\frac{\alpha p}{1+\alpha\theta}. \tag{5}$$

If we denote by γ the ratio of the two specific heats, $\gamma = c/c'$, we find

$$\rho\frac{dq}{d\rho} + \gamma p\frac{dq}{dp} = 0. \tag{6}$$

If γ is assumed to be a constant, that is, independent of p and ρ, then the equation (6) can be integrated with the result

$$q = f(\frac{p^{1/\gamma}}{\rho}), \tag{7}$$

where f is a function to be found.

Poisson writes the solution (7) in the form

$$p = \rho^{\gamma}\phi(q), \tag{8}$$

where ϕ is another function. If p and ρ are transformed into p' and ρ' while q is remains invariant then

$$p' = p\left(\frac{\rho'}{\rho}\right)^{\gamma}. \tag{9}$$

These equations give the change of pressure when the gas is compressed or dilated without variation of heat.

To find the function f, Poisson adopts the Laplace hypothesis contained in the book 12 of Mécanique Céleste that the increase in heat is proportional to the increase in temperature. Replacing (3) in (7) we find that f is a linear function of its argument and the equation (7) is written as

$$q = A + B(\theta_0+\theta)\rho^{-\gamma+1}, \tag{10}$$

where $\theta_0 = 266.67$, and A and B are two constants, and the specific heats are given by

$$c' = B\rho^{-\gamma+1}, \qquad c = \gamma B\rho^{-\gamma+1}, \tag{11}$$

which do not depend on temperature.

The equation (6) and its solution in the form (7) were also found by Laplace by a distinct procedure contained in a publication of 1822 [21]. His point of departure is the equation

$$dp\left(\frac{dq}{dp}\right) + d\rho\left(\frac{dq}{d\rho}\right) = 0, \tag{12}$$

which follows from (2) by considering a process without variation of heat, which can be written as

$$\left(\frac{dp}{d\rho}\right) = -\frac{(dq/d\rho)}{(dq/dp)}, \tag{13}$$

where the differentiation at the left-hand side is carried out at q constant.

Next, Laplace relates the right-hand of this equation to the ratio of the specific heats, arguing as follows. Let us increase the temperature of a unit of mass by one degree at constant pressure. In this process, the density will decrease by a quantity which is $(d\rho/d\theta)$. The increase in heat per unit mass $(dq/d\rho)$ will be the specific heat at constant pressure c' divided by this quantity,

$$\left(\frac{dq}{d\rho}\right) = -\frac{c'}{(d\rho/d\theta)}. \tag{14}$$

Using a similar reasoning,

$$\left(\frac{dq}{dp}\right) = \frac{c}{(dp/d\theta)}, \tag{15}$$

where c is the specific heat at constant volume. Replacing these results in equation (13), we find

$$\left(\frac{dp}{d\rho}\right) = -\frac{(dp/d\theta)}{(d\rho/d\theta)}\frac{c'}{c}. \tag{16}$$

Laplace uses the equation of gases (3) to conclude that the ratio between $dp/d\theta$ and $(d\rho/d\theta)$ is $-p/\rho$, which replaced in equation (16) gives

$$\left(\frac{dp}{d\rho}\right) = \frac{p}{\rho}\frac{c'}{c}. \tag{17}$$

We remark that Laplace identifies the left-hand as the square of the velocity of sound so that the velocity of sound is proportional to the square root of the ratio of the specific heats.

It is worth mentioning that the first fraction on the right hand side of equation (16) equals minus $(dp/d\rho)$ where the derivative is taken at constant temperature, which we denote by k. Then we may write (16) in the form

$$\frac{k'}{k} = \frac{c'}{c}, \tag{18}$$

where k' is the derivative $(dp/d\rho)$ taken at constant heat.

Replacing the result (17) into equation (13) and using the abbreviation $c'/c = \gamma$, we get

$$-\rho\left(\frac{dq}{d\rho}\right) = \gamma p\left(\frac{dq}{dp}\right), \tag{19}$$

which is identical to the equation (6) found by Poisson. Laplace states that by analyzing the experimental data of Gay-Lussac and Welter concerning their experiments on the expansion of gases he could reach the value 1.37244 for γ [21]. Assuming that the ratio of the specific heats γ is constant, Laplace integrates equation (19) obtaining the result given by equation (7).

3. Carnot

Sadi Carnot [23–25] was born in 1796 in Paris at the Petit Luxembourg, and until the age of 16 he was educated at home by his father. He was admitted to the École Polytechnique in 1812 and just after finishing his studies in 1814 he was sent to the School of Artillery at Metz. At the end of two years of study he began to serve as a second lieutenant in the engineering regiment, and in 1819 he was commissioned in the engineer corps in Paris but immediately obtained a permanent leave of absence. In 1821 he became interested on the problem of steam engine and in 1824 he published a book on the subject entitled *Réflexions sur la Puissance Motrice du Feu* [26]. He returned to active service in 1827 but after less than a year he resigned permanently and returned to Paris. He died in 1832 at the age of 36.

In his book, Carnot pursued the laws that govern the production of work by means of heat. The book is not a technical exposition on operation of heat machines but a theoretical treatise on heat and its relationship with mechanical work. In it, Carnot introduced the closed cycle that bears his name, and proposed the fundamental law concerning how much work can be obtained from a certain quantity of heat. In spite of containing new ideas that explained the functioning of thermal machines, the book received little attention [24]. An exception was Clapeyron, who published in 1834 a paper [27] based on the ideas of Carnot, where he reached the same results obtained by Carnot.

Émile Clapeyron [28, 29] was born in 1799 in Paris. He entered the École Polytechnique in the beginning of 1817 and after graduation in the end of 1818 he attended the École de Mines. In 1820 he moved to Saint Petersburg where he remained for eleven years. He returned to Paris at the end of 1831. As the École de Mines did not have the Carnot book, he was still unaware of the publication. In 1832 he was appointed professor at the mine school in Saint-Étiene where did he find a copy of the book. From 1844 he was a professor at the École de Ponts et Chaussés teaching courses on steam engine. He died in Paris in 1864.

The Clapeyron paper also went unnoticed until when it was translated into German in 1843 [30]. The German translation appeared with a preface stating that the essay, until now only notice by a few, was included in the Journal due to its importance. Through this publication, Clapeyron and Carnot reached the physicists [24]. The paper by Clapeyron was cited by Holtzmann in the preface of his book on heat and pressure of gases, published in 1845, where he [31] stated that the paper was based on the work of Carnot which he could not provide.

In 1848, Thomson published a paper on the absolute scale of temperature based on Carnot theory [32]. However, he stated that he had not met with the original book of Carnot and that he had become acquainted with it through the paper of Clapeyron, which he found in 1845 while he was at the Regnault laboratory [29]. Clausius also refers to Carnot in his paper on theory of heat of 1850 saying that he was not able to find a copy of the book and that he was acquainted with the ideas of Carnot through the works of Clapeyron and Thomson [33].

Next we give an account of the heat theory of Carnot contained in his book. We also follow the paper of Clapeyron, which presents the content of the book of Carnot in an entirely analytical form. In the book, the analytical passages are usually reserved for footnotes because he intended the book to be read for all audiences [24]. A distinguish feature of the Clapeyron exposition was the use of the pressure-volume indicator diagram borrowed from Watt [29], which allowed him to describe more clearly the Carnot cycle. He also proposed new results such as the so called Clausius-Clapeyron relation.

The theory of Carnot is based on the caloric conception of heat which means to say that heat obeys the conservation principle. This principle is expressed by stating that the heat of a gas is as state function. Clapeyron choses the state as the volume v and the pressure p. The principle reduces to say that the heat of a gas $q(v,p)$ is a function of v and p.

The relation between heat and work is given by the principle introduced by Carnot which he formulates by considering a cyclic process that bears his name. The gas undergoing the cycle receives a certain quantity of heat q from a hotter body and delivers the same quantity of heat to a colder body, while performing a work w. Notice that the heat received and that delivered are equal by the principle of conservation of heat. The principle of Carnot states that the ratio w/q depends only on the two temperatures and is independent of the substance undergoing the cycle.

From now on we follow Clapeyron [27]. He considers a small cycle in the pv diagram, as shown in Figure 1, and denote by θ the temperature of the colder body which differ from that of the hotter body by $d\theta$. The ratio between the infinitesimal work $dpdv$ and the infinitesimal heat dq is equal to a quantity that depends only on the two temperatures. As the temperature are close to each other, this quantity is proportional to the difference in temperature $d\theta$ and the coefficient of proportionality depends only on θ. The Carnot principle is then expressed by Clapeyron in the form

$$dpdv = \frac{1}{C}dqd\theta, \tag{20}$$

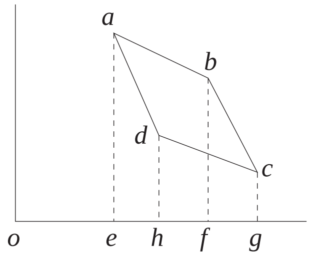


Figure 1: A small Carnot cycle in the pressure-volume diagram. The lines ab and dc represent isothermal processes whereas the lines ad and bc represent process without the intervention of heat. The figure is based on figure 3 of the Clapeyron paper of 1834 [27] and on the similar figure 2 of the Clausius paper of 1850 [33].

where C depends only on θ and is universal. The next step of the theory is to find C.

From the relation (20), and considering that q and θ are functions of v and p, the following relation is obtained by Clapeyron

$$\frac{dq}{dv}\frac{d\theta}{dp} - \frac{dq}{dp}\frac{d\theta}{dv} = C, \tag{21}$$

which is valid no only for gases but also for liquids and solids. In modern terms, C is the Jacobian of the transformation from (v, p) to (q, θ).

The equation of gas used by Carnot and Clapeyron is $pv = R(\theta_0 + \theta)$ where $\theta_0 = 267$ degrees centigrade and R is a constant that is different for each gas. It should be remarked that, as v in this equation is understood as the volume of the gas, the quantity R is a quantity that, for the same gas, varies with the amount of the gas. However, Clapeyron states that if we consider two gases with the same volume, then the constant R will be the same, in spite of the amount gas being different.

From this equation one finds $d\theta/dp = v/R$ and $d\theta/dv = p/R$ which replaced in (21) gives

$$v\frac{dq}{dv} - p\frac{dq}{dp} = RC. \tag{22}$$

Taking into account that C depends only on θ we may understand C as a function of the product pv and (22) may be written as

$$v\frac{dq}{dv} - p\frac{dq}{dp} = f(pv). \tag{23}$$

This equation can be integrated and the result is

$$q = g(pv) - f(pv)\ln p. \tag{24}$$

As the function $g(pv)$ can be understood as a function of θ, we reach the equation

$$q = R(B - C\ln p), \tag{25}$$

where $B(\theta)$ depends only on θ. Thus in addition to the equation $pv = R(\theta_0 + \theta)$, a gas obeys a second equation which is (25).

The differentiations of (25) with respect to the temperature at constant pressure and at constant volume gives the two heat capacities. The difference in the heat capacities is $RC/(\theta_0 + \theta)$. As R is the same for gases with the same volume we conclude that the difference in the heat capacities is the same if the gases are at the same temperature.

Clapeyron applies the equation (21) to the case of a liquid being transformed into its vapor. In this process the temperature remains invariant if the pressure is kept constant, while the volume increases. Therefore, $d\theta/dv$ vanishes and equation (21) becomes $k(d\theta/dp) = C$, or

$$\frac{dp}{d\theta} = \frac{k}{C}, \tag{26}$$

where we have replaced $k = dq/dv$ is the heat absorbed per unit volume, which is understood as the latent heat because it does not modify the temperature. This equation relates $dp/d\theta$ with the latent heat and after a modification by Clausius, it became known as the Clausius-Clapeyron equation.

4. Clausius

Rudolf Clausius [34, 35] was born in 1822 at Köslin, Prussia, now Koszalin, Poland. He studied at the Stettin Gimnasium until he entered the University of Berlin in 1840. After graduation in 1844 he taught for six years at the Friedrich-Werdersches Gymnasium in Berlin. He received his doctorate in 1848 and completed his habilitation at the University of Berlin in 1850, and in the same year he got a teaching position at the Royal Artillery and Engineering School in Berlin. His papers on the theory of heat, published from 1850, led him to be invited to a position of mathematical physics at the newly founded Federal Polytechnic School, Zurich, in 1855. During the stay in Zurich he developed his kinetic theory of gases. In 1867 he returned to Germany, first as a professor at the University of Würzburg and less than two years later as a professor at the University of Bonn. He died in Bonn in 1888.

Clausius published several papers on the theory of heat which were collected in a book which appeared in 1864 [36]. A translation with the title of The Mechanical Theory of Heat was published in 1867 [37]. The use of the term mechanical emphasized the concept of heat as related to the motion of particles. However, the discipline became known as thermodynamics a term coined by Rankine in 1859 [9].

The Clausius theory of heat is based on two principles. The first principle is stated as follows [33, 38]. When heat is created by the expenditure of work or when work is produced by the consumption of heat, then the amount of heat q in both cases is proportional to the work W. This principle is written as $q = aW$ where a is a constant independent of the substance. This principle is the statement of the equivalence of heat and work and was established by Mayer and Joule. Here we use the quantity $Q = q/a$ in which case the principle is written as $Q = W$.

The second principle is stated in terms of a Carnot cycle. If Q is the heat absorbed by the body at the higher temperature and W is the work performed by the body, the ratio W/Q depends only on the higher and lower temperatures and is independent of the substance of the body undergoing the cycle [38]. This is the Carnot principle but here Q is not equal to the heat delivered because heat is not conserved as happens to the Carnot theory. In fact if we denote by Q' the heat delivered, then in a cycle the quantity of heat $Q - Q'$ is transformed into the work W performed by the body, and by the first principle

$$Q - Q' = W. \tag{27}$$

We examine in the following the consequences of the first principle, contained in the first paper on the theory of heat published n 1850 [33]. Let us consider a gas undergoing a certain process which is understood as a path in diagram such as the pressure-volume or temperature-diagram. Along this path, the infinitesimal work is

$$dW = pdV, \tag{28}$$

where p is the pressure of the gas and dV is the differential of the volume V of the gas. The infinitesimal heat, Clausius writes as

$$dQ = MdV + NdT, \tag{29}$$

where dT is is the differential of the temperature T of the gas, and M and N are functions of V and T to be found.

Next, following Clapeyron, Clausius applies the principle to a small Carnot cycle, as the one shown in Figure 1. The work performed by the gas undergoing the cycle, which is the area of the parallelogram abcd, is equal to the heat absorbed by the gas along the isotherm ab minus the heat delivered by the gas along the isotherm cd. Using the small Carnot cycle Clausius shows that the heat developed along the cycle is

$$\left[\left(\frac{dM}{dT}\right) - \left(\frac{dN}{dV}\right)\right] dVdT, \tag{30}$$

and the net work along the cycle is

$$\left(\frac{dp}{dT}\right) dVdT. \tag{31}$$

The demonstration of (30) from (29) following the Clausius reasonings can be found in reference [11]. By the same reasonings one obtains (31) from (28).

By the first principle these two expressions are equal from which follows

$$\left(\frac{dM}{dT}\right) - \left(\frac{dN}{dV}\right) = \left(\frac{dp}{dT}\right). \tag{32}$$

Writing $c = M - p$, it follows from (32) that $(dc/dT) = (dN/dV)$, which is the condition for $cdV + NdT$ being an exact differential. Writing

$$dU = (M - p)dV + NdT, \tag{33}$$

then dU is the differential of a function U of V and T. Recalling that $dQ = MdV + NdT$ and $dW = pdV$, we may write

$$dU = dQ - dW. \tag{34}$$

Clausius adopts the Kelvin terminology and calls U the energy of the body. Thus the equation (34) is understood as the conservation of energy in the differential form, as long as we keep in mind that dU is an exact differential even though dQ and dW are not.

Let us apply the result above to an ideal gas, that obeys the equation $pV = RT$, where we are using the abbreviation $T = \theta_0 + \theta$ where θ is the temperature of the gas and $\theta_0 = 273$ degrees of the centesimal scale, and R is a constant. Equation (34) becomes

$$dQ = dU + \frac{RT}{V} dV. \tag{35}$$

Another result valid for an ideal gas that Clausius uses is that along an isotherm, the heat absorbed is entirely transformed into work. Thus along an isotherm, $dQ = dw$ and $dU = 0$, The equation (33) gives $M = p$, or $dU/dV = 0$ which means that U depends only on T. Writing $dU = CdT$ equation (35) becomes

$$dQ = CdT + \frac{RT}{V} dV. \tag{36}$$

and we recall that dQ is not an exact differential.

From (35), one obtains the heat capacity at constant volume, which is the ratio dQ/dT at constant V,

$$C_v = C, \tag{37}$$

and the heat capacity at constant pressure, which is the ratio dQ/dT at constant p,

$$C_p = C + R, \tag{38}$$

and the difference in the heat capacity of an ideal gas is a constant. As R is the same for two gases having the same volume it follows that the difference in the heat capacities per unit volume is the same for all gases. This result is the same as that obtained from the Carnot theory except that Clausius determines the difference and states that it is a constant.

If we consider a process where there is no exchange of heat then in equation (36) we may set $dQ = 0$ and

$$CdT + \frac{RT}{V} dV = 0. \tag{39}$$

If in addition, the heat capacity is constant then this equation can be integrated with the result

$$T = kV^{-\gamma+1}, \tag{40}$$

where $\gamma = (C+R)/C$ is the ratio of the heat capacities, from which we find

$$p = k'V^{-\gamma}, \tag{41}$$

results that are valid when an ideal gas undergoes a process without the intervention of heat, and also obtained by Poisson.

Next, we examine the consequences of the second principle, contained in his forth paper on the theory of heat published in 1854 [38]. From this principle Clausius demonstrated that dQ/T is an exact differential. In a Carnot cycle, let Q_1 and Q_2 be the heats exchanged at the temperatures T_1 and T_2, and W the work performed. According to the second principle, the ratio W/Q_1 depends only on the two temperatures. As $W = Q_1 + Q_2$ we may say equivalently that Q_2/Q_1 depends only on the two temperature. Writing this dependence in the form $|Q_2|/Q_1 = T_2/T_1$ we obtain

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \tag{42}$$

Applying this result to a cycle approximated by a series of Carnot cycle one obtains

$$\sum_n \frac{Q_n}{T_n} = 0. \tag{43}$$

In the limit of an infinite number of cycles, one finds

$$\int \frac{dQ}{T} = 0, \tag{44}$$

where the integral is performed along a closed path. From relation (44) it follows immediately that dQ/T is an exact differential.

If we divide equation (29) by T, it becomes an exact differential and we conclude that $d(M/T)/dT = d(N/T)/dV$ from which we get with the help of (32) the result

$$M = T\frac{dp}{dT}. \tag{45}$$

Let us apply this equation to coexistence of a liquid with its vapor. In this case as a certain quantity of heat is introduced at a constant pressure, the temperature remains constant and the whole volume V increases. The mass of the vapor is denoted by m and the mass of the liquid is denoted by $m_0 - m$ where m_0 is the total mass of the liquid and vapor. If we represent by ℓ the heat required to vaporize a unit of mass of the liquid then the infinitesimal heat introduced to increase the volume by dV is $dQ = \ell(dm/dV)dV$. If we compare with equation (29), we see that $M = \ell(dm/dV)$. Denoting by v_1 and v_2, the volumes of the unit mass of the vapor and liquid, respectively, then $V = mv_1 + (m_0 - m)v_2$ and $dm/dV = 1/(v_1 - v_2)$, where it is understood that v_1 and v_2 depend only on the temperature. From these results we find $M = \ell/(v_1 - v_2)$ which replaced in (45), gives

$$\frac{dp}{dT} = \frac{\ell}{T(v_1 - v_2)}, \tag{46}$$

which is known as the Clausius-Clapeyron equation. Clausius says this equation represents one of the principal theorems of the mechanical theory of heat.

In his ninth paper on the theory of heat published in 1865 [39], Clausius writes

$$dS = \frac{dQ}{T}, \tag{47}$$

and calls S, which is a state function, the *entropy* of the body. The difference in entropy ΔS between two states is determined by

$$\Delta S = \int \frac{dQ}{T}, \tag{48}$$

and the integral is performed along any path connecting the two states as the integral is the same for any path. Replacing $dQ = TdS$ in the equation (34), we get the expression

$$dU = TdS - pdV. \tag{49}$$

The result $dQ = TdS$ connecting heat and entropy was derived directly from the second principle, which is a modification of the Carnot principle. Clausius says that this second principle can be derived from a more fundamental principle which he stated as follows: *Heat can never pass from a colder to a warmer body, if no other related change occurs at the same time* [38], which we call Clausius principle. We deem that it is more appropriate to keep the second principle independent of the Clausius principle [3]. In deriving the relation $dQ = TdS$ from the second principle, it is implicit in this principle that the body undergoing the cycle is in equilibrium with the source of heat, which means that its temperature is the same or very near the temperature of the source. This situation is distinct from the situation where the Clausius principle applies, which are to be used in systems out of equilibrium.

Let us consider the main consequence of the Clausius principle by considering a body being led from an equilibrium state to another equilibrium state by a process such the intermediary states are not equilibrium states. As the body is in equilibrium in the initial and final state, its entropy in these two states are well defined, and we denote by ΔS their difference. Under these circumstances, Clausius shows that

$$\Delta S \geq \int \frac{dQ}{T'}, \tag{50}$$

where T' is to be understood as the temperature of the environment, and not the temperature of the body.

The equation (34), with the understanding that dU is an exact differential, is understood as the conservation of the energy, usually called the first law of thermodynamics. The equation (50 is usually referred to as the expression of the second law of thermodynamics. We remark that the express of this law needs first the definition of entropy, given by (47), which is valid only if the system is in equilibrium. At the end of his paper of 1865, Clausius summarizes the fundamental laws of thermodynamics in the following brief statements [39]:
Die Energie of der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu.

5. Massieu

François Massieu [40] was born in 1832 at Vatteville, France. At the age of fourteen he entered the Guernet institution in Rouen. In 1851 he was admitted to the École Polytechnique and then at the École de Mines where he spent the three regulatory years. In 1861 he defended at the Sorbonne two theses, one in analytical mechanics, the other in mathematical physics. He was appointed full professor of the Rennes Faculty of Sciences in 1864. He lived in Rennes until 1886 when he was called to Paris and in the following year he became Director of the east railways control. He died in 1896.

In 1869 Massieu published his memoir on the characteristic functions [41]. These functions were later used by Gibbs who called them fundamental equations and by Duhem who called them thermodynamic potentials, and played a central role in the theory of thermodynamics developed by these two physicists. The idea advanced by Massieu is that a single function, the characteristic function of a body, contains all the thermodynamic properties of a body. More precisely, the characteristic function by itself or by partial derivatives express the properties of a body.

Massieu wished the characteristic function to be written in terms of the temperature and volume or the temperature and pressure, which are quantities that are measured directly. This function is not the energy or the entropy but another quantity which is obtained from them. In the following we show how Massieu managed to find this function by the analysis of his paper of 1869 [41] and another longer paper on the same subject published in 1876 [42].

An infinitesimal quantity of heat dQ absorbed by a body is employed to produce an external work and to increase the energy U of the body. Denoting by p the pressure and V the volume, the work is pdV and we may write

$$dQ = dU + pdV. \tag{51}$$

We are omitting in this equation a constant A that multiplies the last term, and which is the mechanical equivalent of work. Following Clausius, $dQ/T = dS$ is an exact differential of a function S called entropy, and the above equation becomes

$$dS = \frac{1}{T}dU + \frac{p}{T}dV, \tag{52}$$

where T is the absolute temperature.

If we choose V and the temperature T as independent variable, then

$$dU = \frac{dU}{dV}dV + \frac{dU}{dT}dT, \tag{53}$$

and

$$dS = \frac{1}{T}\frac{dU}{dT}dT + \frac{1}{T}\left(\frac{dU}{dV} + \frac{p}{T}\right)dV. \tag{54}$$

Since dS is an exact differential, the derivative of the term multiplying dT with respect to V equals the derivative of the term multiplying dV with respect to T. From this relation we obtain

$$\frac{d}{dT}\frac{p}{T} = \frac{d}{dV}\frac{U}{T^2}. \tag{55}$$

If we define the differential $d\Psi$ by

$$d\psi = \frac{U}{T^2}dT + \frac{p}{T}dV, \tag{56}$$

it follows from the equality (55) that it is an exact differential of a function ψ, which Massieu calls the *characteristic function* of the body. Since $d\psi$ is an exact differential, it follows from (56) that

$$\frac{d\psi}{dT} = \frac{U}{T^2}, \qquad \frac{d\psi}{dV} = \frac{p}{T}. \tag{57}$$

Replacing U obtained from the first of the equations (57) in the relation

$$\frac{dS}{dT} = \frac{1}{T}\frac{dU}{dT}, \tag{58}$$

and integrating the resulting equation we find

$$S = \psi + T\frac{d\psi}{dT} = \frac{d}{dT}(T\psi). \tag{59}$$

If the characteristic ψ is known as a function of T and V, then we may obtain S as well as U and p.

Taking into account the first of the equations (57), we may write (59) as

$$\psi = S - \frac{U}{T}. \tag{60}$$

In an analogous manner a characteristic function is obtained by considering T and p as independent function which is

$$\psi' = S - \frac{U'}{T}, \tag{61}$$

where $U' = U + pV$.

In the second publication on the same subject, [42], Massieu simplifies his approach. He adds a term SdT to both sides of the equation $TdS = dU + pdV$ from which follows $d(TS) = dU + pdV + SdT$ which is equivalent to

$$dH = SdT + pdV, \tag{62}$$

where

$$H = TS - U. \tag{63}$$

Since dH is a exact differential so is the right-hand side of this equation and H is understood as a function of T and V and

$$S = \frac{dH}{dT}, \qquad p = \frac{dH}{dV}. \tag{64}$$

Taking into account the first of these equations, then the equation (63) is written in the form

$$U = T\frac{dH}{dT} - H, \tag{65}$$

and S, p and U are expressed in terms of the characteristic function H. The use of H instead of $\psi = H/T$, employed in the publication of 1869, followed a suggestion made by Bertrand [42].

In an analogous manner, Massieu defines a characteristic associated to the temperature and pressure as independent variables. Adding a term Vdp to both sides of the equation $TdS = dU + pdV$, we find

$$dU' = TdS + Vdp, \tag{66}$$

where

$$U' = U + pV. \tag{67}$$

Adding a term SdT to (66) we find

$$dH' = SdT - Vdp, \tag{68}$$

where

$$H' = TS - U', \tag{69}$$

which is the desired characteristic function. From (68),

$$S = \frac{dH'}{dT}, \qquad V = -\frac{dH'}{dp}. \tag{70}$$

6. Maxwell

The major subject of the Maxwell investigations was electromagnetism. However, he gave relevant contributions to the area of the kinetic theory of gases and to the theory of heat. In 1871, he published a book called Theory of Heat [20] that went through several editions. In the fourth edition of 1875 [43], he removed several paragraphs related to entropy that he found to be inappropriate and introduced new ones. The book was written in a language appropriate for a broader audience and contains few analytical expressions [44].

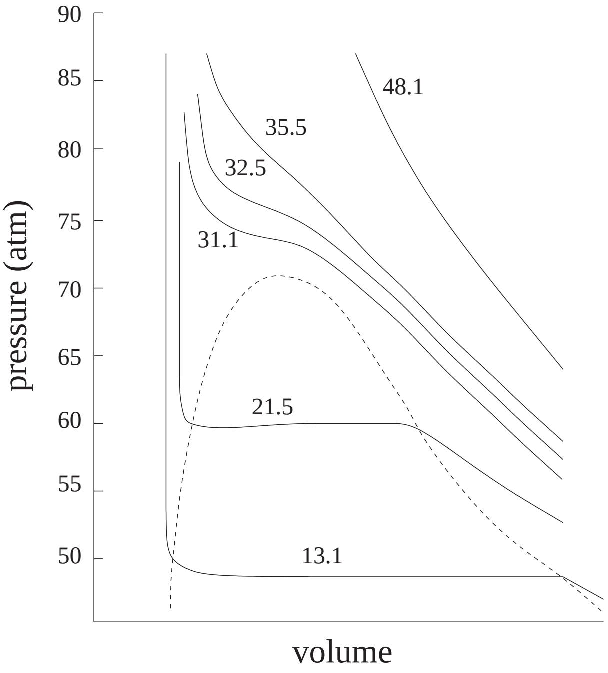


Figure 2: Isotherms of carbon dioxide according to experiments carried by Andrews [45] for various temperatures indicated in degrees Celsius, and pressure in atmospheres. The figure is adapted from the figure 15 of Maxwell book on Theory of Heat [20]. The dashed line is an addition of Maxwell and represents the boundart of the region where the liquid and its vapor coexist.

In the first five chapters of the book, Maxwell discusses the concepts of temperature, heat and work. The temperature of a body is a quantity which indicates how hot of how cold the body is. If two bodies at different temperatures are in contact, heat passes from the hot body to the cold one. The temperature is measured by a thermometer such as the mercurial thermometer or the air thermometer. The heat is measured by a calorimeter such as the ice calorimeter.

The chapter six deals with the isotherms of gases and liquids when represented in the indicator diagram which is the pressure volume diagram. Maxwell analyzes particularly the isotherms of carbon dioxide obtained experimentally by Andrews [45] and shown in Figure 2. The isotherm of 13.1°C has a straight segment at the pressure of 47 atmospheres which is the pressure at which condensation occurs. A point on this line segment represents the state of the fluid as two phases, liquid and vapor, in coexistence. The left and right ends of the segment represent the liquid and vapor, respectively. If we examine the isotherm at 21.5°C, the condensation occurs at about 69 atmospheres and length of the line segment is smaller. When one approaches the temperature of 30.92°C there is no separation between liquid and vapor. At this temperature and pressure between 73

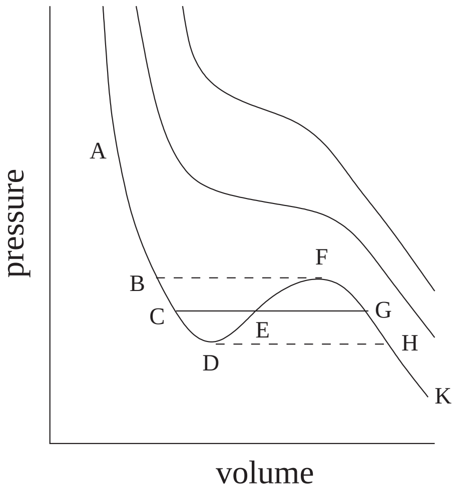


Figure 3: According to James Thomson, the isotherm of a fluid below the critical temperature may have an S shape given by the line ABCDEFGHK, which means that the liquid transforms continuously into vapor. The straight line CG connecting the liquid and vapor states is proposed by Maxwell and describes the coexistence of liquid and vapor. Adapted from figure 16 of Maxwell book on Theory of Heat [20].

and 75 atmospheres the carbon dioxide is in the critical state.

James Thomson, says Maxwell, made the suggestion [46] that the flat portion of the isotherm, that describes the coexistence of liquid and vapor, is apparent and that in fact the isotherms below the critical temperature have a form similar to the curve ABCDEFGHK of Figure 3. This means that the vapor transforms continuously into liquid without coexistence. However, remarks Maxwell, no substance could exist at any state along the points of DEF because they represent unstable states. He proposes to replace the S shaped portion by a straight line CG parallel to the axis of volumes, in accordance with the Andrews experiments. The position of the line CG which represents the vapor pressure is such that the evaporation exactly balances the condensation. The whole isotherm will then consist of the curve ABC, the straight line CG, and the curve GH.

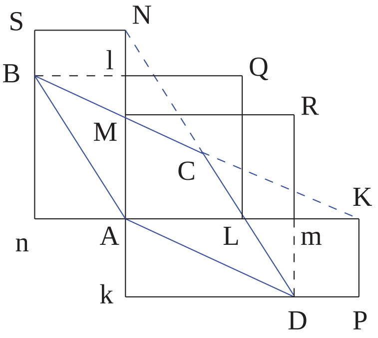


Figure 4: A small Carnot cycle ABCD in the pressure-volume diagram. BC and DA are isothermal and AB and CD are adiabatic. The areas of the rectangles AKPk, ALQl, AMRm, and ANSn are equal to each other and equal to the parallelogram ABDC. The figure is based on figure 24 of the Maxwell book [20].

In chapter nine, Maxwell derives geometrically various thermodynamic relations involving the entropy, some of which are the four relations that bear his name. To this end he uses a Carnot cycle, as shown in Figure 4, represented in the indicator diagram by two adiabatic lines and two isotherms, whose area is the net work W, which equals, by the conservation of energy, to the total heat exchanged Q. The entropy is defined in accordance with Clausius. Along an isothermal, the variation of the entropy is the ratio between the heat and the temperature. Since along an adiabatic line the entropy is invariant, then the variation of entropy along the two isotherms of the Carnot cycle are the same and one concludes that the heat exchanged is equal to the variation of entropy multiplied by the difference in the temperatures of the isotherms, $Q = (T_2 - T_1)(S_2 - S_1)$. Referring to the small Carnot cycle on the pressure-volume diagram of Figure 4, the area ABCD of the cycle, which is the net work, is equal to the heat exchanged, which is equal to $\Delta T \Delta S$, where ΔT and ΔS are the increments in temperature and entropy, respectively.

From the Figure 4 we find that:

1) AK is equal to the increase in volume at constant pressure, $(\Delta V)_p$, and that Ak is equal to the decrease in pressure at constant temperature, $-(\Delta p)_T$. As ABCD is equal to AKPk we find $\Delta T \Delta S = -(\Delta V)_p (\Delta p)_T$ which gives

$$\left(\frac{dS}{dp}\right)_T = -\left(\frac{dV}{dT}\right)_p. \tag{71}$$

2) AL$=(\Delta V)_p$, Al$=(\Delta p)_S$, and as ABCD is equal to ALQl, then $\Delta T \Delta S = (\Delta V)_p (\Delta p)_S$ which gives

$$\left(\frac{dT}{dp}\right)_S = \left(\frac{dV}{dS}\right)_p. \tag{72}$$

3) AM$=(\Delta p)_V$, Am$=(\Delta V)_T$, and as ABCD is equal to AMRm, then $\Delta T \Delta S = (\Delta V)_T (\Delta p)_V$ which gives

$$\left(\frac{dS}{dV}\right)_T = \left(\frac{dp}{dT}\right)_V. \tag{73}$$

4) AN$=(\Delta p)_V$, An$=-(\Delta V)_S$, and as ABCD is equal to ANSn, then $\Delta T \Delta S = (\Delta V)_S (\Delta p)_V$ which gives

$$\left(\frac{dT}{dV}\right)_S = -\left(\frac{dp}{dS}\right)_V. \tag{74}$$

The equations (71), (72), (73), and (74) are the four Maxwell relations of thermodynamics.

Using the illustration of Figure 4, Maxwell also shows the relation between the two types of heat capacities and the two types of elasticities. The line AM represents the increase in pressure at constant volume when the entropy increases by dS and the line AN represents the increase in pressure at constant volume when the temperature increases by dT. Therefore, the heat capacity at constant volume is

$$C_V = T\frac{\mathrm{AM}}{\mathrm{AN}}, \tag{75}$$

where T is the temperature of state A. In an analogous manner, the line AL represents the increase in volume at constant pressure when the entropy increases by dS and the line AK represents the increase in volume at constant pressure when the temperature increases by dT. Therefore, the heat capacity at constant pressure is

$$C_p = T\frac{\mathrm{AK}}{\mathrm{AL}}. \tag{76}$$

Let us consider now the two elasticities. One of them is the ratio of the decrease in pressure and the increase in volume at constant temperature multiplied by the volume, which is denoted by E_T. From Figure 4, the decrease in pressure is Ak and the increase in volume is Am, and

$$E_T = V\frac{\mathrm{Ak}}{\mathrm{Am}} = V\frac{\mathrm{AM}}{\mathrm{AK}}, \tag{77}$$

where we used the equality between the areas of AKPk and AMRm. In an analogous manner, the elasticity E_S at constant entropy is $E_S = V$(Al/An)= V(AN/AL).

$$E_S = V\frac{\mathrm{Al}}{\mathrm{An}} = V\frac{\mathrm{AN}}{\mathrm{AL}}. \tag{78}$$

From the above relations we see that the ratio C_p/C_V equals the ratio E_S/E_T, that is

$$\frac{C_p}{C_V} = \frac{E_S}{E_T}. \tag{79}$$

From the geometrical properties of the Figure 4, we see that the area of the parallelogram ABCD is (Am·Al − Ak·An) or $(\Delta V)_T(\Delta p)_S - (\Delta p)_T(\Delta V)_S$. But the area of ABCD, which is the net work, is equal to the heat $\Delta T \Delta S$ and we reach the relation

$$\left(\frac{dp}{dV}\right)_S - \left(\frac{dp}{dV}\right)_T = \left(\frac{dS}{dV}\right)_T \left(\frac{dT}{dV}\right)_S, \tag{80}$$

which gives

$$E_S(C_p - C_V) = C_V(E_S - E_T) = TV\left(\frac{dp}{dT}\right)_V^2, \tag{81}$$

where the relation (79) was used.

In chapter twelve, Maxwell discusses the available energy or the maximum work one can obtain from a body undergoing a thermodynamic transformation. The conservation of energy along a process connecting two states AB can be understood by representing the process in a pressure volume diagram as shown in Figure 5. In this diagram, the work W performed by the body undergoing the process is the area ABba. As to the heat absorbed by the body, it is represented by the area AB$\beta\alpha$, where Aα and Bβ are isentropic lines. Indeed, if we consider a closed path AB$\beta\alpha$, the heat along this closed path equals the work which is the area of this closed path. But the heat developed along this closed path occurs only along AB as Aα and Bβ are isentropics. The variation of the energy of the body is the difference between the area ABba and AB$\beta\alpha$. If we consider another path connecting the states A and B, we see that the increase in the work in relation to the previous path equals the decrease in the heat and the variation of energy remains invariant.

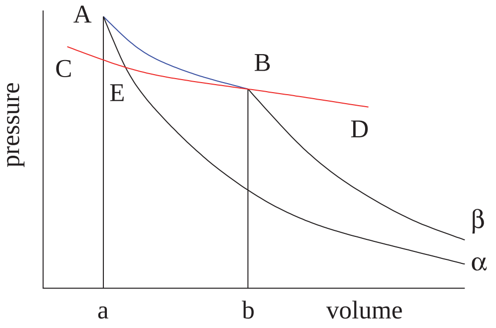


Figure 5: The curve AB represents a process connecting the states A and B, and the lines Aα and Bβ are two adiabatics. The area of ABba represents the work performed and the area AB$\beta\alpha$ represents the heat absorbed by the body undergoing the process AB. The line CBD is an isotherm. The figure is based on figure 26 of the Maxwell book [20].

Let us consider all paths connecting the state A to B and ask for the path which gives the maximum work supposing that the surrounding medium is at the temperature T the same as the body at the final state B. To find this path we draw the isotherm CBD through the state B which corresponds to a temperature T smaller than that of A. Suppose that the body has a temperature higher than T which corresponds to the point of the path is above CBD. In this case it cannot receive heat from the medium and its entropy cannot be higher than that of A which means that the point of the path must be below the isentropic Aα. Analogously, if the point of the path is below CBD it must be above the isentropic Aα. Within these restrictions, the maximum work occurs for the path AEB, where E is the point where the isentropic passing through A meets the isotherm passing through B. This maximum work is equal to the heat received by the body along EB, which is $T(S_0 - S)$, minus the increase in energy $E_0 - E$, that is,

$$E - E_0 - T(S - S_0). \tag{82}$$

We are denoting by E and S the energy and entropy of the initial state A and by E_0 and S_0 those of the final state B. This quantity is the part of the energy which is available to be transformed into work, which for that reason Maxwell called (82) the available energy. If W denotes the work of any process connecting A to B then

$$E - E_0 - T(S - S_0) \geq W. \tag{83}$$

In the first edition of the book of 1871, Maxwell incorrectly identified entropy with the available energy. The error was pointed out by Gibbs in his paper on the geometric representation of thermodynamics, published in 1873. This was corrected by Maxwell in the fourth edition of 1875, who also added a whole section in the chapter twelve to discuss the Gibbs geometric representation [44].

7. van der Waals

Joahnnes Diderik van der Waals [47, 48] was born in 1837 at Leiden, Netherlands. He started a teaching career as an assistant school teacher around 1853. In 1862 he obtained a qualification that allowed him to hold the position of a director of a primary school. He attend the University of Leiden from 1862 but not as a regular student because of his lack of knowledge in the classical languages. He was appointed physics teacher at the advanced schools in Deventer, in 1865, and after in The Hague, in 1867. In 1871, the requirement of classical language was removed and van der Waals could enroll in the doctoral studies at the University of Leiden. He defended his doctoral thesis concerning the equation of state describing the liquid and gas transition in 1873. In 1877, he was nominated professor of physics at the University of Amsterdam. He retired from the university in 1908. He died in Amsterdam in 1923.

The van der Waals thesis [49, 50] concerns the equation of state of a fluid that describes both the liquid and the gas phases as well as its critical point. The equation of state is the expression of the pressure as a function of the temperature and the volume. Van der Waals assumes the molecular structure of fluid and that the molecules moves under the action attractive forces which vanish when the distance between particles is large. The molecules have a finite size which means that they have a strong repulsion when the distance between their centers is of the order their sizes.

The point of departure is the Clausius virial theorem [51]

$$\frac{1}{2}\sum_i mv_i^2 = -\frac{1}{2}\sum(X_i x_i + Y_i y_i + Z_i z_i), \tag{84}$$

where m is the mass, v_i is the velocity, x_i, y_i, and z_i are the coordinates and X_i, Y_i, and Z_i are the components of the force acting on a particle. The left hand side is the total kinetic energy and the term at the right was called the virial by Clausius. The virial can be written as the sum of two parts. One of them is related to the internal forces, considered to be central forces, and reads

$$\mathcal{V} = \frac{1}{2}\sum_{ij} r_{ij} f(r_{ij}), \tag{85}$$

where r_{ij} denotes the distance between two particles and $f(r_{ij})$ the force between them. The second part is related to the external forces which are the reactions of the wall of the vessel due to the impact of the molecules. It equals to $(3/2)pV$ where p is the pressure of the fluid and V the volume of the vessel. The equation (84) becomes

$$\frac{1}{2}\sum_i mv_i^2 = \mathcal{V} + \frac{3}{2}pV, \tag{86}$$

which is written in the form

$$\frac{1}{2}\sum_i mv_i^2 = \frac{3}{2}(p + p')V, \tag{87}$$

where p' represents the molecular pressure.

Van der Waals argues that on account of the extension of the molecule, the volume V should be replaced by $V - Nb$ where N is the number of molecules and b is four times the volume of a molecule, considered to be a sphere. He also argues that the internal molecular pressure p' is proportional to the square of the density, that is proportional to $(N/V)^2$. Defining $v = V/N$, we get

$$\frac{1}{2}\sum_i mv_i^2 = \frac{3}{2}N\left(p + \frac{a}{v^2}\right)(v - b), \tag{88}$$

where the constant a is related to the molecular attraction. Van der Waals assumes that the kinetic energy is proportional to $1 + \alpha t$ where t is the temperature in degrees centigrade, and this equation becomes

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{89}$$

where R is a constant and T is an abbreviation for $1+\alpha t$.

The calculations carried out by van der Waals in the first seven chapters of the thesis is not properly a derivation of his equation from the virial theorem applied to a system of interacting particles, as we would expected. Nonetheless one may consider the calculations to be a justification of the equation that he may already had in mind [48]. But the relevant point here is that his equation contains terms that describe the attraction of the molecules and the repulsion at short distances, which are the basic assumptions of van der Waals concerning the interaction of particles and that are crucial to describe the two states of aggregation of the molecules, the liquid and vapor. In the words of Maxwell, *his attack of this difficult question is so able and so brave, that it cannot fail to give a notable impulse to molecular science* [52].

We write the van der Waals equation in the form

$$p = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{90}$$

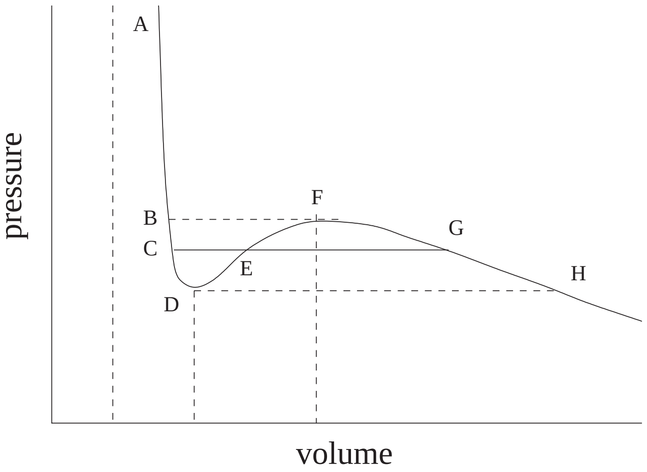


Figure 6: An isotherm at a temperature below the critical temperature according to the van der Waals equation (90). Along the S shaped line CDEFG, the liquid transforms continuously into vapor. But this cannot be realized experimentally because along DEF the body is unstable. Based on the figure 6 of the van der Waals thesis [49].

For high temperatures, the pressures decreases monotonically with the volume. Below a certain temperature the isotherms are of the form given by the Figure 6. For a given pressure there are three possible volumes for a given isotherm, which correspond to the points C, E, and G. Van der Waals recognizes that the volumes of C and G, the smaller and the greater volumes, are the volumes the body acquires in the liquid and gas states, respectively.

To determined the critical point, it suffices to observe that at the critical isotherm the three points C, E, and G coalesce in one point. As the volume of these points are the roots of the cubic equation

$$pv^3 - (RT + bp)v^2 + av - ab = 0, \tag{91}$$

the occurrence of the critical isotherm is obtained when this equation has three equal roots. From this condition van der Waals finds the critical values for the volume $v_c = 3b$, for the pressure $p_c = a/27b^2$, and for the temperature $RT_c = 8a/27b$.

Along any isothermal curve described by the analytical expression (90), the body changes states without ceasing to being homogeneous. In particular, this happens to the line CDEFG which leads us to conclude that along CDEFG the liquid transforms *continuously* into vapor, that is, without being split into coexisting phases. Van der Waals points out that the continuous change of states predicted by his equation is in agreement with the suggestion made by James Thomson [46] of a continuous change from liquid to vapor along an isotherm. However, he remarks that at the intermediate point E and at any point between D and F, dp/dv is positive which means that a homogeneous body is unstable and cannot remain homogeneous. In other terms, a homogeneous body cannot be observed in these conditions.

The comparison of his isotherms to those of the carbon dioxide obtained experimentally by Andrews shows an agreement with the line ABCGH containing the straight line segment CG. The line segments FG and CD, which are not contained in the Andrews isotherms, represent superheated liquid and supercooled vapor observed experimentally. Van der Waals rejected the solution given by Maxwell in his book on the Theory of Heat of joining the C and G by a straight line, and left open this problem.

In the first edition of 1871 of his book on the Theory of Heat, Maxwell proposed the straight line to represent the coexistence of liquid and vapor but did not specify the position of the line. In a publication of 1875 [52], Maxwell proposed to place the straight line in such a way that the areas of the region CDE and EFG be equal. The reasonings given by Maxwell are as follows. Suppose that the body, starting from the state G, follows the hypothetical S shaped line GFEDC and then return to G by the straight line CG. Since the temperature remains the same, no heat is exchanged and, taking into account that the final state is the same as the initial state, the net work vanishes. This means that the area under the curve CDEFG must be equal to the area under the straight line CG, which leads to the equality of the areas CDE and EFG. The equal-areas rule was also proposed independently by Clausius in a publication of 1880, which he obtained by using a reasoning similar to that just presented [53, 54].

8. Gibbs

Josiah Willard Gibbs [56, 57] was born in 1839 at New Haven, United States. In 1849 he entered the Hopkins Grammar School and from 1854 he attended the Yale College from which he graduated in 1858. In the same year he entered the Department of Philosophy and the Arts of Yale as a student of engineering. He received the PhD degree in this area in 1863 and in this year he was appointed as tutor in Yale College for three years. In the period from 1866 to 1869 he traveled to Europe where he attended lectures in Paris and Berlin. After returning to New Haven he was appointed professor of mathematical physics at Yale in 1871 In 1873 he published two papers on the use of geometric surfaces to represent the thermodynamics properties of substances [58, 59]. These papers were followed by his major work on thermodynamics, dealing with the equilibrium of heterogeneous substances, published in two parts, the first in 1876 [60] and the second in 1878 [61]. He also worked on vector calculus and electromagnetic theory of light. In 1902 he published a book on statistical mechanics where he used the theory of probability and Newtonian mechanics to give a rational foundation of thermodynamics. He died in the following year in 1903.

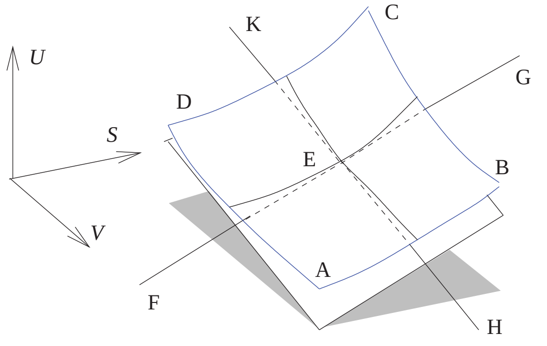


Figure 7: The thermodynamic surface ABCD, which gives the energy U as a function of the entropy S and the volume V. The straight lines FEG and HEK belong to the plane tangent to the thermodynamics surface at the point E. The inclinations of the lines FEG and HEK are related to the temperature T and to the pressure p, respectively. The thermodynamic surface remains above the plane tangent to any point of the surface, which is equivalent to say that it has the convexity property.

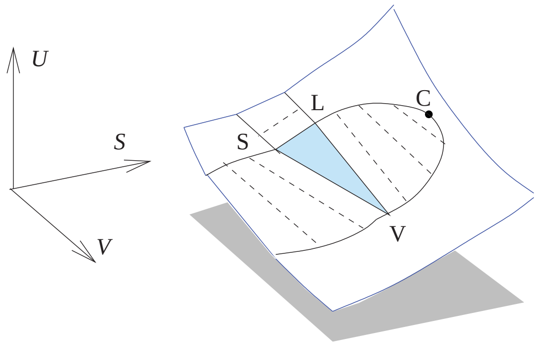


Figure 8: Thermodynamic surface displaying the coexistence of three phases, solid, liquid, and vapor, represented by the plane triangle SLV. Any point of the triangle correspond to the same temperature and the same pressure. It also displays the coexistence of two phases, represented by the dashed straight line segments. Any point of a certain line correspond to the same temperature and pressure. The point C is the critical point where two phases become identical.

8.1. Graphical representation of thermodynamics

We analyze here the two papers of 1873 [58, 59] which deal with the graphical representation of the thermodynamics properties of substances. The first paper starts with the conservation of energy in the differential form

$$dU = dQ - dW, \tag{92}$$

where U is the energy of a given body, Q is the heat received by the body, and W the work done by the body when passing from one state to another. The heat and work are related to entropy S and volume V of the body by $dQ = TdS$ and $dW = pdV$ where T is the absolute temperature and p the pressure of the body. The elimination of dQ and dW gives

$$dU = TdS - pdV. \tag{93}$$

Gibbs remarks that V, p, T, U, and S are state functions and that only two are capable of independent variations. He also remarks that W and Q are not state functions but are determined by the sequence of states by which the body passes along a process.

The main idea of Gibbs contained in the two papers of 1873 lies on the understanding of U as a function of S and V and thus as a surface on the space defined by the rectangular axes U, S, and V, as shown in Figure 7, which he calls the thermodynamics surface. In accordance with the equation (93),

$$T = \frac{dU}{dS}, \qquad p = -\frac{dU}{dV}, \tag{94}$$

and the temperature and pressure are the tangents of the angles of inclination of the lines FEG and HEK, respectively. Gibbs remarks that the points at the surface represents states of thermodynamic equilibrium.

The fundamental property of the thermodynamic surface advanced by Gibbs is its convexity. He states this property by stating that *the surface falls above the tangent plane except at the single point of contact*, as can be seen in Figure 7. This property is expressed by considering a body being placed in a medium with temperature T and pressure p. The medium is large enough so that the exchange of heat and work with the body does not alter its temperature and pressure. If the initial and and final energy, entropy, and volume of the body are, respectively, (U', S', V') and (U'', S'', V'') Gibbs argues by using stability reasoning that [59]

$$U'' - TS'' + pV'' \leq U' - TS' + pV'. \tag{95}$$

We transform this expression as follows.

For a better understanding of this expression, we denote the temperature and pressure of the medium by T_0 and p_0 and we suppose that the body reaches equilibrium and thus attains the temperature T_0 and pressure p_0. As initial state of the body we choose a point (U, S, V) on the thermodynamic surface and denote the final state by (U_0, S_0, V_0). The stability equation becomes

$$U \geq U_0 + T_0(S - S_0) - p_0(V - V_0). \tag{96}$$

The right hand side describes a plane tangent to the thermodynamic surface at the point (U_0, S_0, V_0). Therefore another point of the thermodynamic surface given by $U(S, V)$ lies above the tangent plane.

The Figure 7 shows the thermodynamic surface of a homogeneous body. If the body becomes heterogeneous then there are distinct points of the surface with the same temperature and the same pressure, as the plane triangle and the straight line segments shown in Figure 8. These points correspond to different states of coexistence of two or more thermodynamic phases. As the entropy and volume of the body changes, the size of each phase changes, but the temperature and the pressure remain invariant. Thus the change of states should describe geometric figures with all points with the same inclinations, such as a straight line segment or a plane triangle. The form is related to the coexistence of two phases such as solid and liquid, solid and vapor, and liquid and vapor, and the later with three phases, such solid, liquid, and vapor.

In the case of the liquid-vapor coexistence, the length of the straight line segment eventually vanish at a point C, as shown in Figure 8, when one varies the temperature. This point is called the critical point and is a point where the two phases become identical. Gibbs gives as an example of this point the liquid-vapor critical point of the carbon dioxide obtained experimentally by Andrews in 1869 [45].

8.2. Thermodynamics of heterogeneous substances

We analyze now the Gibbs paper on equilibrium thermodynamics published in two parts, in 1876 and 1878 [60, 61]. A translation of the paper into German appeared in 1892 [62] and into French in 1899 [63]. It is a large paper containing 323 pages dealing with heterogeneous substances which are systems having two or more thermodynamic phases in coexistence. A homogeneous substance contains a single phase. The thermodynamics of Gibbs is founded on the principles upon which Clausius based his own theory of heat. Gibbs acknowledges this at the very beginning of the paper by quoting the last two sentences of the Clausius paper of 1865 [39], which are brief statements of the first and second laws of thermodynamics: *Energie of der Welt ist constant. Die Entropy der Welt strebt einem Maximum zu.*

The point of departure of the Gibbs theory is the two criteria of equilibrium for an isolated system. Let us denote by U and S the energy and entropy of the system and let us suppose that the system is in equilibrium.

I. If we consider all variations of its state which do not alter its energy, then the variation of the entropy is negative or vanishes, $(\delta S)_U \leq 0$.
II. If we consider all variations of its state which do not alter its entropy, then the variation of the energy is positive or vanishes, $(\delta U)_S \geq 0$.

The criteria are direct consequences of the second law of thermodynamics as expressed by Clausius inequality, although Gibbs did not present an explicit derivation of them from the inequality.

Gibbs considers a homogeneous system composed of various substances and assumes that the energy U is a function of the entropy S, the volume V, and the masses $m_1, m_2, \ldots, m_n$, where n is the number of substances. The differential of the energy is

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n, \quad (97)$$

where T is the temperature, p the pressure. The coefficient μ_i is the chemical potential, which Gibbs called the potential for the substance. He did not use the term chemical potential in his major paper on thermodynamics. This term was introduced by Bancroft in a letter to Gibbs of 1899 [64]. It was defined by Gibbs as follows. *If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and the entropy and volume remaining unchanged, the increase in energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered.* That is, $\mu_i = (dU/dm_i)$ where S, V, m_1, $m_2, \ldots, m_n$ remain constant except m_i.

The fundamental consequence of the principle I above is the condition for the equilibrium of a heterogeneous substances, that is, a body composed by two or more thermodynamic phases in coexistence. From this principle it follows that all phases must have the same temperature, the same pressure, the same chemical potential related to the first component substance, the same chemical potential related to the second component substance, and so on. This condition is written as

$$T' = T'' = T''' = \ldots \quad (98)$$

$$p' = p'' = p''' = \ldots \quad (99)$$

$$\mu_i' = \mu_i'' = \mu_i''' = \ldots \quad (100)$$

where the superscripts denote the thermodynamic phases. The last equation is the condition for chemical equilibrium. Notice that Gibbs calls component substance what we call a chemical component.

Looking at the equation (97), we see that U can be considered a function of the $n+2$ variables S, V, $\mu_1, \ldots, \mu_n$. Gibbs calls this function a *fundamental equation* because from it we may obtain the temperature, the pressure, and the chemical potentials by differentiation. Gibbs considered other fundamental equations obtained by using the approached introduced by Massieu [41], who called them *characteristic functions.* Gibbs defines

$$F = U - TS. \quad (101)$$

The differential of F is

$$dF = -SdT - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n, \quad (102)$$

which allows us to consider F as a function of T, V, and $m_1, m_2, \ldots, m_n$. Gibbs also defines $H = U + pV$ which is a function of S, p, and $m_1, m_2, \ldots, m_n$ and $G = U - TS + pV$, which is a function of T, p, and $m_1, m_2, \ldots, m_n$. Gibbs remarks that Massieu introduced two kinds of characteristic functions. One of them is identified with $-F/T$ and the other with $-G/T$. These functions were introduce by Massieu in a paper of 1869 [41]. We remark that in another paper [42], published in 1876, Massieu considers the characteristic functions which are identified with $-F$, H, and $-G$.

Gibbs argues that U can be written in the form

$$U = TS - pV + \mu_1 m_1 + \mu_2 m_2 + \ldots + \mu_n m_n, \quad (103)$$

by assuming that the quantities U, S, V, and $m_1, m_2, \ldots, m_n$ varies in the same proportion. From this relation, one finds

$$F = -pV + \mu_1 m_1 + \mu_2 m_2 + \ldots + \mu_n m_n, \quad (104)$$

$$G = \mu_1 m_1 + \mu_2 m_2 + \ldots + \mu_n m_n, \quad (105)$$

and the relation

$$SdT - Vdp + m_1 d\mu_1 + m_2 d\mu_2 + \ldots + m_n d\mu_n = 0, \quad (106)$$

which is known today as the Gibbs-Duhem relation.

If one considers two states at the same temperature, then $F' - F'' = U' - U'' - T(S' - S'') = U' - U'' - Q = -W$, and the decrease in F is the work done by the system at constant temperature. In an analogous manner, if we consider two states at the same pressure, then $H' - H'' = U' - U'' + p(V' - V'') = U' - U'' + W = Q$, and the increase in H is the heat absorbed by the system at constant pressure. The condition of equilibrium for system that perturbed in such a way that the temperature remains constant is expressed by $(\delta F)_T \geq 0$. If in addition the pressure also remains constant then the condition is $(\delta G)_{T,p} \geq 0$.

As the work is equal to the variation of the internal energy U at constant S, Gibbs asserts that U is the force function for constant entropy. Analogously, as the work is equal to $-F$ at constant T, then $-F$ is the force function for constant temperature. A *force function* is the negative of what we call potential energy function.

Gibbs introduces the rule concerning the number of phase in coexistence, known as the Gibbs phase rule. Let us consider a system consisting of r phase in coexistence. The number of independent of variables capable of being varied is $n + 2 - r$. This is so because the variables are T, p and the n chemical potentials, which sum up to $n + 2$. However, we have r conditions of equilibrium expressed by equations (98), (99), and (100), reducing the number of independent variables by r. The phase rule is expressed by $n + 2 - r \geq 0$. In the case of a simple substance, $n = 1$, the rule implies that we may have at most three phases in coexistence. We should remark that the Gibbs rule is based on the implicit assumption that the r conditions of equilibrium consist of r independent equations. If only $r^* \leq r$ are independent then the rule should read $n + 2 - r^* \geq 0$. This might occur if the system may hold some symmetries which will be reflected in the equation for the conditions of equilibrium. However, this does not seem to be the case of fluid systems that are the main concern of Gibbs.

Let us consider two phase in coexistence in a system one just one component. The condition of equilibrium is $\mu' = \mu''$ or $d\mu' = d\mu''$. Using equation (106), $m' d\mu' = -S' dT + V' dp$ and $m'' d\mu'' = -S'' dT + V'' dp$ from which follows

$$\frac{dp}{dT} = \frac{s' - s''}{v' - v''} = \frac{\ell}{T(v' - v'')}, \quad (107)$$

where s' and s'' are the entropy per unit mass of each phase, and v' and v'' are the volume per unit mass of each phase, and ℓ is the heat absorbed by a unit of mass of the substance in passing from one phase to another. The equation (107) is known as the Clausius-Clapeyron equation.

Let us consider two equilibrium states and let us denote by $\Delta U = U' - U$ the difference in energy of the second and first states. In a similar manner we define $\Delta S = S' - S$, $\Delta V = V' - V$, and $\Delta m_i = m_i' - m_i$. Gibbs writes the general condition of stability for a system with several chemical components as

$$\Delta U > T\Delta S - p\Delta V + \mu_1 \Delta m_1 + \ldots + \mu_n \Delta m_n, \quad (108)$$

where T, p, and μ_i refer to the temperature, the pressure, and the chemical potential of the first state. If V is kept constant then a consequence of the stability condition (108) involve the second derivatives of U with respect to the variables $S, m_1, \ldots, m_n$. If a matrix is set up with these second derivatives, the determinant of any minor is positive.

Gibbs analyzes the properties of a mixture of ideal gases by first considering the fundamental equation of a single ideal gas. To this end he uses the equation that relates the pressure p, the volume V and the temperature T for a ideal gas

$$pV = amT, \quad (109)$$

where m is the mass of the gas and a is a constant. He also uses the equation that related the energy and temperature

$$U = m(cT + \varepsilon), \quad (110)$$

where c and ε denote constants. Using these equations to eliminate T and p in equation (93), one finds

$$\frac{mcdU}{U - m\varepsilon} = dS - \frac{am}{V} dV, \quad (111)$$

The integration of this equation gives

$$c \ln \frac{U - m\varepsilon}{cm} = \frac{S}{m} + a \ln \frac{m}{V} - h, \quad (112)$$

where h is a constant. This is a fundamental equation because U is an implicit function of S, V, and m.

Replacing U, given by (110), into (112) one finds

$$S = m\left(c + h + c \ln T + a \ln \frac{V}{m}\right). \quad (113)$$

From the definition of F, one obtains the fundamental equation

$$F = m\varepsilon + mT\left(c - h - c \ln T + a \ln \frac{m}{V}\right). \quad (114)$$

To reach the fundamental equation for a mixture of ideal gases, Gibbs assumes the following rule. The pressure of a mixture of different gases is equal to the sum of the pressures of each gas at the same temperature and at the same value of the chemical potential. From this rule, Gibbs finds that the function F of the mixture is equal to the sum of these functions by considering each gas separately at the same temperature and with the same volume. Taking into account the expression (104), it is given by

$$F = \sum_i m_i \left[\varepsilon_i + T\left(c_i - h_i - c_i \ln T + a_i \ln \frac{m_i}{V} \right) \right]. \tag{115}$$

From the fundamental equation (115), we determine the chemical potential of the substance i by $\mu_i = dF/dm_i$,

$$\mu_i = \varepsilon_i + T\left(a_i + c_i - h_i - c_i \ln T + a_i \ln \frac{m_i}{V} \right), \tag{116}$$

the pressure by $p = -dF/dV$, or

$$p = \sum_i \frac{a_i m_i T}{V}, \tag{117}$$

and the entropy by $S = -dF/dT$ or

$$S = \sum_i m_i \left(h_i + c_i \ln T + a_i \ln \frac{V}{m_i} \right). \tag{118}$$

Using equation (118),we may determine the increase of entropy when two different gases are mixed at the same temperature and pressure. To meet this condition we suppose that initially each gas occupies one half of the final volume V. The result is

$$(m_1 a_1 + m_2 a_2) \ln 2 = \frac{pV}{T} \ln 2. \tag{119}$$

Gibbs remarks that this expression does not depend on the nature of the gases. In addition, he points out that pV/T is determined by the number of molecules which are mixed. That is, Gibbs is using the Avogadro law of gases.

In the second part of the paper on heterogeneous substances, Gibbs deals with the surface thermodynamics and capillarity. This includes the study of the thermodynamic properties of the interface between two coexistence fluid phases. The Gibbs approach uses the concept of dividing surface, which is a geometrical surface parallel to the interface defined as follows. Let us consider a closed surface within the fluid that contains the interface, and denote by V' and V'' the volume above and below the dividing interface to be found. The densities of each one of the two phases are denoted by ρ' and ρ''. The dividing surface is placed at a point where the mass m of the fluid inside the closed surface equal the sum $V'\rho' + V''\rho''$.

Having defined the dividing surface we may determine the excess of mass m_i^{s} of the substance i by

$$m_i^{\mathrm{s}} = m_i - m_i' - m_i'', \tag{120}$$

where m_i is the mass of the substance i inside the closed surface and $m_i' = V'\rho_i'$ and $m_i'' = V''\rho_i''$, where ρ_i' and ρ_i'' are its densities in each one of the phases.

In an analogous manner, we define the excess energy U^{s} bu

$$U^{\mathrm{s}} = U - U' - U'', \tag{121}$$

where U is the energy of the fluid inside the close surface, and $U' = V'u'$ and $U'' = V''u''$, where u' and u'' are the densities of energy in each phase, and the excess entropy S^{s} by

$$S^{\mathrm{s}} = S - S' - S'', \tag{122}$$

where S is the entropy of the fluid inside the close surface, and $S' = V's'$ and $V''s''$, where s' and s'' are the densities of entropy in each phase.

A quantity related to the whole closed surface such as U growths with the volume V if V is large. However its difference to the quantity $U' + U''$, which also growths with V, does not. In fact the difference, which is the excess energy is much smaller than U or $U' + U''$ and growths with the area A of the dividing surface inside the closed surface. This is so because the difference vanish except in the region very near the interface. Therefore, all the excess quantities are considered to be proportional to A.

The next step is to use the equation (97), with the volume constant, to write

$$dU = TdS + \sum_i \mu_i dm_i, \tag{123}$$

$$dU' = TdS' + \sum_i \mu_i dm_i', \tag{124}$$

$$dU'' = TdS'' + \sum_i \mu_i dm_i'', \tag{125}$$

where the temperature and the chemical potentials are the same in the three equations. From these equations we find

$$dU^{\mathrm{s}} = TdS^{\mathrm{s}} + \sum_i \mu_i dm_i^{\mathrm{s}}. \tag{126}$$

As U^{s} depends on the area A, this equation is in fact valid for constant A. If we allow the area to vary, then

$$dU^{\mathrm{s}} = TdS^{\mathrm{s}} + \sigma dA + \sum_i \mu_i dm_i^{\mathrm{s}}, \tag{127}$$

where *sigma* is the surface tension. Considering that all excess quantities are proportional to A, we may write

$$U^{\mathrm{s}} = TS^{\mathrm{s}} + \sigma A + \sum_i \mu_i m_i^{\mathrm{s}}. \tag{128}$$

Combining (127) and (128), we reach the equation

$$d\sigma = -s^{\mathrm{s}} dT - \sum_i \Gamma_i d\mu_i, \tag{129}$$

where $\Gamma_i = m_i^{\rm s}/A$ is the surface density of the substance i and $s^{\rm s} = S^{\rm s}/A$ surface entropy. The equation (129) relates the surface tension with temperature and the chemical potentials.

9. Thermochemistry

We present here the main laws of thermochemistry, or chemical thermodynamics, understood as the study of systems consisting of many chemical species, and particularly the study of the heat associated to chemical reactions and phase changes [12–16]. These laws were proposed by Lavoisier, by Hess, and by other chemists of the second half of the nineteenth century. In the two sections that follows the present section, we analyze the thermodynamic theories developed by Planck and by Duhem, which include a systematic and analytical approach to the laws of thermochemistry that we present here. It should be remarked that the Gibbs thermodynamics, analyzed above, is a thermochemical theory as the main subject of his theory was the equilibrium of heterogeneous substances.

The conservation of mass in chemical reactions was advocated by Lavoisier as a fundamental principle. He stated this principle in his treatise on Chemistry of 1789 in the following terms [18, 19]: *in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combination of these elements.*

In their memoir on heat of 1784 [17], Lavoisier and Laplace reported experiments on the heat developed in combustion, understood as a chemical reaction involving oxygen as proposed by Lavoisier. They measured the heat of combustion of some substances including coal, and the heat associated to animal respiration, understood as a very slow combustion. In one of these experiments, a guinea pig was placed inside a bell jar with air enriched with oxygen for one hour and one quarter, and the heat developed measured by an ice calorimeter.

Within the caloric theory employed by Laplace and Lavoisier, heat was understood as a conserved quantity, which is equivalent to say that the heat involved along any process depends only on the initial and final states. This principle when applied to chemical reactions was established and verified experimentally by Hess in 1840 [65, 66]. Hess proposed that the heat released by a chemical combination is the same no matter whether the combination is direct or carried out indirectly through an intermediate step. He stated the principle in the following terms [65, 66]: *When a combination takes place, the quantity of heat released is always constant, whether the combination takes place directly or indirectly, and repeated differently.*

In a paper on the bases of thermochemistry of 1854 [67], Thomsen proposed that the force that holds a compound united, which he called affinity, can be measured by the amount of heat developed in its decomposition. This heat is equal to the amount of heat developed in the opposite process, the formation of the compound. He proposed the following general rule [67]: *every simple or compound action of a purely chemical nature is accompanied by the development of heat.*

A similar rule was proposed independently by Berthelot in 1869 [68], and in 1873 [69] he stated it as fundamental principle of thermochemistry in the following terms: *Any chemical change, accomplished without the intervention of energy from the outside, tends to that which produces the most heat.* In a publication of 1875 [70], he called it the principle of maximum work. In the same publication he stated another principle: *if a system undergoes a chemical transformation from one state to another, without any external mechanical work, the amount of heat developed depends solely on the initial and final state.* Berthelot differentiated clearly reactions accompanied with absorption of heat from those with release of heat, which he termed endothermic and exothermic reactions, respectively [68].

In 1884 van 't Hoff published a book [71] which dealt with chemical equilibrium and its relation with the rates of reactions. He pointed out the distinction between two types of chemical reactions. In the first, the reactants transform completely into the products of the reaction. In the second, the reactants transform only partially into the products, and eventually a *chemical equilibrium* is reached. To denote the equilibrium, van 't Hoff proposed the notation $\rightleftarrows$ as in the chemical equation $\mathrm{N_2O_4} \rightleftarrows 2\mathrm{NO_2}$. This equation comprises two opposite reactions, denoted by $\mathrm{N_2O_4} = 2\mathrm{NO_2}$ and by $2\mathrm{NO_2} = \mathrm{N_2O_4}$.

In this book, he proposed the following equation that relates the equilibrium constant K to the change in the temperature, for homogeneous systems. Denoting by q the heat developed, at constant volume, in the chemical reaction, the relation reads

$$\frac{d\ln K}{dT} = \frac{Q}{RT^2}, \tag{130}$$

where Q is measured in calories, and van 't Hoff wrote the number 2 in the place of R. We recall that 2 is the approximate value of R when heat is measured in calories. If k_1 is the rate constant for the reaction $\mathrm{N_2O_4} = 2\mathrm{NO_2}$ and k_2 for the opposite reaction $2\mathrm{NO_2} = \mathrm{N_2O_4}$, then the equilibrium constant is $K = k_1/k_2$. Denoting by x and y the concentrations of $\mathrm{N_2O_4}$ and $2\mathrm{NO_2}$, then the rate of the first reaction is k_1x whereas the rate of the second reaction is k_2y^2. In equilibrium both rates are equal and $k_1x = k_2y^2$, which is similar to a relation obtained by Guldberg and Waage, by Pfaunder, and by Horstmann, says van 't Hoff. Thus the equilibrium constant can be written in terms of concentration as $K = y^2/x$. We remark that van 't Hoff defines the concentration as the number of molecules per unit volume.

If the variation in K is positive and the temperature decreases, then according to equation (130), Q is negative and heat is released. Based on this results, van 't Hoff proposed the following general principle, which he calls principle of mobile equilibrium: *Any equilibrium between two different states of matter shifts, by lowering the temperature, towards that whose formation develops heat.* It is valid not only for chemical equilibrium but also for physical equilibrium such as the equilibrium of thermodynamic phases.

In a paper of 1884 [72], Le Chatelier extended the principle by allowing the variation of variables other than temperature such as pressure and concentration, which he called condensation. He stated the principle in the form: *Any system in stable chemical equilibrium subjected to the influence of an external cause which tends to vary either its temperature or its condensation can only undergo internal modifications, which, if they occurred alone, would bring about a change in temperature or of condensation of opposite sign to that resulting from the external cause.*

In a paper of 1886 [73], van 't Hoff proposed a formula for the osmotic pressure of dilute solutions, which is analogous to the combined laws of Boyle and Gay-Lussac for ideal gases,

$$pv = RT, \tag{131}$$

where p is the pressure, v the volume of the solution containing a molecular mass of the solute, T the temperature, and R is the ideal gas constant. When dissociation occurs, the equation is modified to $pv = iRT$ where i depends on the case considered.

10. Planck

Max Planck [74] was born in 1858 at Kiel, Germany. In 1867, his family moved to Munich, where he attend the Maximilian Gymnasium until 1874. In this same year, he entered the University of Munich from which he got his doctorate degree in 1879 with a thesis on the second law of thermodynamics. One year later, he obtained the habilitation at the University of Munich. In 1885, Planck was appointed professor of theoretical physics at the University of Kiel. In 1888, he was appointed assistant professor at the University of Berlin becoming a full professor in 1892. He retired in 1926 but it did not reduce his teaching and lecturing. For the last two and half years of his life he lived in Göttingen where he died in 1947.

Planck is most remembered for his researches on thermal radiation which led him to the law of black body radiation at the end of 1900 [75, 76]. He also did researches on thermodynamic and thermochemistry, the subject of his doctoral and habilitation theses. These researches are the bases of his book on thermochemistry of 1893 [77] and his book on thermodynamics of 1897 [78–82], which we analyze here. The book went through nine editions during Planck's lifetime, the last one being published in 1930. In the third edition of 1911 [79], he included a new section about the new heat theorem introduced by Nernst in 1906, known as the third law of thermodynamics.

10.1. Fundamental principles

The first law of thermodynamics is expressed by considering the increase in energy of a system that undergoes any process passing from a state 1 to a state 2,

$$U_2 - U_1 = Q + W, \tag{132}$$

where U_1 and U_2 are the energy corresponding to states 1 and 2, Q is the mechanical equivalent of the heat absorbed by the system and W is the work expended by the system. The sum $Q + W$ is independent of the type of the transition from state 1 to state 2. For infinitely small changes, the work done by the the system is $-pdV$, where p is the pressure and V is the volume, and equation (132) becomes

$$dU = dQ - pdV. \tag{133}$$

Planck did not write dQ for an infinitesimal quantity of heat as we have just written, but wrote simply Q. He explained in a footnote that the notation dQ might lead to the understanding that it is the differential of a function, which is not the case of heat. He says that some authors use the notation $d'Q$. We stick to the notation dQ.

The conservation of energy in the forms given by (132) and (133) are valid not only for mechanical systems but also for systems that in addition undergo internal chemical reactions. If we consider a process such that at the final state both the temperature and the volume are the same as those of the initial state, then for a pure mechanical system $U_2 = U_1$. This happens because a pure mechanical system the state can defined by temperature and volume and if they are the same, then the states are the same and so are the internal energies. However, in a system undergoing chemical reactions, in addition to the temperature and volume there are other variables that describe the chemical states. The values of these variables may change due to the reaction and the final state might be distinct from the initial states, and U_2 might not be equal to U_1 In this case $U_2 - U_1 = Q$, and Q is the heat of reaction. We might also consider the case where the temperature and pressure are kept constant. In this case the heat of reaction is $Q = (U_2 + pV_2) - (U_1 + pV_1)$ where V_2 and V_1 is the initial and final volumes. Planck states that the quantity $U + pV$ was called heat function at constant pressure by Gibbs.

The above considerations lead to the conclusion that the heat of reaction depends only on the initial and final states if T and V are kept constant or if T and p are kept constant. If a compound B is obtained from a compound

A through an intermediate compound C, the heat of the reaction does not depend on C. This is a brief statement of the law established by Hess in 1840 concerning the heat released in chemical reactions [65, 66].

Planck defined entropy using a reasoning similar to that used by Clausius a concluded that the change of entropy by the absorption of heat is $dS = dQ/T$. He then states the second principle as follows. *Every physical or chemical process in nature takes place in such a way as to increase the sum of the entropies of all the bodies taking any part in the process.* According to Planck, this is the most general statement of the second law of thermodynamics.

If a system is in contact with a body which performs work dW but exchanges no heat then the increase of energy is $dU = dW$ and the increase in entropy is $dS \geq 0$. Let us suppose that in addition the system in contact with a body at temperature T while it exchanges a quantity of heat dQ with the system. Then the variation of the entropy of the system plus the body is $dS - dQ/T \geq 0$ or $TdS - dQ \geq 0$. As $dQ = dU - dW$, we find $dU - TdS \leq dW$ If the temperature is kept constant and defining

$$F = U - TS, \tag{134}$$

then $dF = dU - TdS$ and $dF \leq dW$, or $F_2 - F_1 \leq W$. Planck states that the function F was called free energy by Helmholtz.

If the work along the isothermal process vanish, as may occur in most chemical reactions, then $F_2 - F_1 \leq 0$. A reaction that spontaneous occurs within a vessel maintained at a constant temperature is thus that which lowers the free energy. In chemical processes, says Planck, the first term in $F_2 - F_1 = (U_2 - U_1) - T(S_2 - S_1)$ is usually much greater then the second in which case $U_2 - U_1 \leq 0$. Since there is no work, the difference in energy is the heat released by the system, and the inequality becomes $Q \leq 0$. Planck states that this leads to the Berthelot principle that in the absence of external work, chemical reactions occurs as to give the greatest heat. However, for high temperatures the second term cannot be neglected and chemical reactions may take place even with the absorption of heat.

If the temperature and the pressure are kept constant, one defines the function

$$\Phi = S - \frac{1}{T}(U + pV). \tag{135}$$

Considering that $d\Phi = dS - (dU + pdV)/T$ for T and p constant, it follows from the inequality $dU - TdS \leq dW$, that $d\Phi \geq 0$.

10.2. Systems with several components

In the fourth part of the book, Planck considers a system consisting of α components and β phases, and derives the Gibbs rule using a reasoning similar to that used by Gibbs. He also states that the rule was amply verified experimentally by Roozeboom. The Gibbs rule states that the number of phases that may coexist cannot exceed the number of components plus two, $\beta \leq \alpha + 2$. The demonstration starts by considering the characteristic function Φ, defined by (135), which is written as a sum of the characteristic functions of each phase,

$$\Phi = \sum_k \Phi^k, \tag{136}$$

and Φ^k is a homogeneous function of the masses M_1^k, M_2^k, ..., M_α^k of the α components. As one varies the masses keeping the temperature and pressure constant then $\delta\Phi = 0$ subject to the invariance of the masses of each component,

$$\sum_k M_i^k = M_i. \tag{137}$$

This condition of equilibrium gives the equations

$$\frac{\partial \Phi^1}{\partial M_i^1} = \frac{\partial \Phi^2}{\partial M_i^2} = \ldots = \frac{\partial \Phi^\beta}{\partial M_i^\beta}. \tag{138}$$

We remark that these equations are equivalent to the Gibbs condition (100). From these equations Planck derives the Gibbs rule.

From $\partial\Phi/\partial T = (U + pV)/T^2$ and $\partial\Phi/\partial p = -V/T$, Planck derives the dependence of the equilibrium on the temperature and pressure.

10.3. Gas mixture

To determine the properties of a mixture, of ideal gases, Planck seeks to find the characteristic function $\Phi = S - (U + pV)/T$. The volume and the energy are related to the numbers of molecules n_1, $n_2, \ldots$ of each type of idea gas by

$$V = \frac{RT}{p} \sum_i n_i, \tag{139}$$

$$U = \sum_i n_i(c_i T + h_i), \tag{140}$$

where c_i and h_i are constants.

Now it is necessary to determine the entropy S. Considering that $dS = (dU + pdV)/T$ and using the two equations above, we find after integration on T and p,

$$S = \sum_i n_i(c_i' \ln T - R \ln p + k_i) + C, \tag{141}$$

where $c_i' = c_i + R$, k_i is a constant and C does not depend on T and p but may depend on n_i. To determine C, Planck uses the following proposition first established by Gibbs: *The entropy of a mixture of gases is the sum* *of the entropies which the individual gases would have, if each at the same temperature occupied a volume equal to the total volume of the mixture.* This proposition leads to the following value of C,

$$C = -\sum_i n_i \ln x_i, \tag{142}$$

where k_i is a constant, and $x_i = n_i/(n_1 + n_2 \ldots)$.

Collecting the results for S, U, and V, we reach the result

$$\Phi = \sum_i n_i(\phi_i - R \ln x_i), \tag{143}$$

where

$$\phi_i = c_i' \ln T - R \ln p + k_i - c_i' - \frac{h_i}{T}. \tag{144}$$

In equilibrium the characteristic function Φ is a maximum when we vary the numbers of molecules n_i, that is, $\delta\Phi = 0$, which gives

$$\sum_i (\phi_i - R \ln x_i)\delta n_i = 0. \tag{145}$$

We suppose that the variations in the number of molecules are proportional to integer ν_1, $\nu_2, \ldots$, which leads to

$$\sum_i (\phi_i - R \ln x_i)\nu_i = 0. \tag{146}$$

The quantities ν_1, $\nu_2, \ldots$ are understood as the number of molecules that simultaneously pass to the mass of each constituent and may be positive or negative. The equation (146) is written as

$$\prod_i x_i^{\nu_i} = K, \tag{147}$$

where K depends only on the temperature and pressure, and given by

$$\ln K = \frac{1}{R} \sum_i \nu_i \phi_i. \tag{148}$$

The equation (147) determines the concentration of the various gases that react among themselves in the state of equilibrium.

10.4. Diluted solutions

Let us consider a system with several components and denote by n_0 the number of molecules of the solvent and by n_1, $n_2, \ldots$ the number of molecules of dissolved substances. The energy U of the system is a homogeneous function of the number of particles from which we may conclude that $u = U/n_0$ may considered as a function of the concentrations $y_i = n_i/n_0$. In a diluted solution n_0 is much large compared to n_1, $n_2, \ldots$ which means that y_i is very small in this case we may expand u up to linear term in y_i to reach the expression

$$u = u_0 + y_1 u_1 + y_2 u_2 + \ldots \tag{149}$$

where u_0, $u_1, \ldots$ do not depend on the number of molecules but only on the temperature and the pressure. The energy is written as

$$U = n_0 u_0 + n_1 u_1 + n_2 u_2 + \ldots \tag{150}$$

Planck states that u_0 corresponds to the interactions between the molecules of the solvent and thus depend only on the nature of the solvent, and u_i corresponds to the interactions between the molecules of dissolved substance i and the molecules of the solvent. In an analogous reasoning, the volume V is written as

$$V = n_0 v_0 + n_1 v_1 + n_2 v_2 + \ldots \tag{151}$$

To determine the entropy one uses the relation $dU = TdS - pdV$ and the definition of the characteristic function Φ to get

$$\Phi = n_0\phi_0 + n_1\phi_1 + n_2\phi_2 + \ldots + C, \tag{152}$$

where ϕ_i depends only on T and p, and C does not depend on T and p, but may depend on n_i. To find C, it suffices to consider the system at high temperature and small pressure since C does not depend on these two variables. In this regime we suppose that the system behaves as an ideal gas. Comparing (152) with (143), we find

$$C = -R \sum_i n_i \ln x_i, \tag{153}$$

where $x_i = n_i/(n_0 + n_1 + \ldots)$. The equation (152) together with (153) determine the thermodynamic properties of a diluted solution.

To find the equilibrium conditions, we determine $\delta\Phi$ in terms of the variations δn_i in the number of molecules. Using the condition of equilibrium $\delta\Phi = 0$, valid at constant temperature and pressure, and that δn_i is proportional to ν_i, we find

$$\sum_i (\phi_i - R \ln x_i)\nu_i = 0. \tag{154}$$

Defining

$$\ln K = \frac{1}{R} \sum_i \nu_i \phi_i, \tag{155}$$

which depends on T and p, but is independent of n_i, we find

$$\sum_i \nu_i \ln x_i = \ln K. \tag{156}$$

To find the influence of the temperature and pressure we perform the following calculations

$$\frac{\partial \ln K}{\partial T} = \frac{1}{R}\sum_i \nu_i \frac{\partial \phi_i}{\partial T}, \tag{157}$$

$$\frac{\partial \ln K}{\partial p} = \frac{1}{R}\sum_i \nu_i \frac{\partial \phi_i}{\partial p}. \tag{158}$$

Using the relations $\partial\phi_i/\partial T = h_i/T^2$, $h_i = u_i + pv_i$, and $\partial\phi_i/\partial p = -v_i/T$, we get

$$\frac{\partial \ln K}{\partial T} = \frac{L}{RT^2}, \qquad \frac{\partial \ln K}{\partial p} = -\frac{v}{RT}, \tag{159}$$

where L is the heat absorbed at constant temperature and pressure, and v is the change in volume, and are give by

$$L = \sum_i \nu_i h_i, \qquad v = \sum_i \nu_i v_i. \tag{160}$$

The equations (159) say that the influence of the temperature on K is controlled by the heat effect, that is, by the heat evolved L, whereas that of the pressure is controlled by the change of volume v. If the reaction does not absorb or release heat, $L = 0$ and the temperature has no influence on the equilibrium. If no change of volume occurs, $v = 0$ and the pressure has no influence on the equilibrium.

11. Duhem

Pierre Duhem [83–86] was born in 1862 at Paris. At eleven years of age he was sent to the Collège Stanislas where he studied for ten years. In 1882 he was enrolled at the École Normale, and in 1884, before his graduation which occurred in 1885, he presented a doctoral thesis in physics concerning the concept of the thermodynamic potential. The thesis was rejected by the committee of examiners but Duhem managed to get the thesis published as a book in 1886 [87]. Another thesis was presented by Duhem, now in the area of magnetism, for which he received his doctorate degree in 1888. He taught at the Lille Catholic University in the period 1887–1893, at the University of Rennes in 1893–1894 and at University of Bordeaux in 1894–1916. He died at Cabrespine in 1916.

Duhem worked on thermodynamics, thermochemistry, hydrodynamics, elasticity, electricity, magnetism, and made contributions to the history of science, particularly to the science of the Middle Ages, and to the philosophy of science. He hold the opinion that physical theories are descriptions organized in a systematic manner by the use of a deductive reasoning from which the laws are derived from the fundamental principles of the theory [84, 88]. In his book on energetics [89], he attempt to built a generalized thermodynamics which would include the other physical theories in addition to thermodynamics [84]. His writings include about four hundred papers and about twenty books. *Le Système du Monde* about the cosmological doctrines from Plato to Copernicus comprises ten volumes, some of which published posthumously.

The Duhem approach to thermodynamics, like that of Gibbs, is founded on the principle of the conservation of energy and on the principle of the increase of entropy in the analytical form put forward by Clausius. In both approaches, a central role is played by the functions which were introduced by Massieu, who called them characteristic functions. Gibbs showed that the state of equilibrium is represented by a minimum of these functions. For this reason, Duhem called a function of this type a *thermodynamic potential* and Gibbs a force function, a term that has the same meaning of potential function, except for a minus sign.

In the following we analyze his treatise on thermodynamics and thermochemistry published in four volumes in the period 1897–1899 [90]. In it we found the derivation of the laws of thermochemistry that were proposed by physicists and chemists during the second half of the nineteenth century. The treatise contains nine books and an introductory chapter where Duhem summarizes the main concepts of mathematical analysis, that is, differential and integral calculus, and the analytical mechanics, pointing out the role of the exact differential and the potential function.

11.1. Thermochemical principle

The state of a system is defined by the temperature θ and some other variables α, β, and γ such that the elementary work of the external forces is

$$dW = Ad\alpha + Bd\beta + Cd\gamma, \tag{161}$$

where the actions A, B, and C are functions of θ, α, β, and γ. The internal energy U is also a function of these variables. The principle of the conservation of energy is expressed by $U' - U = Q + W$ where W is the work of the external forces and Q is the heat absorbed by the system along a modification, and U and U' are the initial and final internal energy. We are using here the term *modification* employed by Duhem for a sequence of changes of the state of the system, that is, a process.

We remark that Duhem writes Q multiplied by a constant that represents the mechanical equivalent of heat. In differential form the conservation of energy reads

$$dU = dQ + dW. \tag{162}$$

If a fluid is under the action of a pressure p, the elementary work is $dW = -pdV$ where dV is the increment of the volume V of the fluid.

As we have mentioned above, Hess established experimentally in 1840 that the heat released by a chemical combination is the same no matter whether the combination is direct or carried out indirectly through an intermediate step [65, 66]. Within the caloric theory this rules is an immediate consequence of the conservation of the caloric. As in thermodynamics this laws in no longer valid, one may ask whether the Hess rule remains valid. Duhem assumes that this rule remains valid within thermodynamics provided either the pressure or the volume is kept constant, and calls it the *thermochemical principle*. Duhem says that the principle was admitted by Lavoisier and Laplace, and was verified by Hess.

The following remark is necessary here. In addition to the temperature T and the volume V, the state of the system is represented by other variables that describe the chemical state. As the chemical state changes, these variables change and the forces related to these changes would perform a work, which we may call call chemical work. The thermochemical principle is equivalent to say that the chemical work of the type (161) is zero, which allows us to write $dQ = dU + pdV$ since the only work involved is the mechanical work. If the pressure is kept constant, then $dQ = d(U + pV)$. If the volume is kept constant, then $dQ = dU$. In both cases dQ is an exact differential and Q becomes a state function, which is a statement of the thermochemical principle. We also remark that the principle can be extended to processes in which the work is independent of the path, which occurs when the volume or the pressure are kept constant. In this case dW is an exact differential and so is $dQ = dU - dW$.

From the thermochemical principle, Duhem derives the Kirchhoff formula as follows. Let us consider four states A, B, A′, and B′ that are connected by processes occurring at constant volume. The process AB is isothermal at a temperature T and releases a quantity of heat Q. The process A′B′ is also isothermal at a temperature T' and releases a quantity of heat Q'. The processes AA′ and BB′ involve, respectively, the heats

$$q = \int_T^{T'} CdT \qquad q' = \int_T^{T'} C'dT, \tag{163}$$

where C and C' are the heat capacities at constant volume. Since $Q + q' = Q' + q$ by the thermochemical principle, we find

$$Q' - Q = \int_T^{T'} (C' - C)dT, \tag{164}$$

which is the formula proposed by Kirchhoff in 1858 [91]. A similar expression can be obtained by any process occurring at a constant pressure. In this case the C' and C represent the heat capacity at constant pressure.

11.2. Thermodynamic potentials

To introduce the second law of thermodynamics, Duhem defines a reversible process as a sequence of equilibrium states. In accordance with Clausius, the integral

$$\int \frac{dQ}{T}, \tag{165}$$

along a reversible cycle vanishes. It should be noted that the integral is carried out along a path on the space consisting not only by the variables T and V but also by the chemical variables. The vanishing of the integral above is equivalent to say that there exists a function S of these variables, called entropy by Clausius, such that $dQ/T = dS$. An immediate consequence of the vanishing of the integral (165) is that the heat exchanged along an isothermal cycle vanishes.

Duhem adopts the Clausius principle of the increase of entropy which he writes in the form

$$S_1 - S_0 = \int \frac{dQ}{T} + P, \tag{166}$$

where S_0 and S_1 denote the initial and final entropies, P is a positive quantity and dQ is the heat absorbed by the system. For an isolated system the first term on the right-hand side vanishes and $S_1 - S_0 = P$. That is, for any modification of an isolated system, the entropy of the system increases. Considering that the internal energy remains constant, we also have $U_1 - U_0 = 0$. In a short form, $dS > 0$ for $dU = 0$. If the system is in equilibrium then any virtual modification will decrease the entropy, that is, for virtual modifications such that $dU = 0$ then $dS \leq 0$. According to Duhem, this condition of equilibrium was proposed by Horstmann in 1873 [92].

If the modification is isothermal, then the equation (166) becomes

$$T(S_1 - S_0) = Q + TP, \tag{167}$$

and since $Q = U_1 - U_0 - W$ we find $T(S_1 - S_0) = U_1 - U_0 - W + TP$ which can be written in the form

$$F_1 - F_0 = W - TP, \tag{168}$$

where $F = U - TS$ is a function which Duhem called *internal thermodynamic potential.* As $P \geq 0$, this equation can be written as the inequality, $F_1 - F_0 \leq W$, valid for an isothermal modification. If the system is in equilibrium, then for an isothermal virtual modification, $dF \geq dW$, which is the equilibrium condition for isothermal modification.

Duhem also defines the thermodynamic potential Φ at constant actions, or the total thermodynamic potential, by

$$\Phi = F + \Omega, \tag{169}$$

where $\Omega = -(A\alpha + B\beta + C\gamma)$. For a modification carried out maintaining the actions A, B, and C invariant, and at constant temperature

$$\Phi_1 - \Phi_0 = -TP, \tag{170}$$

which can be written as the inequality $\Phi_1 - \Phi_0 \leq 0$. In equilibrium any virtual modification at constant actions and at constant temperature, $d\Phi \geq 0$.

For a system under the action of a pressure, $dW = -pdV$. In this case one defines the thermodynamic potential at constant pressure $G = F + pV$ and one reaches the result $G_1 - G_0 \leq 0$, valid for modification carried at constant temperature and constant pressure. The condition for equilibrium is $dG \geq 0$, valid for virtual modifications at constant temperature and constant pressure.

The conditions of equilibrium involving F and G were obtained by Gibbs, says Duhem, in his capital memoire in 1876 [60]. Duhem adds that Gibbs demonstrated these conditions from the condition of equilibrium proposed by Horstmann, mentioned above. A few years later, in 1882, continues Duhem, Helmholtz [93] considered again the potential F, which he called *free energy*. If we consider a reversible isothermal modification, the relation $F_1 - F_0 = W$ tells us that the variation in F is the work performed on the system by the external forces or that F is the part of U that is free to be converted into useful work, justifying the term free energy. If the modification is irreversible the variation in F is smaller than the work performed on the system.

The idea that only a part of the energy can be converted into useful work, says Duhem, seems to be perceived by Maxwell in the first edition of his Theory of Heat of 1871, who called it available energy. We add that in the fourth edition of the book of 1875, Maxwell showed that the available energy, which is the maximum work that one can extract along an isothermal process is $(U_0 - TS_0) - (U_1 - TS_1)$ as shown by equation (82), but he did not attributed a symbol for $U - TS$.

Let us write the equation (167) in the following form

$$Q' + T(S_1 - S_0) \geq 0, \tag{171}$$

where $Q' = -Q$ is the heat released by the system. This relation means that a spontaneous isothermal process occurs whenever this inequality is fulfilled. If the first term is positive and large compared to the second, which means that a great amount of heat is released, the inequality becomes $Q' > 0$, which means that a spontaneous process is exothermic. This was the rule proposed by Thomsen in 1854 [67] and independently by Berthelot in 1873 [69] in the following terms: "Any chemical change, accomplished without the intervention of energy from the outside, tends to that which produces the most heat." However, it is possible to have Q' negative provided the second term in (171) is positive and large enough. In this case we are faced to an spontaneous process which is endothermic, and the Thomsen-Berthelot principle cannot be considered generally valid.

11.3. Law of equilibrium displacement

The stability of a system was analyzed by Duhem by considering the total thermodynamic potential Φ given by (169), that is,

$$\Phi = F - A\alpha - B\beta, \tag{172}$$

where F is a function of α and β. If A and B are maintained constant, Φ is a minimum for modifications on α and β. The condition for a minimum is

$$A = \frac{\partial F}{\partial \alpha}, \qquad B = \frac{\partial F}{\partial \beta}, \tag{173}$$

and

$$\frac{\partial^2 F}{\partial \alpha^2} a^2 + 2\frac{\partial^2 F}{\partial \alpha \partial \beta} ab + \frac{\partial^2 F}{\partial \beta^2} b^2 > 0, \tag{174}$$

for arbitrary values of a and b.

Let us submit the system to variation on A and B. We find,

$$dA = \frac{\partial^2 F}{\partial \alpha^2} d\alpha + \frac{\partial^2 F}{\partial \alpha \partial \beta} d\beta, \tag{175}$$

$$dB = \frac{\partial^2 F}{\partial \beta \partial \alpha} d\alpha + \frac{\partial^2 F}{\partial \beta^2} d\beta. \tag{176}$$

If we sum the first equation multiplied by $d\alpha$ with the second mutiplied by $d\beta$ and comparing the result with (174), we conclude that

$$dAd\alpha + dBd\beta > 0, \tag{177}$$

which is valid for constant temperature and called law of equilibrium for isothermal displacement.

Duhem calls dA and dB disturbing actions and $d\alpha$ and $d\beta$ the corresponding disturbances. The left hand side of (177) he calls the disturbing work. Using this terminology, he states the law in the following terms. If a system in equilibrium at a certain temperature is perturbed by disturbing actions, it changes to a new equilibrium which is accompanied by a positive disturbing work. Applying this result to the case of mechanical work we find $-dpdV \geq 0$. That is, a decrease in the volume results in an increase in the pressure.

The law of equilibrium displacement just presented was proposed by Le Chatelier in 1884 [72] but, according to Duhem, in a summary manner and without proof.

Let us make the replacements $a = d\alpha/dT$ and $b = d\beta/dT$ in the inequality (174). We find the following inequality

$$R_\alpha \frac{d\alpha}{dT} + R_\beta \frac{d\beta}{dT} > 0, \tag{178}$$

where R_α and R_β are the thermal coefficients given by

$$R_\alpha = -T\frac{\partial^2 F}{\partial \alpha \partial T} = T\frac{\partial S}{\partial \alpha}, \tag{179}$$

$$R_\beta = -T\frac{\partial^2 F}{\partial \beta \partial T} = T\frac{\partial S}{\partial \beta}. \tag{180}$$

The coefficient R_α is the heat absorbed by the system when the variable α increases by $d\alpha$ at constant temperature and β. The coefficient R_β has a similar interpretation. If we suppose an isothermal modification from the state of equilibrium, the heat absorbed by the system is

$$dQ = \left(R_\alpha \frac{d\alpha}{dT} + R_\beta \frac{d\beta}{dT} \right) dT. \qquad (181)$$

Since the expression between parentheses is positive by (178), then an increase in the temperature will result in an absorption of heat, and a decrease in the temperature will result in a release of heat by the system. In other terms, if the temperature is increased, the equilibrium will dislocated in the direction where the heat is absorbed, and if the temperature is decreased, the equilibrium will dislocated in the direction where the heat is released. This important law was proposed by van 't Hoff in his book on chemical dynamics [71] and received from him, says Duhem, the name law of equilibrium displacement by variation of temperature.

11.4. Mixture of ideal gases

The equation that relates the pressure p and the specific volume v of an ideal gas is

$$p = \frac{rT}{v}, \qquad (182)$$

where r is a constant. The equation (182) encloses the laws of gases of Boyle-Mariotte and of Gay-Lussac. Considering that $p = -\partial f/\partial v$, then the thermodynamic potential f per unit mass is obtained by integration. The result is

$$f = -rT \ln v + f^*, \qquad (183)$$

where f^* depends only on T. The thermodynamic potential $g = f + pv$ is

$$g = rT \ln p + g^*, \qquad (184)$$

where g^* depends only on T and is given by

$$g^* = -rT \ln rT + rT + f^*. \qquad (185)$$

Duhem states the law of Avogadro and Ampére in the following terms. Consider several gases at the same temperature and pressure. If the mass of each gas is equal to its molecular mass then the volumes occupied by the gases are equal. If we denote by V_0 the volume of a mass of the hydrogen gas equal to its molecular mass at the atmospheric pressure p_0 and at the temperature of the melting ice T_0, then the ratio $p_0 V_0/T_0 = R$ is the same for all gases. From (182) it follows that $r = R/\varpi$ where ϖ is the molecular mass of the gas.

To determine the internal potential F of a mixtures of gases, Duhem follows Gibbs [60] and assumes that F is equal to the sum of the internal potential of each gas as if they occupy separately the vessel. According to this assumption,

$$F = \sum_i M_i f_i, \qquad (186)$$

where

$$f_i = -r_i T \ln \frac{V}{M_i} + f_i^* \qquad (187)$$

is the thermodynamic potential per unit mass of gas i. The pressure $p = -\partial F/\partial V$ is

$$p = \sum_i M_i \frac{r_i T}{V}. \qquad (188)$$

From F we may determine the potential $G = F + pV$, which is

$$G = \sum_i M_i g_i, \qquad (189)$$

$$g_i = r_i T \ln p_i + g_i^*, \qquad (190)$$

where

$$g_i^* = r_i T(1 - r_i T) + f_i^*, \qquad (191)$$

and p_i is related to p by

$$p_i = \frac{M_i r_i}{\sum_i M_i r_i} p. \qquad (192)$$

Duhem states that this definition leads to a contradiction that he calls the Gibbs paradox. Let us determine the difference in the thermodynamic potential G that results from the mixing of ideal gases at the same temperature T and pressure p. After the mixing, G is given by (189) and (190). Before the mixing we may use the same formulas provided we replace p_i by p in (190). The resulting difference in the the thermodynamic potential can be put in the form

$$-T \sum_i M_i r_i \ln \frac{p}{p_i}. \qquad (193)$$

The term that multiplies $(-T)$ is positive and is the variation in entropy. In this formula, says Duhem, there is nothing that identifies the nature of the gases and could as well be valid for gases of the same type. But this is incorrect because in the mixture of gases of the same type, at the same temperature and pressure, the entropy remains invariant, which constitutes the Gibbs paradox. It should be remarked, however, that at the beginning of the derivation of the free energy for distinct gases, the Gibbs hypothesis presupposes that the gases are distinct, otherwise the phrase "occupy separately the vessel" makes no sense.

11.5. Diluted solutions

We consider a system consisting of a solvent of mass M_0 and n solutes of masses M_1, $M_2, \ldots, M_n$. The thermodynamic potential under constant pressure G is a function of M_i, T, and p. Since G is a homogeneous function of the first order, it can be written in the form

$$G = M_0 g_0 + M_1 g_1 + \ldots + M_n g_2, \qquad (194)$$

where g_i depends on the masses only through the concentrations $s_i = M_i/M_0$ of the solutes. The question posed by Duhem is the determination of g_i for diluted solutions, which means that s_i is very small.

If the solution was a mixture of ideal gas then g_i for a solute is given by the expression (190), which we write as

$$g_i = r_i T \ln \frac{r_i s_i p}{r_0} + g_i^*, \qquad (195)$$

where we have kept only the leading terms in s_i. Since s_i is small, we expand g_0 up to linear terms in s_i. From (190), we find

$$g_0 = -T(r_1 s_1 + \ldots + r_n s_n) + g_0^* + r_0 T \ln p. \qquad (196)$$

To determine g_i for the general case, Duhem makes the following assumptions. The solutes behaves as ideal gases which means that g_i are given by (195). As to the the function g_0, it is taken to be similar to (196), that is,

$$g_0 = g^* - T(r_1 s_1 + \ldots + r_n s_n), \qquad (197)$$

where g^* is the thermodynamic potential per unit mass of the pure solvent and depends on p and T only.

Duhem states that the various considerations about the infinitely diluted solutions are intimately linked to the ideas expressed about them by van 't Hoff [73].

11.6. Osmotic pressure

We consider a vessel with two compartment separated by a membrane and maintained at a constant temperature T. The first compartment contains a dilute solution with just one solute, and is subject to a pressure p. The mass of the solvent is M_0 and of the solute is M_1. The second compartment contains only the solvent of mass M_0' and is under the pressure p'. The membrane is permeable only to the solvent. The total thermodynamic potential is

$$\Phi = G + G', \qquad (198)$$

where G and G' are the thermodynamic potentials of the two parts.

Using the results of the previous section we write

$$G = M_0 g_0 + M_1 g_1, \qquad (199)$$

$$g_0 = g^*(T,p) - T r_1 s, \qquad (200)$$

$$g_1 = r_1 T \ln \frac{r_1 s p}{,} r_0 + g_i^* \qquad (201)$$

where $s = M_1/M_0$ and $g^*(T,p)$ is the thermodynamic potential per unit mass of the pure solvent, and

$$G' = M_0' g^*(T,p'). \qquad (202)$$

As the membrane is permeable only to the solvent, the mass M_1 is invariant. The masses M_0 and M_1 may vary but their sum is constant. The equilibrium is determined by the minimum of Φ as one varies the masses, or by $\partial G/\partial M_0 = \partial G'/\partial M_0'$, which gives

$$g^*(T,p) - r_1 T s = g^*(T,p'). \qquad (203)$$

As s is small the osmotic pressure $\overline{p} = p - p'$ is also small. Taking into account that the specific volume v is $\partial g_0/\partial p$ we may write $g^*(T,p) - g^*(T,p') = \overline{p}v$ and

$$\overline{p}v = s r_1 T. \qquad (204)$$

Recalling that $s = M_2/M_1$, this equation is equivalent to

$$\overline{p}V = \frac{R M_1 T}{\varpi_1}, \qquad (205)$$

where V is the volume of the compartment containing the solute and ϖ_1 is the molecular mass of the solute. The result (205) is due to van 't Hoff who called it law of Mariotte and Gay-Lussac for dilute solutions [73].

11.7. Law of Guldberg and Waage

We consider a system composed by five chemical species which react among themselves. The reaction is such that n_1 molecules of the first type react with n_2 molecules of the second to form n_3 molecules of third and n_4 of the fourth. The components 1 and 2 are the reactants and 3 and 4 the products of the reaction. Denoting by ϖ_1, ϖ_2, ϖ_3 and ϖ_4 the molecular masses of the chemical species, the variation of their masses M_1, M_2, M_3, and M_4 are given by

$$\frac{dM_1}{n_1\varpi_1} = \frac{dM_2}{n_2\varpi_2} = -\frac{dM_3}{n_3\varpi_3} = -\frac{dM_4}{n_4\varpi_4}. \qquad (206)$$

At constant pressure p and constant temperature T, the variation of the thermodynamic potential Φ, which is a function of T, p, M_1, M_2, M_3, M_4 is

$$d\Phi = g_1 dM_1 + g_2 dM_2 + g_3 dM_3 + g_4 dM_4. \qquad (207)$$

Using the condition (206), we may write

$$d\Phi = A\frac{dM_1}{n_1\varpi_1}, \qquad (208)$$

where

$$A = g_1 n_1 \varpi_1 + g_2 n_2 \varpi_2 - g_3 n_3 \varpi_3 - g_4 n_4 \varpi_4, \qquad (209)$$

and we remark that A is a function of M_1, M_2, M_3, and M_4. In equilibrium $d\Phi = 0$ and we reach the following condition for equilibrium

$$A = 0, \qquad (210)$$

which determines the relation between M_1, M_2, M_3, and M_4 at equilibrium.

Considering that $d\Phi < 0$, then if $A > 0$ then $dM_1 < 0$ and the reaction will be shifted towards the decrease of the first component, that is, towards the products of the reaction. If $A < 0$ then $dM_1 > 0$ and the reaction will be shifted towards the the increase of the first component, that is, towards the reactants.

We suppose now that the chemical system includes another component with mass M_0 that does not take part in the reaction. In addition we suppose that the system is dilute which means that the masses M_1, M_2, M_3, and M_4 are very small compared to M_0. Under these conditions we may use the thermodynamic potentials given by (195), which replaced in (209) and setting the result to zero, we reach the following condition for equilibrium involving the concentrations $s_i = M_i/M_0$,

$$\frac{s_1^{n_1} s_2^{n_2}}{s_3^{n_3} s_4^{n_4}} = K, \tag{211}$$

where we have used the relation $r_i = R/\varpi_i$. The quantity K depends only on p and T. The equation (211) expresses the law proposed by Guldberg and Waage in 1864 for the chemical equilibrium [94–96]. Duhem states that similar laws were then proposed by Lemoines [97] and by van 't Hoff [98].

12. Nernst

Walther Nernst [99, 100] was born in 1864 at Briesen, Prussia, now Wąbrzeźno, Poland. The family moved to Graudenz, now Grudziądz, where he went to school at the Gymnasium in 1874, graduating in 1883. Nernst pursued his studies in various universities. He went to Zürich, Berlin, Graz and Würzburg, where he received his doctorate in 1887. He then moved to Leipzig where an assistantship was offered to him. After two years, he obtained his habilitation at the University of Leipzig in 1889. In the following year he moved to Göttingen to take up a position of professor of physical chemistry at the University of Göttingen. In 1905 he moved to Berlin and started his position as the chair of physical chemistry at the University of Berlin. In 1924 he was appointed to the chair of experimental physics, holding this position until 1933, when he retired. He died in 1941 at Zibelle, now Niwica.

The main contribution of Nernst was to the development of physical chemistry. His views concerning this field of research are contained in his book on theoretical chemistry based on the Avogadro law and on thermodynamics [101, 102]. The book appeared in 1893 and went through fifteen editions until 1926. In 1905, Nernst proposed a new law of thermodynamics, which he called the new heat theorem. In fact it is not properly a theorem but a fundamental law, independent of the first and second laws, as insisted Nernst himself. The Nernst law was reported in a publication the following year [103], and included in the later editions of his theoretical chemistry, and was also the subject of a book published in 1918 [104, 105].

In his book on theoretical chemistry, after introduction the law of conservation of energy, Nernst expresses the second law of thermodynamics in the following terms [101, 102]. 1) Every process that takes places in any system by itself, that is, without the supply of energy in any form, can provide a finite amount of work when properly used. 2) A process yields the maximum amount of work when it is reversible. By a self-acting process, Nernst means a spontaneous process such as the mixing of two liquids or gases, and all chemical processes that take place on their own.

The variation of energy along a process is $dU = dQ - dW$ where dQ is the heat absorbed by the system and dW the work performed by the system. If the process is reversible $dQ = TdS$ where T is the absolute temperature and S the entropy. Defining the free energy by $F = U - TS$, and taking into account that $\partial U/\partial T = T(\partial S/\partial T)$, then

$$\frac{\partial F}{\partial T} = -S. \tag{212}$$

Replacing (212) in $F = U - TS$, this equation becomes

$$F = U + T\frac{\partial F}{\partial T}. \tag{213}$$

A criterion for the occurrence of a spontaneous isothermal process is the decrease in the free energy, called the principle of maximum work by Nernst, which is a consequence of the second law. It is worth pointing out that Nernst states that the change of the free energy is the measure of affinity. A similar principle was advanced by Thomsen in 1854 and independently by Berthelot in 1867, which Nernst writes in the following form. Every chemical reaction gives rise to the formation of those substances which generate the greatest amount of heat. This principle received recognition but it was proven to be untenable, says Nernst.

The principle of maximum work is written in the form $W \leq -\Delta F$ or in the equivalent form $Q - T\Delta S \leq 0$. If it is possible to neglect the last term, we see that it becomes $Q \leq 0$, which is the expression of the Thomsen-Berthelot principle. Nernst observes that the Thomsen-Berthelot principle holds remarkably well for condensed system at low temperatures. Writing equation (213) as

$$\Delta F = \Delta U + T\frac{\partial \Delta F}{\partial T}, \tag{214}$$

then at low temperatures the last term of this equation vanishes, and ΔF becomes equal to ΔU. In addition not only do ΔF and ΔU become equal but they approach each other asymptotically at low temperatures, which meanst that, when $T \to 0$,

$$\frac{\partial \Delta F}{\partial T} = \frac{\partial \Delta U}{\partial T}, \tag{215}$$

which is the first expression of the Nernst law [103].

Assuming that the energy at low temperatures can written as a power series in the temperature, and after integration equation (214), Nernst concludes that each term in equation (215) vanishes, that is, when $T \to 0$,

$$\frac{\partial \Delta F}{\partial T} \to 0, \tag{216}$$

which is the second expression of the Nernst law [103], and

$$\frac{\partial \Delta U}{\partial T} \to 0. \tag{217}$$

Taking into account (212), then (216) takes the form $\Delta S \to 0$ when $T \to 0$, that is, in the neighborhood of absolute zero all process proceed without the alteration of entropy [104, 105]. The second consequence (217) means that the specific heat vanishes at abolute zero of temperature [104, 105].

The quantities ΔU, ΔF, and ΔS are understood as the variation of the energy, the free energy, and the entropy at constant temperature such as that occurring in chemical reactions or in change of states. When applied to distinct allotropic forms of a substance, $\Delta S = 0$ means that the entropy is the same for both forms.

The Nernst law was included by Planck in the third edition of his book on thermodynamics of 1911 [79], which he expressed in the following terms. As the zero point of the absolute temperature, the entropy of a chemical homogeneous solid or liquid body attains a value that is independent of the state of aggregation and the specific chemical modification. Planck states that this conception of the Nernst law is more comprehensive than that given by Nernst himself.

Planck proceeds saying that as the entropy contains an additive arbitrary constant, then without loss of generality it can be chosen equal to zero. The Nernst law becomes: at the zero point of the absolute temperature, the entropy of every chemical, homogeneous solid or liquid body has a zero value [79].

In their book on thermodynamics of 1923 [106], Lewis and Randall emphasized the use of free energy in chemical thermodynamics. They also pointed out that some authors used the energy U when they meant $H = U + pV$, and $F = U - TS$ when they meant $G = H - TS$. We remark that Lewis and Randal used the term free energy to G and not to F. Thus an equation analogous to (213), which we write as

$$\Delta F = \Delta U - T\Delta S, \tag{218}$$

is the equation

$$\Delta G = \Delta H - T\Delta S, \tag{219}$$

and by the Nernst law, ΔG approaches ΔH asymptotically at low temperatures. Let us suppose that we have measured the heat Q developed in a chemical process. If the process is carried out at constant volume, then we have to use equation (218) because in this case $Q = \Delta U$, but if the process is carried out at constant pressure, $Q = \Delta H$, and we have to use (219), which can be written in the form analogous to (214),

$$\Delta G = \Delta H + T\frac{\partial \Delta G}{\partial T}. \tag{220}$$

An important example where the pressure is constant is the change of phases of a pure substance, in which case ΔH is the latent heat.

It is worth mentioning the statement of the third law by Lewis and Randall [106]. If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

13. De Donder

Théophile De Donder [107–109] was born in 1872 at Schaerbeek, Belgium. He pursued his studies at the École Normale in Brussels and graduated in 1891. He entered the University of Brussels where he got this doctorate in physical and mathematical sciences in 1899. In 1904, he was nominated professor at the Communal Atheneum at Saint-Gilles, where he remained until 1918. In 1914, he was appointed professor at the University of Brussels but his duties only began in 1918. He reached the age limit in 1942 but was promoted to honorary only in 1944. He died in Brussels in 1957.

De Donder gave contributions to the fields of relativity, integral invariants, and chemical thermodynamics by the introduction of his own concept of chemical affinity and that of extension of reaction. He wrote several books in these fields. Here we analyze his treatises on the theory of affinity contained in a book published in 1927 [110]. A second and a third part of this treatise was published in 1931 and 1934 [111, 112]. A new edition of the first part was published in 1936 [113].

Let us consider a chemical system consisting of c constituents under the action of a chemical reaction, which transform a set of molecules of the constituents into another set of molecules. We denote by ν_i the variation in the number of moles n_i of the constituent i due to the reaction. These quantities can be positive, in which case n_i increases, or negative, in which case n_i decreases. We assume that the backward reaction is also present which makes n_i to vary by an amount $-\nu_i$. In equilibrium, n_i remains constant, what means that the backward reaction occurs as many times as the forward reaction, or that they are balanced.

Due to the reaction, the variations in the number of molecules of each type cannot be arbitrary. The connection between them is written in the parametric form as

$$dn_i = \nu_i d\xi, \tag{221}$$

where ξ is the *extension of reaction*, which De Donder calls the degree of the advancement of the reaction. The differentials are to be interpreted as *variations occurring during an interval of time* $dt > 0$. Therefore, if $d\xi$ is positive the reaction is shifted to the right, that is, toward the products of the reaction. If it is negative, the reaction is shifted to the left, that is, toward the reactants.

It is assumed that the energy U is a function of entropy S, the volume V, and the number of moles n_i of each constituent. Then the infinitesimal increase of energy is

$$dU = TdS - pdV + \sum_i \mu_i dn_i, \tag{222}$$

where $T = \partial U/\partial S$ is the temperature, $p = -\partial U/\partial V$, and $\mu_i = \partial U/\partial n_i$ is the chemical potential of the constituent i. The terms of the summation are understood as the variation in the energy due to flux of molecules from the environment.

Replacing (221) into equation (222) we get

$$dU = TdS - pdV - Ad\xi, \tag{223}$$

were A is a quantity that De Donder calls the *affinity*, given by

$$A = -\sum_i \nu_i \mu_i, \tag{224}$$

and we notice that

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{SV}. \tag{225}$$

For a closed system, De Donder assumes the following relation

$$dU = TdS - pdV. \tag{226}$$

In a closed system no reactants of products of the reaction are exchange with the environment. This does not mean that the number n_i of molecule of each chemical species remains constant. It may vary due to the chemical reaction occurring inside the system, which is induced by variation of pressure or temperature. We remark that this fundamental assumption is equivalent to the thermochemical principle that we have discussed above. It is independent but consistent with the fundamental laws of thermodynamics. If we consider a cyclic process in the variables S and V, the equation (226) says that the final and initial energy are the same. The assumption represented by the equation(226) is not obvious because the chemical state defined by the number n_i of molecules of each species might not be the same, and the final energy could not be equal to the initial energy.

The equation (226) is valid for equilibrium or for reversible processes. For out of equilibrium of irreversible process De Donder assumes the following relattion

$$dU = TdS - pdV - dQ', \tag{227}$$

where dQ' is related to the irreversible process and called by Clausius as the uncompensated heat. According to Clausius, says De Donder, $dQ' \geq 0$ which is a consequence of the second principle of thermodynamics.

Comparing (227) with (223) we find

$$dQ' = Ad\xi, \tag{228}$$

which De Donder writes in the form

$$\frac{dQ'}{dt} = A\frac{d\xi}{dt}. \tag{229}$$

Considering that in irreversible process $dQ'/dt > 0$, then if the affinity A is positive, the velocity of reaction $d\xi/dt$ is positive and the reaction is shifted to the right. If the affinity is negative, the velocity of reaction is negative and the reaction is shifted to the left. The equilibrium occurs when $A = 0$, that is, when

$$\sum_i \mu_i \nu_i = 0. \tag{230}$$

Replacing (228) in the equation (227),

$$dU = TdS - pdV - Ad\xi. \tag{231}$$

Defining $F = U - TS$, $H = U + pV$, and $G = U - TS + pV$, we have

$$dF = -SdT - pdV - Ad\xi, \tag{232}$$

$$dH = TdS + Vdp - Ad\xi, \tag{233}$$

$$dG = -SdT + Vdp - Ad\xi. \tag{234}$$

From these equations, we may write

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{SV}, \qquad A = -\left(\frac{\partial F}{\partial \xi}\right)_{TV}, \tag{235}$$

$$A = -\left(\frac{\partial H}{\partial \xi}\right)_{Sp}, \qquad A = -\left(\frac{\partial G}{\partial \xi}\right)_{Tp}. \tag{236}$$

The condition of equilibrium is represented by $\partial A/\partial \xi \leq 0$. For T and p held constant this condition gives

$$\Omega = -\left(\frac{\partial A}{\partial \xi}\right)_{Tp}. \geq 0 \tag{237}$$

Taking into account that

$$-\left(\frac{\partial A}{\partial \xi}\right)_{Tp} = \frac{(\partial A/\partial T)_{\xi p}}{(\partial \xi/\partial T)_{Ap}}, \tag{238}$$

and defining

$$R = T\left(\frac{\partial S}{\partial \xi}\right)_{Tp} = T\left(\frac{\partial A}{\partial T}\right)_{\xi p}, \tag{239}$$

which is the heat of reaction, we may write

$$\left(\frac{\partial \xi}{\partial T}\right)_{Ap} = \frac{\Omega R}{T}. \tag{240}$$

An analogous relation can be obtained for variation in pressure. Defining

$$\Lambda = -\left(\frac{\partial V}{\partial \xi}\right)_{Tp} = \left(\frac{\partial A}{\partial p}\right)_{\xi T}, \tag{241}$$

we may write

$$\left(\frac{\partial \xi}{\partial p}\right)_{AT} = \Omega\Lambda. \tag{242}$$

De Donder states that (240) and (242) are generalizations of the relations due to Le Chatelier and van 't Hoff.

De Donder applies his theory to the mixture of ideal gases and derives the van 't Hoff equation related to the equilibrium constant as well as the law of mass action of Guldberg and Waage.

The relevant points of De Donder theory are the concepts of extent of reaction and affinity, and the relation he obtained between the Gibbs chemical potentials and his affinity. Above we presented the case of a system with just one chemical reaction. For several chemical reaction, one should define one extent of reaction ξ_γ for each reaction. The variation in the number of moles becomes

$$dn_i = \sum_\gamma \nu_{i\gamma}\xi_\gamma, \tag{243}$$

where $\nu_{i\gamma}$ are the coefficients related to the reaction γ. Also one defines an affinity for each reaction by relations (235) and (236). The affinity related to reaction γ is obtained by these equations where the derivation is respect to ξ_γ, and equation (228) becomes

$$dQ' = \sum_\gamma A_\gamma d\xi_\gamma. \tag{244}$$

The condition of equilibrium occurs when this expression vanishes, that is,

$$\sum_\gamma A_\gamma \xi_\gamma = 0. \tag{245}$$

14. Prigogine

A further development of the De Donder theory was carried out by Ilya Prigogine. A distinct feature of Prigogine approach is that he intended to describe open systems, understood as systems that are permanently out of thermodynamic equilibrium, and thus are irreversible systems. To this end he base his theory on two important concepts, the *flux of entropy* and *production of entropy*, which may have been introduced by Jaummann. Previous works on irreversibility, says Prigogine [114], were limited to the use of the Clausius relation, without an explicit determination of the uncompensated heat which is related to the production of entropy. To study open system it is necessary to explicitly consider the production of entropy. The importance of uncompensated heat was recognize by Duhem, Natanson, and Jaummann, but the real development of the study of the thermodynamics of irreversible process started with De Donder.

We analyze here his book on the thermodynamic of irreversible phenomena published in 1947 [114], which was his thesis presented in 1945 at the Free University of Brussels for obtaining the degree of Agrégé in higher education. We also analyze his book on the same subject published in 1955 [115]. The starting point of the Prigogine theory is the Clausius relation

$$dS = \frac{dQ}{T} + \frac{dQ'}{T}, \tag{246}$$

where dS is the variation of the entropy of a system at a temperature T during an interval of time dt, dQ is the heat exchanged with the environment and dQ' is the uncompensated heat. This second quantity is due to irreversible processes and is always positive.

Prigogine *interpreted* the firs term on the right hand side of equation (246) as the entropy exchanged with the environment, which he denoted by d_eS, but we write it as Φdt, that is, $dQ/T = \Phi dt$, where Φ is the flux of entropy, a quantity that can be positive, negative or zero. The second term, he interpreted as the production of entropy inside the system, which he denoted by d_iS, but we write it as $\mathcal{P}dt$ where $\mathcal{P}$ is the production of entropy per unit time. This quantity is positive for irreversible processes and vanishes for reversible processes, that is, $\mathcal{P} \geq 0$. Thus equation (246) becomes

$$dS = \Phi dt + \mathcal{P}dt. \tag{247}$$

The variation of the energy of an open system with several chemical species during an interval of time dt is

$$dU = dQ - pdV + \sum_i \mu_i dn_i', \tag{248}$$

where dQ is the heat absorbed, pdV is the work performed by the system, and dn_i' is the number of moles of species i that enter the system during the interval of time dt. The quantity dn_i' is related to the increase dn_i in the number of moles of species i by

$$dn_i = dn_i' + \nu_i d\xi, \tag{249}$$

and we are considering just one chemical reaction.

Recalling that $dQ = T\Phi dt$, we eliminate Φ from the two equations (248) and (247), and use (249) to eliminate dn'_i. The resulting equation is

$$dU = TdS - pdV + \sum_i \mu_i dn_i + Ad\xi - T\mathcal{P}dt, \qquad (250)$$

where A is the affinity, given by (224). At the stationary state the variations of U, S, V, and n_i vanish and we find the following expression for the production of entropy

$$\mathcal{P} = \frac{1}{T}Av, \qquad (251)$$

where $v = d\xi$ is the velocity of reaction. Proceeding in an analogous manner we reach the following equation for the case of multiple reactions,

$$\mathcal{P} = \frac{1}{T}\sum_\gamma A_\gamma v_\gamma, \qquad (252)$$

which is equivalent to the De Donder equation (244), and is a definite-positive quadratic form.

Let us consider now that a closed system is in contact with two heat reservoirs at temperatures T_1 and T_2. In this case the variation of energy during an interval of time dt is

$$dU = dQ_1 + dQ_2 - pdV, \qquad (253)$$

where dQ_1 and dQ_2 are the heats coming from the two reservoirs and are related to the entropy fluxes Φ_1 and Φ_2 from the two reservoirs by $dQ_1 = T_1\Phi_1 dt$ and $dQ_2 = T_2\Phi_2 dt$. The total flux of entropy is $\Phi = \Phi_1 + \Phi_2$ and equation (247) becomes

$$dS = (\Phi_1 + \Phi_2)dt + \mathcal{P}dt. \qquad (254)$$

In the stationary state, the variations of U, S, and V vanish and we find

$$T_1\Phi_1 + T_2\Phi_2 = 0, \qquad (255)$$

and

$$\mathcal{P} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\Phi_q, \qquad (256)$$

where $\Phi_q = T_1\Phi$ is the heat flux from the first reservoir.

From the the two cases studied above we see that the rate of entropy production is a sum of products

$$\mathcal{P} = \sum_k J_k X_k, \qquad (257)$$

where X_k is a generalized force, such as the affinity, and J_k is a generalized rate, such as the velocity of reaction. At equilibrium $J_k = 0$ and $X_k = 0$ for all k. Near equilibrium we may assume that the rates are linear in the forces, that is,

$$J_k = \sum_j L_{kj} X_j. \qquad (258)$$

Replacing (258) in (257), the entropy production becomes the quadratic form

$$\mathcal{P} = \sum_{kj} L_{kj} X_k X_j. \qquad (259)$$

Since $\mathcal{P} \geq 0$, the eigenvalues of the matrix with elements L_{jk} has nonnegative eigenvalues. The non-diagonal elements may be positive or negative but the diagonal must be non-negative. A theorem due to Onsager [116] asserts that the coefficient matrix is symmetric, that is,

$$L_{kj} = L_{jk}. \qquad (260)$$

We remark that the demonstration is outside the realm of the theories of thermodynamics analyzed here. It is based on a dynamic approach to thermodynamics and that the equilibrium corresponds to a dynamic that obeys detailed balance.

15. Discussions

15.1. Thermodynamic potentials

The thermodynamic potentials were introduced by Massieu in 1869 with the name of *characteristic functions* [41]. The main idea advanced by Massieu was that a single characteristic function could enclose all properties of a body. This idea was embraced by Gibbs who stated in his treatise on thermodynamics of 1876 that *Massieu has shown how all the properties of a fluid which are considered in thermodynamics may be deduced from a single function* [60].

Massieu introduced two characteristic functions which are $\Psi = S - U/T$ and $\Phi = S - (U + pV)/T$. Gibbs instead introduced the functions $F = U - TS$ and $G = H - TS$ which together with $H = U + pV$ and U he called *fundamental equations* [60]. We remark that, in a later paper of 1876, using a suggestion of Bertrand, Massieu simplified his previous approach by introducing two characteristic functions that are identical to F and G except for a minus sign [42, 117, 118].

A distinguishing feature of the Gibbs approach in comparison with that of Massieu is that he considered the thermodynamic potentials to be applied to systems with variable composition, as pointed out by Gibbs himself. The second and most important feature showed by Gibbs is that the thermodynamic potentials hold the conditions of equilibrium, which he wrote as $(\Delta U)_S \geq 0$, $(\Delta F)_T \geq 0$, and $(\Delta G)_{Tp} \geq 0$, as well as the convexity properties.

Duhem used the term *thermodynamic potential* to name the Massieu characteristic function, a concept that became central in his thermodynamics [87, 90]. The name was borrowed from mechanics. Duhem explains that if the work of a force depends only on the final and the initial state, there exists a function called potential such that the forces are obtained by differentiation [87]. The main property of the potential is that it is a minimum in a state of stable equilibrium, as shown by Lagrange and demonstrated by Dirichlet, says Duhem [87]. Gibbs used the same concept of potential but he associated it to a function with the reverse sign of the potential, which he called force function [60]. Thus $-F$ is the force function of a system at constant temperature, $-U$ is the force function at constant entropy. By analogy he called H the *heat function* for constant pressure because the variation of H at a constant pressure equals the heat. In this sense U might as well be the heat function at constant volume, says Gibbs.

The quantity $U - TS$ was called available energy by Maxwell in 1875 although he did not ascribe a letter to it [43]. Helmholtz introduced the thermodynamic potential F in 1882 and called it the *free energy* [93]. In a publication of the following year Helmholtz acknowledges that Massieu had already introduced the function F in 1876, except for the minus sign, but without relating it with chemical processes as he did [119]. Duhem called F the internal thermodynamic potential [90]. In addition to free energy [78–80, 101, 110, 120–126], other terminologies are *Helmholtz free energy* [113, 127–130], work function [131], Helmholtz function [132] and Helmholtz potential [133].

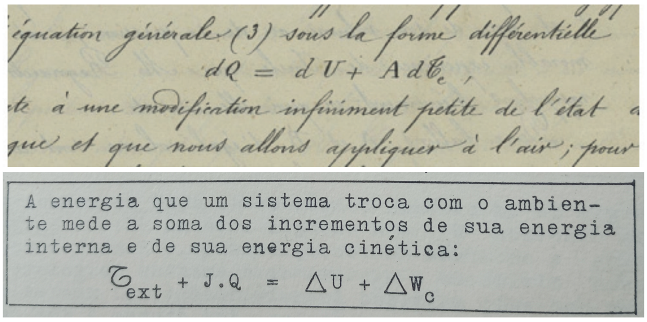
Planck [78–80] and others [120, 121, 125, 126, 130, 131], called H the heat function as did Gibbs, whereas Lewis and Randall [106], called it the heat content. The name *enthalpy* was proposed by Kamerling Onnes in 1908 [134, 135] and was widely adopted [110, 113, 120, 122, 124, 128, 129, 131–133].

Lewis and Randall [106] called G the free energy. Other terminologies for G are thermodynamic potential [120, 125], *Gibbs free energy* [121, 127–129], Gibbs thermodynamic potential [113], Gibbs function [130, 132, 133] and free enthalpy [124].

Guggenheim [130] and Kubo [129] called the potential Ψ the Massieu function and Φ the Planck function. Both potentials were called Massieu functions by Callen [133].

In Table 1 we show the notation for the thermodynamic potentials used by several authors together with the notation for temperature, heat, and work. In the present paper, starting from the section on the Gibbs thermodynamics, we employed the notation shown in the first line of Table 1 instead of the original notations used by the authors.

We remark that Massieu [136], Duhem and some other French authors used for work the symbol $\mathscr{T}$, which is a French cursive capital letter 'T'. In French, the word for work (*travail*) begins with the letter 't', as is the case of Portuguese (*trabalho*) and Spanish (*trabajo*). It is interesting to note that the symbol $\mathscr{T}$ is also used for work in physics textbooks for the secondary school in Brazil, which sometimes is called 'tau' due to the resemblance with the Greek letter [137], as illustrated in Figure 9.



équation générale (3) sous la forme différentielle

$$dQ = dU + Ad\mathscr{T}_e ,$$

té à une modification infiniment petite de l'état a

que et que nous allons appliquer à l'air ; pour

A energia que um sistema troca com o ambiente mede a soma dos incrementos de sua energia interna e de sua energia cinética:

$$\mathscr{T}_{ext} + J.Q = \triangle U + \triangle W_c$$

Figure 9: Top panel. Massieu handwriting [136] of 1873 for the first law of thermodynamics in differential form, $dQ = dU + Ad\mathscr{T}_e$. The symbol $\mathscr{T}$ for work is a French cursive capital letter 'T', and A is the heat equivalent of work. Bottom panel. Illustration of the first law in a secondary school book of 1965 [137].

Table 1: Notations for temperature θ, absolute temperature T, heat Q, work W, entropy S, energy U, Helmholtz free energy F, enthalpy H, Gibbs free energy G. An asterisk* indicates that the author mentions the Legendre transformation.

author	θ	T	Q	W	S	U	F	H	G	year	ref.
Poisson	θ		q							1823	[22]
Clapeyron	t		Q							1834	[27]
Clausius	t		Q			U				1850	[33]
Clausius	t	T	Q	W		U				1854	[38]
Clausius		T	Q	W	S	U				1865	[39]
Massieu	t	T	Q		S	U		U'		1869	[41]
Maxwell	t	T	H	W	ϕ	E				1871	[20]
Gibbs		t	H	W	η	ϵ				1873	[58]
Massieu	t	T	Q	$\mathscr{T}$	S	U	$-H$	U'	$-H'$	1876	[42]
Gibbs		t	Q	W	η	ϵ	ψ	χ	ζ	1876	[60]
Helmholtz		ϑ	Q	W	S	U	$\mathfrak{F}$			1882	[93]
Duhem		T	Q	$\mathscr{T}$	S	U	$\mathscr{F}$		Φ	1886	[87]
Bertrand	t	T	Q		S	U	$-H$		$-H'$	1887	[117]
Poincare	t	T	Q	τ	S	U	$-H$		$-H'$	1892	[118]
Nernst		T	Q		S	U	A			1893	[101]
Duhem	ϑ	T	Q	$\mathscr{T}$	S	U	$\mathscr{F}$		$\mathscr{H}$,Φ	1897	[90]
Planck	t	ϑ	Q	A	S	U	F			1897	[78]
Planck	t	T	Q	A	S	U	F	W		1911	[79]
Partington	θ	T	Q	A	S	U	Ψ	W	ϕ	1913	[126]
Planck	t	T	Q	A	S	U	F	W		1922	[80]
Lewis and Randall		T	q	w	S	E	A	H	F	1923	[106]
Partington	θ	T	Q	A	S	U	F	H	Z	1924	[120]
De Donder		T	Q	W	S	U	F	Ψ	H	1927	[110]
Schottky		T	Q	A	S	U	F	W	G	1929	[121]
van Lerberghe		T	Q	$\mathscr{T}$	S	U	F	I	H	1931	[122]
Guggenheim		T	q	w	S	E	F	H	G	1933	[127]
De Donder		T	Q		S	E	F	H	G	1936	[113]
Epstein*		T	Q	W	S	U	Ψ	X	Φ	1937	[131]
Fermi		T	Q	L	S	U	F		Φ	1937	[123]
Zemansky		T	Q	W	S	U	F	H	G	1937	[132]
Guggenheim		T	q	w	S	U	F	H	G	1949	[130]
Sommerfeld*		T	Q	W	S	U	F	H	G	1952	[124]
Landau and Lifshitz		T	Q	R	S	E	F	W	Φ	1958	[125]
Callen*		T	Q	W	S	U	F	H	G	1960	[133]
ter Haar and Wergeland*		T	Q	L	S	U	F	H	G	1966	[128]
Kubo*		T	Q	W	S	U	F	H	G	1968	[129]

15.2. Legendre transformation

The recognition that the thermodynamic potentials are connected to a Legendre transformation was made by

Ehrenfest in a paper on the Le Chatelier-Braun principle published in 1911 [138]. He adds that it is the same transformation used to pass from the equations of Lagrangian to the equations of Hamilton. Later it was also recognized by Epstein in his book on thermodynamics of 1937 [131]. He says that the method of replacing ydx by the term $-xdy$ through the subtraction of $d(xy)$ is called a Legendre transformation.

Sommerfeld in his book on thermodynamics of 1952 [124] used the Legendre transformation and pointed out the same observations made by Epstein and Ehrenfest concerning this transformation. Thereafter, it was used by Callen in his textbook on thermodynamics of 1960 [133] and by Tisza in a paper on thermodynamics of 1961 [139]. The transformation was also used by ter Haar and Wergeland in his book on thermodynamics of 1966 [128], where they remarked that it is a special case of a Lie contact transformation, and by Kubo in his book on thermodynamics published in 1968 [129], which is a translation of the Japanese edition of 1961. It should be remarked that many books do not refer to the Legendre transformation, as seen in Table 1, including the book of Landau and Lifshitz on statistical mechanics published in 1958 [125], which includes a section about thermodynamics.

The origin of the transformation associated to the name of Legendre is found in his publication of 1787 [140] about the integration of some partial differential equations. Legendre introduced a change of variable to simplify a partial differential equation of the type

$$A\frac{\partial^2 z}{\partial x^2} + B\frac{\partial^2 z}{\partial x \partial y} + C\frac{\partial^2 z}{\partial y^2} = 0, \tag{261}$$

where A, B and C are functions of $p = \partial z/\partial x$ and $q = \partial z/\partial y$. The variable z depends on x and y and its differential is

$$dz = pdx + qdy. \tag{262}$$

Legendre then proposes to regard x, y, and z as functions of p and q. To this end, he defines a function ω by

$$\omega = px + qy - z, \tag{263}$$

from which follows that

$$d\omega = xdp + ydq, \tag{264}$$

and as $d\omega$ is an exact differential, one finds $x = \partial\omega/\partial p$ and $y = \partial\omega/\partial q$. From these results Legendre reaches the equalities

$$\frac{\partial^2 z}{\partial x^2} = \frac{1}{D}\frac{\partial^2 \omega}{\partial q^2}, \qquad \frac{\partial^2 z}{\partial y^2} = \frac{1}{D}\frac{\partial^2 \omega}{\partial p^2}, \tag{265}$$

$$\frac{\partial^2 z}{\partial x \partial y} = -\frac{1}{D}\frac{\partial^2 \omega}{\partial p \partial q}, \tag{266}$$

where

$$D = \frac{\partial^2 \omega}{\partial p^2}\frac{\partial^2 \omega}{\partial q^2} - \left(\frac{\partial^2 \omega}{\partial p \partial q}\right)^2. \tag{267}$$

Replacing these results in equation (261), the following equation is obtained

$$A\frac{\partial^2 \omega}{\partial q^2} - B\frac{\partial^2 \omega}{\partial p \partial q} + C\frac{\partial^2 \omega}{\partial p^2} = 0, \tag{268}$$

which is simpler than (261) in that it does not contain partial differentials of the first order.

We see that the equation (263), which defines the change of variable proposed by Legendre, is identical to the change of variables given by equations (60), (61), (63), and (69) proposed by Massieu. Thus, the change of variable employed by Massieu to obtain the several thermodynamic potentials, which has become common practice in the development of thermodynamics since Gibbs, is the same transformation used by Legendre. Considering that Massieu was the origin of the thermodynamic potential used by Gibbs, Helmholtz, Duhem and others, we find no reference to Legendre in these authors, as the reference was Massieu. Only later was the reference to Legendre recognized, as stated above.

Let us examine the transformation proposed by Legendre and independently by Massieu. Given $U(S)$, considered a continuous function of S, we obtain $F(T)$ by

$$F = U - TS, \tag{269}$$

where $T = \partial U/\partial S$. If $U(S)$ is convex than T will be a single-valued function of S and we can invert $T(S)$ to obtain S as a function of T, which replaced in (269) gives $F(T)$. If $U(S)$ is not convex then T may not be a single-valued function and the same may happen to F. To remedy this problem an appropriate way of defining the Legendre transformation is [55, 141–144]

$$F = \min_S\{U(S) - TS\}. \tag{270}$$

Using this definition, then $F(T)$ will be be single-valued and will be a concave function.

An illustration of the transformation defined by (270) is shown in Figure 10. If $U(S)$ is convex than $F(T)$ will be concave. We remark that convex and concave functions have convexity properties. A convex function is facing upwards, as in Figure 10a, and a concave function, facing downwards, as in Figure 10d. Thus the transformation (270) preserves the convexity property. The inverse transformation of (270) is

$$U^* = \min_T\{F(T) + ST\}. \tag{271}$$

If $U(S)$ in equation (270) has the convexity properties, than $U^*(S)$ will coincide with $U(S)$. If not then U^* will be the convex hull of U. The procedure of finding the convex hull is equivalent to the Maxwell construction [55].

Another important feature of the transformation defined by (270) is that it is also valid when the derivative of F does not exist as happens in a discontinuous thermodynamic phase transition as shown by the function F in Figure 10d.

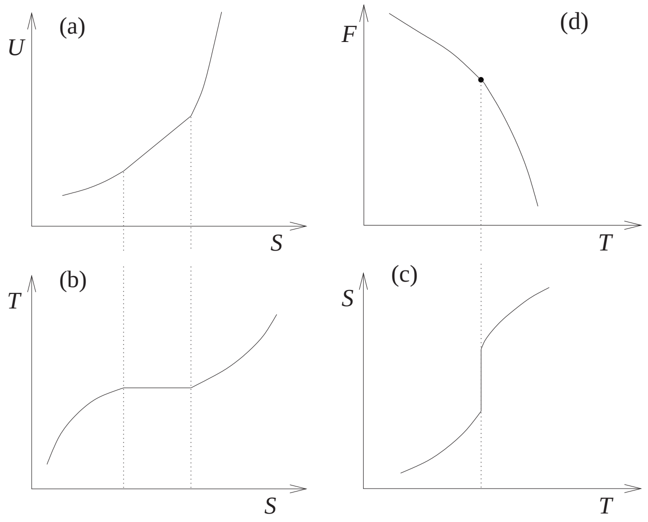


Figure 10: Illustration of a Legendre transformation. (a) Energy U versus entropy S, (b) temperature $T = \partial U/\partial S$ versus S, (c) entropy $S = -\partial F/\partial T$ versus T, (d) free energy F versus T. The curves in (a) and (d) are Legendre transforms of each other, and both hold the convexity property. The functions shown in (b) and (c) are inverse of each other. The full circle in (d) indicates that the left and right derivatives are distinct. The dot lines are guides to the eyes.

The Legendre transformation in the form (269) is used in many text-books on thermodynamics. The form (270), which is very useful in the study of phase transitions, is less employed. Nevertheless, this form is found in the chapter on thermodynamics contained in the book on statistical physics by Salinas [143], in the book on thermodynamics by Wreszinski [144], and in the book on equilibrium thermodynamics by the present author [55].

It is noteworth that the equivalence of descriptions by distinct thermodynamic potentials can be captured by looking at the Figure 10. We clearly see that the derivatives, which are conveniently located below the plots of the potentials, are inverse functions of each other.

15.3. Carathéodory

In 1909, Carathéodory published a paper [145] where he presented a derivation of the Clausius principle that $dQ/T = dS$ is an exact differential. He demonstrated this statement from a postulate that he introduced and which reads: *In any arbitrary neighborhood of a given initial state, there are states that cannot be arbitrarily reached by an adiabatic process.* This postulate is the main result of the Carathéodory approach, which he claimed to be an axiomatic treatment of thermodynamics [145, 146].

To better understand the Carathéodory approach we first formulate his main result as a theorem of mathematical analysis. Let us consider the differential equation, called Pfaffian,

$$\sum_i X_i dx_i = 0, \tag{272}$$

where X_i are given functions of the variables x_i which constitute a space x. Of all trajectories in space x, those that obey (272) we call a Pfaff trajectory.

Given a point A belonging to a Pfaff trajectory we may ask whether there exist a point B in an arbitrary neighborhood of the point A that is not connected by the Pfaff trajectory. If the answer is affirmative then the differential form on the left hand side of equation (272) can be integrated. That is, if we write

$$dS = \lambda \sum_i X_i dx_i, \tag{273}$$

then there exists a quantity λ such that dS is an exact differential, which means that S is a function of x. The quantity λ is a function of x and is called an integration factor. The main consequence of the theorem just presented is that the Pfaff trajectories will belong to surfaces in space x, described by $S(x) = k$ where k is a constant. Distinct surfaces are described by distinct values of k and they do not intercept each other.

To interpret this theorem in thermodynamics terms, we begin by writing the conservation of energy U along an adiabatic process in the differential form is written as

$$dU = -\sum_k f_k dx_k, \tag{274}$$

where each term $f_k dx_i$ represents one type of work performed by the system. This equation is identified with equation (272) and an adiabatic process as a Pfaff trajectory. With this interpretation we may conclude that

$$dS = \frac{dQ}{T}, \tag{275}$$

where

$$dQ = dU + \sum_k f_k dx_k, \tag{276}$$

where T is the inverse of the integration factor λ. Interpreting dQ as the heat developed along a trajectory and T as the temperature, then S is the Clausius entropy and (275) is the Clausius principle.

It should be remarked that, according to Born [147, 148], who supported the Carathéodory approach, the definition of adiabatic process does not use the notion of heat. That is, the equality (274) which describes an adiabatic process does not follow by setting the heat dQ in (276) equal to zero. The equality (274) *defines* an adiabatic process and the heat dQ is defined by (276). It should be noted however that this does not distinguish the Carathéodory approach from that of Clausius as the same interpretation can be said about the Clausius approach. In fact, we have emphasized the viewpoint that heat is defined by means of adiabatic process which is understood as a primitive concept and not defined as the a process without the exchange of heat [9, 10].

Table 2: The author and the abbreviated title of the work that we have analyzed together the year of its publication and references.

author	work	year	ref.
Laplace	Theory of elastic fluids	1822	[21]
Poisson	Heat of gases and vapors	1823	[22]
Carnot	Motive Power of Fire	1824	[26]
Clapeyron	Motive power of heat	1834	[27]
Clausius	Mechanical theory of heat	1850	[33]
Maxwell	Theory of Heat	1871	[20]
van der Waals	Continuity of the Gaseous and Liquid States	1873	[49]
Gibbs	Equilibrium of heterogeneous substances	1876	[60]
Planck	Treatise on Thermodynamics	1897	[78]
Duhem	Chemical Mechanics	1897	[90]
Nernst	New Heat Theorem	1906	[103]
De Donder	Affinity	1927	[110]
Prigogine	Irreversible Phenomena	1945	[114]

The theories of thermodynamics analyzed here used the Clausius principle as a fundamental law. As any scientific theory, the fundamental laws which are the starting point on the development of the theory, can be replaced by other equivalent laws if they exist. The Carathéodory approach is an example of this type. It is possible if we wish to replace the Clausius principle by the Carathéodory. However, we find it more natural to take the Clausius principle as fundamental and consider the Charathéodory postulate stated above as a consequence. That is, the existence of states near a given state that cannot be reached by means of an adiabatic process only is a consequence of the Clausius principle.

16. Conclusion

We have presented a critical analysis of the analytical theories of heat that included the caloric theories of Laplace, Poisson and Carnot, and the thermodynamic theories founded on the energy conservation and on the principle of the increase of entropy formulated by Clausius, which are summarized in Table 2. They were analyzed from the viewpoint that a scientific theory consists of a theoretical framework and an interpretation. The theoretical framework contains primitive concepts and fundamental laws from which other concepts and other laws are derived by a deductive reasoning. The fundamental laws must not contradict each other but an actual demonstration of consistency is not required.

Another feature of the theories of heat presented here is that they incorporate some laws that are not derived from the fundamental laws but are consistent with them. This is the case of the laws related to the ideal gases, such as the equation of state associate to the names of Boyle and Gay-Lussac, the Avogadro law, and the Gibbs rule used to determined the free energy of a mixture of ideal gases. Another important example is the Gibbs phase rule.

The way in which the laws are presented in some scientific treatises is made through a textual statement. This is particularly true in the case of thermodynamics where it became a tradition to state the second law in a textual form known as the Kelvin and Clausius statements. Sometimes other equivalent forms are also presented such as the Planck statement and the Charathéodory postulate. Usually a textual presentation needs an interpretation of its terms in order to be translated into an analytical form. In the theories presented above, the second law is formulated in the analytical form in terms of the entropy. However, the textual forms are still present in many textbooks.

The textual forms of the second law, such as those stated in terms of the efficiency of machines, have been argued to be inadequate to the construction of a theoretical framework of thermodynamics and a reconstruction of the theory is said to be necessary. The problem is not properly the reference to devices such as the heat engine. The problem lies in the lack of accuracy of the terms used in the statement and also on the unclear reasonings employed to reach the analytical forms. The principle of Carnot, which was stated originally in textual form, when interpreted by Clapeyron and by Clausius lead them to the desired analytical expressions (20) and (47).

At the end of this paper it is worth reproducing the words of Nernst concerning the study of theoretical physics, but we think it can be applied to the study of any scientific theory or any science. It the preface of his book on the New Heat Theorem, Nernst says [104, 105]: "In times of trouble and distress, many of the old Greeks and Romans sought consolation in philosophy, and found it. Today we may well say that there is hardly any science so well adapted as is theoretical physics to divert the mind from the mournful present and to lead it into other spheres; it can, however, offer this attraction only to the few who have studied it for years". The mournful present refers to the first world war but the quote could as well be alluded to the present time of the pandemic.

Acknowledgement

I wish to acknowledge Tânia Tomé for the critical reading of the manuscript and Dora Izzo for presenting me with a book containing the Gibbs scientific papers.

References

[1] M.J. de Oliveira, Rev. Bras. Ens. Fis. **43**, e20200506 (20021).

[2] M.J. de Oliveira, Rev. Bras. Ens. Fis. **43**, e20210160 (20021).

[3] M.J. de Oliveira, Rev. Bras. Ens. Fis. **41**, e20180174 (2019).

[4] D.S.L. Cardwell, *From Watt to Clausius* (Cornel University Press, Ithaca, 1971).

[5] R. Fox, *The Caloric Theory of Gases* (Clarendon Press, Oxford, 1971).

[6] E. Segrè, *From Fallling Bodies to Radio Waves* (Freeman, New York, 1984).

[7] A.S.T. Pires, *Evolução das Idéias da Fisica* (Editora Livraria da Física, São Paulo, 2011), 2 ed.

[8] L.R. Evangelista, *Perspectivas em História da Física, Da Física dos Gases à Mecânica Estatística* (Editora Livraria da Física, São Paulo, 2014).

[9] M.J. de Oliveira, Braz. J. Phys. **48**, 299 (2018).

[10] M.J. de Oliveira, Rev. Bras. Ens. Fis. **41**, e20180307 (2019).

[11] M.J. de Oliveira, Rev. Bras. Ens. Fis. **42**, e20190192 (2020).

[12] G.S. Parks, J. Chem. Educ. **26**, 262 (1949).

[13] M.W. Lindauer, J. Chem. Educ. **39**, 384 (1962).

[14] V.M. Schelar, Chymia **11**, 99 (1966).

[15] R.G.A. Dolby, History of Science **22**, 375 (1984).

[16] A. Ya. Kipnis, in: *Thermodynamics: History and Philosophy, Facts, Trends, and Debates*, edited by K. Martinás, L. Ropolyi and P. Szegedi (World Scientific, Singapore, 1991), p. 492.

[17] A. Lavoisier and P. S. Laplace, Memoires de l'Académie des Sciences, année 1780, 355 (1784).

[18] A. Lavoisier, *Traité Élementaire de Chimie* (Cuchet, Paris, 1789).

[19] A. Lavoisiser, *Elements of Chemistry* (Creech, London, 1790).

[20] J.C. Maxwell, *Theory of Heat* (Longmans, London, 1871).

[21] P.S. Laplace, *Connaissance des Tems, ou des Mouvements Célestes, a l'Usage des Astronomes et des Navigateurs, pour l'an 1825* (Forgotten Books, Paris, 1825), p. 219, 302.

[22] S.D. Poisson, Annales de Chimie et de Physique **23**, 337 (1823).

[23] C.C. Gillispie, *Dictionary of Scientific Biography* (Scribner, New York, 1971), v. 3, p. 79.

[24] E. Mendoza, *Reflections on the Motive Power of Fire by Sadi Carnot and other Papers on the Second Law of Thermodynamic* (Dover, New York, 1960).

[25] R. Taton, in: *Sadi Carnot et l'Essor de la Thermodynamique* (Éditions du Centre National de la Recherche Scientifique, Paris, 1976), p. 35.

[26] S. Carnot, *Réflexions sur la Puissance Motrice du Feu* (Bachelier, Paris, 1824).

[27] E. Clapeyron, Journal de l'École Royale Polytechnique **14**, 153 (1834).

[28] C.C. Gillispie, *Dictionary of Scientific Biography* (Scribner, New York, 1971), v. 3, p. 286.

[29] A. Birembaut, in: *Sadi Carnot et l'Essor de la Thermodynamique* (Éditions du Centre National de la Recherche Scientifique, Paris, 1976), p. 191.

[30] E. Clapeyron, Annalen der Physik und Chemie **59**, 446 (1843).

[31] C. Holtzmann, *Ueber die Wärme und Elasticität der Gase und Dämpfe* (Loeffler, Mannheim, 1845).

[32] W. Thomson, Philosophical Magazine **33**, 313 (1848).

[33] R. Clausius, Annalen der Physik und Chemie **79**, 368, 500 (1850).

[34] C.C. Gillispie *Dictionary of Scientific Biography* (Scribner, New York, 1971), v. 3, p. 303.

[35] G. Ronge, Gesnerus **12**, 73 (1955).

[36] R. Clausius, *Abhandlungen über die Mechanische Wärmertheorie* (Vieweg, Braunschweig, 1864).

[37] R. Clausius, *The Mechanical Theory of Heat* (John van Voorst, London, 1867).

[38] R. Clausius, Annalen der Physik und Chemie **93**, 481 (1854).

[39] R. Clausius, Annalen der Physik und Chemie **125**, 353 (1865).

[40] E. Nivoit, Annales de Mines **11**, 350 (1897).

[41] F. Massieu, Comptes Rendus **69**, 858, 1057 (1869).

[42] F. Massieu, Mémoires Présentés par Divers Savants a l'Académie de Sciences de l'Institut Nationale de France **22**, 2 (1876).

[43] J.C. Maxwell, *Theory of Heat* (Longmans, London, 1875), 4rd.

[44] J.C. Maxwell, *Theory of Heat* (Dover, New York, 2001).

[45] T. Andrews, Philosophical Transactions of the Royal Society of London **159**, 575 (1869).

[46] J. Thomson, Proceedings of the Royal Society of London **20**, 1 (1872).

[47] C.C. Gillispie *Dictionary of Scientific Biography* (Scribner, New York, 1976), v. 14, p. 109.

[48] A.Ya. Kipnis, B.E. Yavelov and J.S. Rowlinson, *Van der Waals and Molecular Science* (Clarendon Press, Oxford, 1996).

[49] J.D. van der Waals, *Over de Continuitet van den Gasen Vloeistoftoestand* (Sijthoff, Leiden, 1873).

[50] J.S. Rowlinson, *J.D. van der Waals: On the Continuity of the Gaseous and Liquid States* (North-Holland, Amsterdam, 1988).

[51] R. Clausius, Philosophical Magazine **40**, 122 (1870).

[52] J.C. Maxwell, Nature **11**, 374 (1875).

[53] R. Clausius, Annalen der Physik **9**, 337 (1880).

[54] R. Clausius, Philosophical Magazine **9**, 393 (1880).

[55] M.J. de Oliveira, *Equilibrium Thermodynamics* (Springer, Berlin, 2013).

[56] L.P. Wheeler, *Josiah Willard Gibbs* (Yale University Press, New Have, 1951).

[57] C.C. Gillispie *Dictionary of Scientific Biography* (Scribner, New York, 1972), v. 5, p. 386.

[58] J.W. Gibbs, Transactions of the Connecticut Academy of Arts and Sciences **2**, 309 (1873).

[59] J.W. Gibbs, Transactions of the Connecticut Academy of Arts and Sciences **2**, 382 (1873).

[60] J.W. Gibbs, Transactions of the Connecticut Academy of Arts and Sciences **3**, 108 (1876).

[61] J.W. Gibbs, Transactions of the Connecticut Academy of Arts and Sciences **3**, 343 (1878).

[62] J.W. Gibbs, *Thermodynamische Studien* (Engelmann, Leipzig, 1892).

[63] J.W. Gibbs, *Équilibre des Systèmes Chimiques* (Gauthiers-Villars, Paris, 1899).

[64] R. Baierlein, Am. J. Phys. **69**, 423 (2001).

[65] G.H. Hess, Bulletin de l'Académie des Sciences de Saint Pétersbourg **7**, 257 (1840); **8**, 81 (1841).

[66] G.H. Hess, Annalen der Physik und Chemie **50**, 385 (1840); **52**, 97 (1841).

[67] J. Thomsen, Annalen der Physik und Chemie **92**, 34 (1854).

[68] M. Berthelot, Annales de Chimie et de Physique **18**, 5 (1869).

[69] M. Berthelot, Comptes Rendus **76**, 94 (1873).

[70] M. Berthelot, Annales de Chimie et de Physique **4**, 5 (1875).

[71] J.H. van 't Hoff, *Études de Dynamique Chimique* (Frederik Muller, Amsterdam, 1884).

[72] H. Le Chatelier, Comptes Rendus **99**, 786 (1884).

[73] J.H. van 't Hoff, Archives Néerlandaises des Sciences Exactes et Naturelles **20**, 239 (1886).

[74] C.C. Gillispie *Dictionary of Scientific Biography* (Scribner, New York, 1975), v. 11, p. 7.

[75] M. Planck, Verhandlungen der Deutschen Physikalischen Gesellschaft **2**, 202 (1900).

[76] M. Planck, Verhandlungen der Deutschen Physikalischen Gesellschaft **2**, 237 (1900).

[77] M. Planck, *Grundriss der Allgemeinen Thermochemie* (Trewendt, Breslau, 1893).

[78] M. Planck, *Vorlesungen über Thermodynamik* (Von Veit, Leipzig, 1897).

[79] M. Planck, *Vorlesungen über Thermodynamic* (von Veit, Leipzig, 1911), dritten Auflage.

[80] M. Planck, *Vorlesungen über Thermodynamic* (Gruyter, Berlin, 1922), siebente Auflage.

[81] M. Planck, *Treatise on Thermodynamics* (Longmans, London, 1903).

[82] M. Planck, *Treatise on Thermodynamics* (Longmans, London, 1927), 3rd ed.

[83] Hèlène Pierre-Duhem, *Un Savant Français: Pierre Duhem* (Librairie Plon, Paris, 1936).

[84] D.G. Miller, Physics Today **19**, 47 (1966).

[85] C.C. Gillispie *Dictionary of Scientific Biography* (Scribner, New York, 1971), v. 4, p. 225.

[86] S.L. Jaki, *Uneasy Genius: The Life and Work of Pierre Duhem* (Martinus Nijhoff, Dordrecht, 1987).

[87] P. Duhem, *Le Potentiel Thermodynamique et ses Applications à la Mécanique Chimique et à l'Étude des Phénomènes Électriques* (Hermann, Paris, 1886).

[88] J.R.N. Chiappin, *Duhem's Theory of Science: an Interplay between Philosophy and History of Sceince.* Ph.D. thesis, University of Pittsburgh, Pittsburgh (1989).

[89] P. Duhem, *Traité d'Energetique* (Gauthier-Villars, Paris, 1911), v.2.

[90] P. Duhem, *Traité Élémentaire de Mécanique Chimique Fondée sur la Thermodynamique* (Hermann, Paris, 1897-1899), 4 vols.

[91] G. Kirchhoff, Annalen der Physik und Chemie **103**, 177 (1858).

[92] A.F. Horstmann, Annalen der Chemie und Pharmacie **170**, 192 (1873).

[93] H. von Helmholtz, Sitzungsberichte der Königlich preussischen Akademie der Wissenschaften zu Berlin **XXVI**, 1 (1882), p. 22.

[94] P. Waage and C.M. Guldberg, Forhandlinger I Videnskabs-selskabet I Christiania 1864, **35** (1865).

[95] P. Waage, Forhandlinger I Videnskabs-selskabet I Christiania 1864, 92 (1865).

[96] P.C.M. Guldberg, Forhandlinger I Videnskabs-selskabet I Christiania 1864, 111 (1865).

[97] G. Lemoine, *Études sur les Équilibres Chimiques* (Dunot, Paris, 1881).

[98] J.H. van 't Hoff, Kongliga Svenska Vetenskaps-Akademiens Handlingar **21**, 1 (1885).

[99] K. Mendelssohn, *The World of Walther Nernst, The Rise and Fall of German Science* (Macmillan, London, 1973).

[100] H.-G. Bartel and R.P. Huebener, *Walther Nernst Pioneer of Physics and of Chemistry* (World Scientific, Singapore, 2007).

[101] W. Nernst, *Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik* (Ferdinand Enke, Stuttgart, 1893).

[102] W. Nernst, *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics* (Macmillan, London, 1895).

[103] W. Nernst, Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen **Jahre 1906**, 1 (1906).

[104] W. Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes* (Wilhelm Knapp, Halle, 1918).

[105] W. Nernst, *The New Heat Theorem, its Foundations in Theory and Experiment* (Methuen, London, 1926).

[106] G.N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill, New York, 1923).

[107] J. Géhéniau, in: *Florilège des Sciences en Belgique* (Académie Royale de Belgique, Brussels, 1968), p. 169.

[108] J. Géhéniau, Biographie Nationale de l'Académie Royale de Belgique **37**, 240 (1971).

[109] P. Glansdorff, J. Bosquet and J. Géhéniau, *Notice sur Théophile De Donder* (Annuaire de l'Académie Royale de Belgique Bruxelles, 1987).

[110] T. De Donder, *L'Affinité* (Gauthier-Villars, Paris, 1927).

[111] T. De Donder, *L'Affinité*, seconde partie, (Gauthier-Villars, Paris, 1931).

[112] T. De Donder, *L'Affinité*, troisième partie, (Gauthier-Villars, Paris, 1934).

[113] T. De Donder, *L'Affinité*, première partie (Gauthier-Villars, Paris, 1936), 2 ed.

[114] I. Prigogine, *Étude Thermodynamique des Phénomènes Irreversibles* (Desoer, Liège, 1947).

[115] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Charles C. Thomas, Springfield, 1955).

[116] L. Onsager, Phys. Rev **37**, 405; **38**, 2265 (1931).

[117] J. Bertrand, *Thermodynamique* (Gauthier-Villars, Paris, 1887).

[118] H. Poincaré, *Thermodynamique* (Georges Carré, Paris, 1892).

[119] H. von Helmholtz, Sitzungsberichte der Königlich preussischen Akademie der Wissenschaften zu Berlin, (1883), p. 647 .

[120] J.R. Partington, *Chemical Thermodynamics* (Constable, London, 1924).

[121] W. Schottky, *Thermodynamik* (Springer, Berlin, 1929).

[122] G. van Lerberghe, *Calcul des Affinités Physico-Chimiques* (Gauthier-Villars, Paris, 1931).

[123] E. Fermi, *Thermodynamics* (Prentice-Hall, New York, 1937).

[124] A. Sommerfeld, *Vorlesungen über theoretische Physik, Thermodynamik und Statistik* (Dieterische, Wisbaden, 1952), band V.

[125] L.D. Landau and E.M. Lifshitz, *Statistical Physics* (Pergamon Press, London, 1958).

[126] J.R. Partington, *A Text-Book of Thermodynamics* (Constable, London, 1913).

[127] E.A. Guggenheim, *Modern Thermodynamics by the method of Willard Gibbs* (Methuen, London, 1933).

[128] D. ter Haar and H. Wergeland, *Elements of Thermodynamics* (Addison-Wesley, Reading, 1966).

[129] R. Kubo, *Thermodynamics* (North-Holland, Amsterdam, 1968).

[130] E.A. Guggenheim, *Thermodynamics* (North-Holland, Amsterdam, 1949).

[131] P.S. Epstein, *Textbook of Thermodynamics* (Wiley, New York, 1937).

[132] M.K. Zemansky, *Heat and Thermodynamics* (McGraw-Hill, New York, 1937).

[133] H.B. Callen, *Thermodynamics* (Wiley, New York, 1960).

[134] I.K. Howard, J. Chem. Educ. **79**, 697 (2002).

[135] H.C. van Ness, J. Chem. Educ. **80**, 486 (2003).

[136] F. Massieu, *Exposé des principes fondamentaux de la théorie mécanique de la chaleur*, 1873; https://iris.univ-lille.fr/handle/1908/4877.

[137] T.N.O. Folmer-Johnson, *Elementos de Termologia* (Nobel, São Paulo, 1965).

[138] P. Ehrenfest, Zeitschrift für physikalische Chemie **77**, 227 (1911).

[139] L. Tisza, Annals of Physics **13**, 1 (1961).

[140] A.-M. Legendre, Histoire de l'Académie Royale des Sciences, avec les Mémoires de Mathématique et de Physique (Imprimerie royale, Paris, 1787), p. 309.

[141] R.B. Griffiths, J. Math. Phys. **6**, 1447 (1965).

[142] V.I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer, New York, 1978).

[143] S.R. Salinas, *Introdução à Física Estatística* (EDUSP, São Paulo, 1997).

[144] W.F. Wreszinski, *Termodinâmica* (EDUSP, São Paulo, 2003).

[145] C. Carathéodory, Mathematische Annalen **67**, 355 (1909).

[146] L. Pogliani and M.N. Berberan-Santos, Journal of Mathematical Chemistry **28**, 313 (2000).

[147] M. Born, Physikalische Zeitschrift **22**, 218, 249, 282 (1921).

[148] M. Born, *Natural Philosophy of Cause and Chance* (Clarendon Press, Oxford, 1949).