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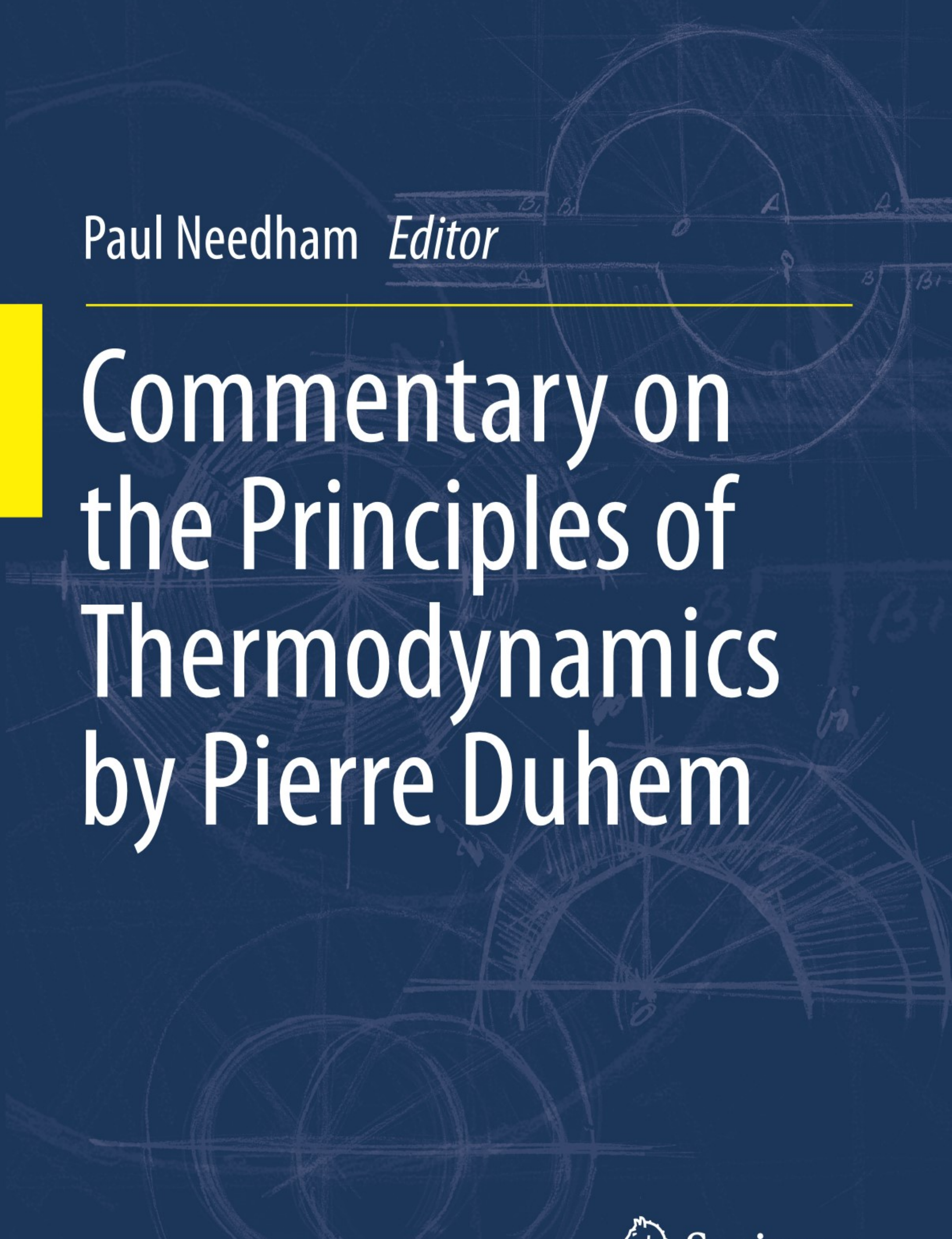
Commentary on the Principles of Thermodynamics by Pierre Duhem



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COMMENTARY ON THE PRINCIPLES OF THERMODYNAMICS BY PIERRE DUHEM

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COMMENTARY ON THE PRINCIPLES OF THERMODYNAMICS BY PIERRE DUHEM

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Introduction

Pierre Maurice Marie Duhem (1861–1916) held the chair of physics (changed to chair of theoretical physics in 1895) at Bordeaux from 1894 to his death. He established a reputation in both the history and philosophy of science as well as in science (physics and physical chemistry). His pioneering work in medieval science opened up the area as a new discipline in the history of science, and his *La théorie physique* (Duhem 1906) is a classic in the philosophy of science which is still read and discussed today. Although his work in these two fields is now well represented in English with a number of translations that have appeared in recent decades (Duhem 1892b, 1903, 1902, 1905–1906, 1906, 1908, 1915, 1985, 1996), there is little of his scientific work available in English. The original manuscript of Duhem (1898) was translated by J. E. Trevor, one of the editors of *The Journal of Physical Chemistry*, for its first issue. But his work almost invariably appeared in French. The present volume contains translations of some of his important early work in thermodynamics, which I hope will contribute to a more balanced picture in English of the breadth of Duhem's publications and provide a further source of insight into his thought.

Duhem's first book, *Le potentiel thermodynamique* (1886) furthers work initiated by Massieu, Helmholtz and Gibbs on the application of thermodynamics in chemistry. Clausius had shown that the second law was associated with a function of state which he called entropy, just as the first law was associated with a more familiar function of state, energy. But he made no real use of his new concept of entropy in his own work on the development of thermodynamics, eliminating energy and entropy as soon as possible in favour of the original thermodynamic concepts of heat and work (Klein 1978, pp. 331–2). It was Gibbs (1876–1878) who put the new concept of entropy to serious use in his now familiar combined form of the first and second laws, which characterises systems entirely in terms of functions of state. This was the form that made perspicuous these application of the science first formulated to articulate the principles governing the working of steam engines and seemingly having nothing to do with chemistry.

Duhem (1886)[1] exploits the application of Euler's theorem on homogeneous functions, from which the association of Duhem's name with the Gibbs-Duhem equation derives. The following year he began to explore the foundations of thermodynamics on which Gibbs built his theory in his "Study of the thermodynamic works of J. Willard Gibbs" (1887), which was the first critical study of Gibbs (1876–1878). It is translated here because it is something of a predecessor to the principal work translated here, Duhem's three-part study "Commentary on the principles of thermodynamics" (1892a, 1893a and 1894), henceforth referred to simply as *Commentary*. In the 1887 essay Duhem presents a first rigorous definition of the notion of a reversible process. This was problematic because thermodynamics provides a characterisation of matter (or radiation) at equilibrium. It is paradoxical how any process connecting two equilibrium states could itself comprise just equilibrium states, as thermodynamicists had supposed, because once in a state of equilibrium, the system never changes. Real processes only occur as a result of an imbalance of forces between a system and its environment. Duhem suggested that in the limit, now called a quasi-static process, in which the imbalance is successively reduced, each step is an equilibrium state, but he emphasised that the totality of such steps cannot itself represent a process, however slow. If such a limit in the process of getting from state A to state B coincides with the limit for getting from B to A, Duhem (1887, pp. 132–4)[2] defines it as a reversible change (*transformation réversible*), observing that this cannot be an actual change.

Duhem introduced this conception in his physical chemistry textbooks. In his *Introduction à la mécanique chimique*, he began his presentation of thermodynamics with an account of reversible change (*modification réversible*), emphasising that real changes are never reversible (1893b. pp. 93–9). And in later works he devotes several pages to carefully describing the notion (1897, pp. 56–60; 1910, pp. 59–82), always stressing the impossibility of any such process. Rechel (1947, p. 301) was later to bemoan the fact that the standard English term "reversible process" "contains a contradiction within itself ... which text book writers are prone to ignore" but exonerates Duhem from this charge.

Duhem sharpens the definition of a *modification réversible* in §8 of the second part of his *Commentary* (Section 6.8 here), having argued in the preceding §7 that a sequence of equilibrium states can be regarded as a virtual change which, as distinct from a real change, doesn't occur in time with the independent variables on which the state of the system depends being functions of time and having determinate rates of change. As Miller (1966, 1971) notes, Duhem points out in this more extended discussion that there are circumstances in which the limiting quasi-static processes are not the same in each direction, so that it is a substantial restricting assumption to speak of "systems for which all changes ..., which are sequences of

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[1] Jaki (1984, pp. 50–3) argues Duhem (1886) must be identical with the doctoral thesis which he submitted in 1884 but was not accepted.

[2] The original page numbers to Duhem's works translated here are preserved in the translation, and references to these works in this Introduction are to the original pagination.

equilibrium states, are reversible changes" (Duhem 1893a, p. 307). A more comprehensive development of thermodynamics in which this restriction is lifted is pursued in Duhem (1896a). Another definition given in the 1887 paper and repeated in the first part of *Commentary* is noteworthy for providing for the first time a definition of the amount of heat in terms of energy and work.

The earlier 1887 paper professed to address the circumstance that "Mathematicians regret that the principles of Thermodynamics should have been developed in general with so little precision that the same proposition can be regarded by some as a consequence, and by others as a negation, of these principles" (p. 123). This task is more earnestly pursued in the later three-part *Commentary*, where he sets about articulating the theory in axiomatic form which provides a framework in which definitions can be properly formulated and from which he rigorously establishes the standard results of thermodynamics such as the existence of a function serving as the entropy (Chapter 8 here). Earlier on in the nineteenth century, mathematicians had turned to the axiomatic method in order to clarify the foundations of the differential and integral calculus in the real number system. But the axiomatic foundations of Euclidean geometry and the status of the non-Euclidean geometries were only being developed around the time Duhem was writing, and as Miller (1971) says, his application of this approach in physics was truly pioneering in making the assumptions (what he calls conventions) explicit and formulating them rigorously.

Duhem had another goal in his *Commentary*, in addition to providing a clear and adequate foundation for thermodynamics. He was writing at a time when many physicists accepted the vision of all physical phenomena as essentially mechanical, and several were actively engaged in the project of demonstrating this by reducing physical theory to mechanics. There was some opposition to this in the development of schools of energetics. In Germany, the two leading figures, Georg Helm (1851–1923) and Wilhelm Ostwald (1853–1932) promoted a theory of energetics inspired by thermodynamics at the end of the nineteenth century, but with rather different motivations. Whereas Ostwald offered a realist conception of energy as the fundamental thing or substance in terms of which the properties of matter were to be reduced, Helm advocated an instrumentalist or phenomenological conception. Their theories were heavily criticised by Boltzmann and Planck at a famous meeting in Lübeck in 1895 (Deltete 1999), in view of which it is somewhat surprising that Duhem later used the term (Duhem 1911). But Duhem cannot be criticised, as they were, for misunderstanding the basic principles of thermodynamics. Nor did he adopt either Ostwald's stance of treating energy as the only ultimate real object or Helm's phenomenal view. Although he was in agreement with them in opposing universal reduction to mechanics, he didn't offer an alternative form of reduction instead (to phenomena, like Helm, or to energy, like Ostwald), and never appeals to their writings. The person he acknowledges for introducing the term "energetics" is Rankine (1855) (see, for example, Duhem 1896b, p. 498 or Duhem 1911, vol. I, p. 3). He states his conception at the end of the third part of the *Commentary*, where he offers a view of science as unified by supplementing mechanical conceptions with new ones which are incorporated into a single overarching theory adequate to deal with mechanical and non-mechanical phenomena alike. Thus he brings his three-part study to a close by surmising

> It seems to us that a general conclusion arises from this study. If the science of motion ceases to be the first of the physical Sciences in logical order, and becomes just a particular case of a more general science including in its formulas all the changes of bodies, the temptation will be less, we think, of reducing all physical phenomena to the study of motion. It will be better understood that change of position in space is not a more simple change than change of temperature or of any other physical quality. It will then be easier to get away from what has hitherto been the most dangerous stumbling block of theoretical physics, the search for a mechanical explanation of the Universe. (Duhem 1894, p. 285)

The English reader might well turn to the article Duhem (1898) referred to above after these translations. It was the first rigorous proof, without any restrictions, of Gibbs' phase rule, which gives a condition on the number of independent intensive variables specifying temperature, pressure and concentration of each substance in each phase in a heterogeneous mixture. He also extends the result, giving necessary conditions for the masses of each phase, in what has come to be called Duhem's theorem.

Although Duhem would make minor changes in wording when republishing a text, he seems to have been in the habit of writing out his manuscripts for first publication without revising. This is apparent in turgid formulations and sentences that can be convoluted, which would naturally have been rewritten. I have resisted any such temptation and sought to reduce adjustments to a minimum in these translations, giving as literal a translation as possible. His very long sentences have often been broken down, however, but his division into paragraphs is retained, even though many of them comprising just one or two lines would normally be integrated into larger paragraphs in modern English. Page numbers of the original texts are given in square brackets, except for the numbers of the first pages, which are given in the reference to the original name and place of publication accompanying each article. Together with the retention of the original paragraphs, the original pagination should facilitate comparison with the original text and following references in the secondary literature. Remarks and additions to the text in square brackets are my own. Whenever a change has been made to a mathematical formula, this is indicated in the footnotes.

In the 1887 paper Duhem uses both the expressions *demi-force vivre* and *force vivre*, and in the *Commentary* he uses both the expressions *force vivre* and *énergie cinétique*. Whilst this varying usage is often indicated in the footnotes, these terms have been uniformly rendered as "kinetic energy". The term introduced by equation (14) of the first *Commentary* paper (Duhem 1892, p. 305), which he calls *force vivre*, is precisely how kinetic energy is defined in modern texts.

In the *Commentary* Duhem uses both *oeuvre* and *travail*, each normally translated into English as *work*, as distinct technical terms. I have systematically translated *oeuvre* as "mechanical work" and reserved the plain "work" for *travail* in order to preserve this distinction in the translation. Since *oeuvre* figures only in the second chapter of the first part of the *Commentary* (except for a sporadic appearance in the third part), the two-word English term is confined to a relatively short portion of the translation. Duhem distinguishes between variables $\alpha, \beta, \ldots, \lambda$ on which the shape and motion of the system under consideration depends, and variables $a, b, \ldots, l$ not affecting shape and motion. The discussion of *oeuvre* (mechanical work) in the second chapter of the first part of the *Commentary* is concerned only with the former, those affecting shape and motion, and is due to the actions of bodies external to the system. Duhem points out at the beginning of section 3 of this second chapter that the *oeuvre* (mechanical work) is the increase in total energy of the system, and includes the kinetic energy.

Since Duhem's symbols, which with one exception I have tried to reproduce as nearly as possible, differ from those now in common use, I enumerate here a glossary of his principal symbols with a page reference to an occurrence in one of the articles (indicated by year of publication). (The exception is W, for work, which replaces Duhem's symbol which for typographical reasons I can't reproduce.)

Symbol	Meaning	Page reference
E	Mechanical equivalent of heat	p. 173 (1887)
$\mathscr{F}$	Internal thermodynamic potential	p. 207 (1894)
$\mathfrak{F}$	Internal thermodynamic potential	p. 214 (1894)
P	Uncompensated transformation	p. 146 (1887)
	But also used for pressure	
Q	Amount (quantity) of heat	p. 6 (1887)
$\mathfrak{Q}$	Total calorific effect	p. 298 (1893)
$R_\alpha, R_\beta,$	Calorific coefficients	p. 208 (1894)
S	Entropy	p. 46 (1887)
	But is also used to denote a state or a series of states	pp. 133–4 (1887)
$\sum_1, \sum_2$	Entropy (of parts of a system)	p. 234 (1894)
$\mathfrak{T}$	Kinetic energy	p. 305 (1892)
τ	Work done by inertial forces	p. 297 (1893)
τ	Instant of time	p. 301 (1893)
W	work	p. 312 (1893)
U	Internal energy	p. 3 (1887)
$\mathfrak{U}$	Internal energy	p. 212 (1894)

Finally, I would like to acknowledge the help and advice on numerous points that I have received from Robert Deltete, Donald Miller, and, last but in Swedish alphabetical order, Jan Österberg for their help and advice on numerous points. Don has gone through the translation of the 1887 article and Rob the *Commentary* papers (1892, 1893 and 1894), comparing them with the orginal papers and giving me many suggestions which have been incorporated into the final version published here. At an earlier stage, I was able to discuss many of Duhem's less easily penetrated passages with Jan. To these three gentlemen I would like to extend a heartfelt thanks.

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Contents

Part I
Study of the Thermodynamic Works of J. Willard Gibbs (1887)*

In 1875 Gibbs published *On the equilibrium of heterogeneous substances*, a memoir which introduced a new method into thermodynamics. Just as Lagrange based all statics on the single principle of virtual velocities, so Gibbs was able to base the entire study of equilibrium in thermodynamics on a principle analogous to that of virtual velocities and which includes the latter as a special case. In this way, mechanics and thermodynamics are [123] joined together more closely than in the past, and a whole section of physical science is taken to a higher degree of unity. At the same time, at the same hands of Gibbs, the new theory confirms its fecundity by making considerable progress, on the one hand, in the study of dissociation, and on the other, in the study of the voltaic cell.

In the now appreciable time since their publication, Gibbs' ideas have stimulated much research, some of which, like that of H. von Helmholtz, are intended to confirm them, while others, on the contrary, have the object of criticising either the very principles of the new theory or some of its applications. Accordingly, many minds have yet to be made up about the value of Gibbs' theory. Mathematicians regret that the principles of thermodynamics are developed in general with so little precision that the same proposition can be regarded by some as a consequence, and by others as a negation, of these principles. Experimentalists have but little confidence in consequences of a theory whose principles are disputed in this way and resist appealing to it for the explanation of phenomena which they observe or for the prediction of facts that it might lead them to discover.

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*"Étude sur les travaux thermodynamiqes de M. J. Willard Gibbs", *Bulletin des Sciences Mathématiques*, 11 (1887), 122–148, 159–176.

On the equilibrium of heterogeneous substances, 1st Part [*Transactions of the Connecticut Academie* [sic.] *of Arts and Sciences*, vol. III, Part I, pp. 108–248 (1875–1876); 2nd Part, ibid., vol. III, Part II, pp. 343–524 (1877–1878)]. Abstract of the same (*American Journal of Sciences and Arts*, vol. XVI, p. 441; 1878). *On the density of vapour* (*American Journal of Sciences and Arts*, vol. XVIII; 1879). *Graphical methods in the thermodynamics of fluids* (*Transact. of the Connecticut Academy of Arts and Sciences*, vol. III, Part II, p. 310; 1873). *A method of geometrical representation of the thermodynamics* [sic.] *properties of surfaces by means of surfaces* (ibid., p. 382; 1873).

Under these circumstances is seems appropriate to return to the very foundations of the principles of this controversial theory. It is true that this task is an arduous one, because it involves redoing afresh an exposition of the second law of thermodynamics. But isn't it useful to submit the principles of the various branches of physics to a rigorous discussion if this science is to approach more closely the precision of mathematical sciences?

We will, therefore, in the first place show how the first principles of thermodynamics lead to Gibbs' new method. In the second place, we will describe the history of the previous attempts in the same direction, and the applications which have since been made of this method.

Chapter 1
An Examination of the Second Law of Thermodynamics

1.1 The Principle of the Equivalence of Heat and Work

Gibbs' [124] method is a logical consequence of Clausius' thoughts on Carnot's principle. Gibbs indicated this connection of ideas himself, and we have tried elsewhere to make this more precise. But several physicists have raised doubts about these ideas of Clausius, or rather about those which serve as the point of departure for Gibbs' work. Since it is impossible to know what an edifice is worth before being assured of the solidity of its foundations, we must call a halt to the discussion of Clausius' theories and go over them again from their point of departure.

Thermodynamics rests on two principles: the principle of the equivalence of heat and work, and Carnot's principle. It is the second law which is the subject of the discussions which divide many physicists today. The first, on the contrary, presents little difficulty. Suffice it here to recall the proposition and deduce from it a consequence which will be indispensable in the remainder of this study.

We will suppose, first of all, that the meanings of the terms *temperature*[1] and *amount of heat* have been precisely defined. These definitions present more than one difficulty which it would be interesting to examine. But we cannot take up this matter here without inordinately lengthening this article.

All systems studied in thermodynamics are defined by the temperature ϑ at each of its points, and by a limited or unlimited number of parameters $\alpha, \beta, \ldots$, such that in order to know the entire series of modifications that the system undergoes, it is necessary and sufficient to know the temperature of each point and the parameters $\alpha, \beta, \ldots$ as a function of time. From [125] this definition it follows that, among the parameters $\alpha, \beta, \ldots$ the coordinates of the various points of the system can be found, but not the velocities of these points.

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[1] I intend here to speak of a temperature read on an arbitrary thermometer and not the *absolute temperature* which will be taken up later.

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An infinitesimal change of the system considered is accompanied by the release of an amount of heat dQ. At the same time, the kinetic energy[2] of the system increases by $d\sum mv^2/2$ and the external forces applied to the system do a certain work dW.[3] The first law of thermodynamics consists in assuming that

$$dQ + Ad\sum \frac{mv^2}{2} = -dU + dW, \tag{1}$$

A being a constant, the *calorific equivalent of work*, the inverse of which is called the *mechanical equivalent of heat*,[4] and U is a function of the values of ϑ at each point of the system and of α, β, ... This function, introduced into thermodynamics by Clausius, is now known by the name *internal energy* given to it by Sir W. Thomson.

For infinitesimal changes, we can write to a second order of approximation

$$dW = \sum (Xdx + Ydy + Zdz),$$

X, Y and Z being the components of the exterior force which act at the coordinates x, y and z, and dx, dy and dz being the components of the displacement of this point. Therefore, from the equality (1) we can derive the following consequence:

Designating by the symbols (0) and (1) two infinitesimally close states of the system, we imagine passing from state (0) to state (1) in two different ways, under the action of the same exterior forces and leading to the same change of kinetic energy,[5] each of these transformations being constituted by a limited number of infinitesimal changes. The amount of heat released is the same in each of these two transformations.

We will not show here the importance of this remark for the exposition of thermodynamics. We will in any case have occasion to make use of it in the course of this study. We merely observe that it explains how Laplace and Poisson, who assumed along with all their contemporaries the erroneous hypothesis that the quantity of heat released in a change [126] depends solely on the initial and final states of the system, were able to obtain exact results whenever they applied this hypothesis just to infinitesimal transformations.

Such are the notions relating to the equivalence of heat and work that it will be necessary for us to recall. Now we move on to examine the second law, which will detain us much longer.

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[2] *la demi-force vive*.

[3] [Duhem's symbol for work is a script "T" (for *travail*) which for typographical reasons is replaced here by the symbol W usual in modern thermodynamics texts.]

[4] [Denoted by E later on in the paper.]

[5] *force vive*.

1.2 Clausius' Postulate

Clausius based Sadi Carnot's proposition on a very simple postulate, obtained by generalising the most common notions concerning conduction.

Let us imagine a metal bar whose surfaces are surrounded by a non-conducting substance which doesn't allow any exchange of heat between the bar's surface and the surroundings. One end of the bar is at a base temperature ϑ, the other is submitted to the action of a source of heat with a temperature ϑ', higher than ϑ. After a certain time, a permanent regime is established. The temperature of each point in the bar and the state of each element of volume of the bar then remain invariable. If, therefore, starting from the moment that the permanent regime is established, the bar is observed for a certain time, its internal energy will not vary, the external forces acting on it will do no work, its kinetic energy will remain equal to 0. At the same time, the bar will have absorbed heat at its hot end and released heat at its cold end.

This is the simple observation that Clausius[6] has generalised in such a way as to give the following fundamental postulate.

Suppose that a system undergoes a change subject to the following four restrictions:

1. The internal energy of the system has the same value at the beginning and the end of the change. [127]
2. The kinetic energy of the system has the same value at the beginning and the end of the change.
3. The external forces applied to the system during the course of the change produce as much positive as negative work.
4. The exchange of heat between the system and the surroundings takes place exclusively either while all the points of the system have the same temperature ϑ, or while all the points of the system have the same temperature ϑ' higher than ϑ.

Under these conditions, *it is impossible that the system has absorbed heat at the temperature* ϑ *in order to release it at the temperature* ϑ'.

This is, in its most precise form, Clausius' postulate. After having been discussed for a long time, it is now accepted by all physicists. We will allow ourselves to introduce a slight modification which, although apparently trifling, suffices in fact to eliminate all the difficulties which can be raised against certain of Clausius' ideas. This modification will, moreover, have the advantage of approaching more strictly the statement of the postulate about conduction phenomenon which suggested the idea. The new form that we propose for Clausius' postulate is the following:

> *In a change subject to the restrictions indicated, the system necessarily absorbs more heat at the temperature* ϑ' *than it releases at the same temperature, and necessarily releases more heat at the temperature* ϑ *than it absorbs at the same temperature.*

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[6] R. Clausius, *Poggendorff's Annalen der Physik und Chemie*, vol. LXXIX; 1859. *Mémoires sur la theéorie mécanique de la chaleur*. Trad. Folie, vol. I, p. 54.

1.3 The Carnot Cycle and the Postulate of Sir W. Thomson

A system is said to traverse a *closed cycle* when it undergoes a series of changes which bring it back to its initial state with its initial kinetic energy.

A closed cycle is called a Carnot cycle when it satisfies the following restriction:

While traversing the cycle, the exchange of heat between the system and the environment only takes place when all the points of the system are [128] at the same temperature ϑ, or else when all the points of the system have the same temperature ϑ' higher than ϑ.

A steam engine in which all the points of the furnace are at the same temperature ϑ', while all the points of the condenser are at the same temperature ϑ lower than ϑ', in which, moreover, the cylinder is impermeable to heat, provides an image of a system traversing a Carnot cycle.

A system which traverses a Carnot cycle in such a way that during the cycle the external forces acting on the system do *negative* work provides an image of the simplest conceivable heat engine.

Generalising our experience of the most common heat engines, Sir W. Thomson[7] has stated the following postulate:

> *When a system describes a Carnot cycle during which the external forces acting on the system perform a total negative work, it is impossible for the system to absorb more heat at the temperature ϑ than it releases at the same temperature.*

We will subject Sir W. Thomson's postulate to a very slight modification, analogous to that introduced to Clausius' postulate, and say:

> *When a system describes a Carnot cycle during which the external forces acting on the system perform a total negative work, the system releases more heat at the temperature ϑ than it absorbs at the same temperature.*

Sir W. Thomson had proposed the postulate which we have just adjusted as a proposition equivalent to Clausius' postulate. We will, in the following exposition, make use of both postulates at the same time.

1.4 Carnot's Theorem and Absolute Temperature

We propose [129] first of all to introduce a classification of Carnot cycles whose existence is compatible with the first law of thermodynamics and with the two postulates that we have stated.

We designate by Q the total amount of heat exchanged between the system and the surroundings while all the points are at the temperature ϑ, and by Q' the total amount of heat exchanged between the system and the surroundings while all the points are at the temperature ϑ'. We take the two quantities Q and Q' to be positive

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[7] W. Thomson, *Transactions of the Royal Society of Edinburgh*, vol. XX, p. 255; 1851.

when they represent heat released from the system, and negative when they represent heat absorbed by the system.[8]

We designate the work done during the traversal of the cycle by the external forces acting on the system by W.[9]

We then have, by virtue of the first law,

$$W = E(Q + Q') \tag{2}$$

From this follow the propositions:

1. If the external work is zero, the two quantities Q and Q' have opposite signs and equal absolute values.
2. If the external work is positive, then at least one of the quantities Q and Q' is positive, and if only one, then that is the one with the greater absolute value.
3. If the external work is negative, then at least one of the quantities Q and Q' is negative, and if only one, then that is the one with the greater absolute value.

On the other hand, the two postulates of Clausius and Sir W. Thomson lead to the following proposition:

When the external work is zero or negative, the quantity Q is necessarily positive.

From these propositions, it is easy to conclude that all Carnot cycles can be classified in the following way:

1. The work done by the external forces is zero; Q is positive, Q' is negative and equal to Q in absolute value.
2. The work done by the external forces is negative; Q is positive, Q' is negative and greater than Q in absolute value.
3. [130] The work done by the external forces is positive; three cases can then arise:
    a. Q is positive, Q' is negative and less than Q in absolute value.
    b. Q is negative, Q' is positive and greater than Q in absolute value.
    c. Q and Q' are positive.

Now we propose to compare, for the various kinds of cycles, the values of the ratio

$$\rho = \frac{Q' + Q}{Q},$$

and to demonstrate that, *for cycles described between the temperatures ϑ and ϑ' corresponding to a positive or zero external work, the ratio ρ is greater than*

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[8] [It is more usual in modern thermodynamics to define Q, the heat absorbed by the system *from* the surroundings, as positive.]

[9] [Again, it is more usual in modern thermodynamics to define W, the work done by the system *on* the surroundings, as positive.]

for cycles described between the same temperatures corresponding to a negative external work.

This theorem is evident, except for cycles with positive external work where Q is negative and Q' is positive. In fact, for all the other cycles where the external work is positive, the ratio ρ is positive. It is zero for cycles where the external work is zero, and negative for cycles where the external work is negative.

Let us therefore compare a cycle described between the temperatures ϑ and ϑ' where the external work is positive, the quantity Q is negative and the quantity Q' is positive, with a cycle described between the temperatures ϑ and ϑ' where the external work is negative, the quantity Q is positive and the quantity Q' is negative.

Designating the values of the quantities W, Q and Q' for the first cycle by W_1, Q_1 and Q'_1, and for the second cycle by W_2, Q_2 and Q'_2, we wish to demonstrate that

$$\frac{Q'_1 + Q_1}{Q_1} > \frac{Q'_2 + Q_2}{Q_2}.$$

Let m_1/m_2 be a commensurable number greater than or equal to $W_1/|W_2|$,[10] where m_1 and m_2 are whole numbers.

Let [131] us consider a system comprising m_2 systems identical to that which describes the first cycle and of m_1 systems identical to that which describes the second cycle. The m_2 first systems are made to describe the first cycle and the m_1 systems the second cycle. The total system describes a Carnot cycle in which the exchanges of heat still take place at temperatures ϑ and ϑ'. The work done by the external forces during the course of the cycle will have the value

$$m_2 W_1 + m_1 W_2.$$

From the way m_1 and m_2 were chosen, it is negative, unless the ratio $W_1/|W_2|$ is commensurable and m_1/m_2 is identical with this ratio. In this case, the external work in question will be zero. In every case, in view of the fundamental postulates, the cycle in question should release heat at the temperature ϑ. We therefore have

$$m_2 Q_1 + m_1 Q_2 > 0.$$

From this inequality, we deduce

$$\frac{m_2}{Q_2} < \frac{m_1}{|Q_1|}.$$

Putting

$$\frac{m_1}{m_2} = \frac{W_1}{|W_2|} + \varepsilon,$$

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[10] The notation $|W_2|$ signifies the absolute value of W_2.

ε will be zero or a positive quantity that can be made as small as one may wish. The preceding inequality becomes

$$\frac{|W_2|}{Q_2} < \frac{W_1 \; + \; \varepsilon \, |W_2|}{|Q_1|}.$$

This inequality cannot tend towards an equality when ε tends towards 0. We therefore have

$$\frac{W_1}{Q_1} > \frac{W_2}{Q_2}$$

or, in virtue of the equalities

$$\begin{aligned} W_1 &= E\,(Q_1 + Q_1') \\ W_2 &= E\,(Q_2 + Q_2') \end{aligned}$$

given [132] by the first law of thermodynamics,

$$\frac{Q'_1 \; + \; Q_1}{Q_1} > \frac{Q'_2 \; + \; Q_2}{Q_2}.$$

This is precisely the inequality we wished to demonstrate.

Summarising, *if all the Carnot cycles are considered for which the exchanges of heat take place at the same temperatures* ϑ *and* ϑ', ϑ' *being greater than* ϑ, *then for all those cycles that correspond to a negative work by the external forces, the ratio* $\rho = (Q' \; + \; Q)\big/Q$ *takes a value less than a certain negative quantity* A. *For those that correspond to a positive or zero work by the external forces, the ratio* $\rho = (Q' \; + \; Q)\big/Q$ *takes a value greater than a certain negative quantity,* A′. A′ *is greater than or equal to* A.

We will now demonstrate that

$$\mathrm{A}' = \mathrm{A}.$$

In order to arrive at this important proposition, it is necessary for us to introduce the concept of a *reversible transformation*. This concept, one of the most important in thermodynamics, is at the same time one of those least easy to make precise. It will therefore be necessary for us to dwell on this for some time.

Let us imagine a system having the same temperature at all its points, under the action of certain external forces and subject to certain connections[11] expressed by the equalities and inequalities between the various parameters defining the state of the system. We will say that such a system is in *equilibrium* in a certain state if, put in this state without kinetic energy, it remains there perpetually.

Let (1) and (2) be two states of equilibrium of the same system. Suppose that an infinite series of its equilibrium states can be put in a linear series beginning with

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[11] *liaisons*.

the state (1) and finishing with state (2) in such a way that the following conditions are met:

1. The parameters which determine the state of the system undergo [133] variations which are continuous and compatible with the connections on passing from one state to the neighbouring state.
2. The external forces acting on the system vary continuously in magnitude and direction.
3. The equalities and inequalities expressing the connections of the system undergo continuous variations of form.

Such a series $\sum$ will be called a *continuous series of equilibrium states*.

If the external forces acting on the system in the state of equilibrium (1), and the connections to which it is subjected in this state, are changed, or even if it is simply placed in this state without its kinetic energy becoming zero, the system will no longer be able to remain perpetually in this state. It will undergo changes.

Suppose that it is possible to arrange infinitesimal initial velocities[12] of various points, of external forces and of the connections in such a way as to form an infinity of ways of passing from state (1) without kinetic energy to state (2) without kinetic energy. Each of these transitions is constituted of a linear and continuous series of states. Let S, S′, ... be these series, whose number is supposed to be unlimited.

We also suppose, analogously, that it is possible to set up an infinity of ways of passing from state (2) to state (1), corresponding to an infinity of linear and continuous series s, s′, ... of states of the system.

Now suppose that amongst the series S, S′, ... it is possible to choose in at least one way an infinity of them which, along with the series $\sum$, can be arranged as a series in linear sequence possessing the following properties:

It is possible to establish a unique correspondence between a state of each of the series and a state of each of the others and of the series $\sum$.

The ensemble of states corresponding to the same state of the series $\sum$ forms a linear and continuous series of states ending in the state of the series $\sum$, and whose kinetic energy tends towards 0.

Let [134] us suppose that the series s, s′, ... exhibits a property analogous to that we have just supposed for the series S, S′, ...

We will briefly express all the properties that we have just attributed to the series $\sum$ by saying that *it constitutes a reversible change allowing the passage either from state* (1) *to state* (2) *or from state* (2) *to state* (1).

We will say that a reversible change $\sum$ is *isothermal* when it is possible to form two continuous sequences of isothermal changes from, on the one hand, the series S, S′, ..., and on the other hand, the series s, s′, ..., having the sequence $\sum$ as a common limit, in the way we have indicated. It is clear that such a sequence $\sum$ is

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[12] When the initial speeds are infinitesimal, the initial kinetic energy is infinitesimal to the second order. It can therefore be regarded as zero.

formed from equilibrium states all corresponding to one and the same temperature of the system.

We will say that a reversible change $\sum$ is *adiabatic*[13] when it is the same common limit of two sequences of adiabatic changes in oppossite directions. Taking two neighbouring states from a reversible sequence $\sum$, the two states will correspond to the values U and $U + dU$ of the internal energy of the system. If the system is transported from one of these states to the other, the external forces will perform a virtual work dW. In general, *the amount of heat released in a reversible passage from one of these states to the other* will be referred to by

$$dQ = \mathrm{A}\ dW - dU.$$

This quantity does not represent an actual release of heat because a reversible change does not represent an actual change. It is only the limit of the amount of heat released in one of the changes S or s which have as their limit the sequence $\sum$ during which the interval is crossed between the two states having as their correspondents the two states considered in the sequence $\sum$.

Following the definition just given, in the case of a reversible adiabatic change, we have

$$dQ = 0.$$

[135] Having stated these definitions, we now return to the properties of the Carnot cycle.

Given two temperatures, ϑ and ϑ', ϑ' being greater than ϑ, let us suppose that it is always possible to find four reversible changes of a certain system exhibiting the following properties:

The first is a reversible isothermal change $\sum_1^2$ corresponding to the temperature ϑ', and taking the system from a state (1) to another state (2).

The second is a reversible adiabatic change $\sum_2^3$ taking the system from the state (2), where it has the temperature ϑ', to the state (3) where its temperature is ϑ.

The third is a reversible isothermal change $\sum_3^4$ taking the system from a state (3) to another state (4) at the same temperature ϑ.

The fourth is a reversible adiabatic change $\sum_4^1$ returning the system from the state (4) to the state (1).

We have thus constructed a *reversible Carnot cycle* described between the temperatures ϑ and ϑ'.

In accordance with the definition of reversible transformations, there are infinitely many ways of passing from state (1) to state (2), among which are found an infinity of isothermal changes $\mathrm{S}_1^2,\ \mathrm{S'}_1^2,\ \ldots$ forming a linear series whose limit is the sequence $\sum_1^2$. Similarly, there are infinitely many ways of passing from state (2) to state (1), among which are found an infinity of isothermal changes $\mathrm{S}_2^1,\ \mathrm{S'}_2^1,\ \ldots$

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[13] An *adiabatic change* is a change in which heat is neither absorbed nor released at any time.

forming a linear series whose limit is the sequence $\sum_2^1$. Analogous considerations apply to the three other reversible changes $\sum_2^3$, $\sum_2^3$ and $\sum_4^1$

Let us take one of the isothermal changes S_1^2, one of the adiabatic changes S_2^3, one of the isothermal changes S_3^4, and one of the adiabatic changes S_4^1. We have a Carnot cycle passing through the four states (1), (2), (3) and (4) and described between the temperatures ϑ and ϑ' in the direction (1), (2), (3), (4). Clearly, it is possible to form infinitely many similar cycles, and it is possible, in infinitely many different ways, to form from these cycles a linear series of cycles having the reversible cycle as a limit. Let C(1,2,3,4) be such a series of Carnot cycles.

In the same way, it is possible, from the changes S_1^4, S_4^3, S_3^2 and S_2^1 to form [136] an infinite linear series of Carnot cycles, described between the temperatures ϑ and ϑ' passing through the four states (1), (2), (3) and (4) in the direction (4), (3), (2), (1), transforming continuously from the one to the other and having the reversible cycle as a limit. Let C(4,3,2,1) be such a series of Carnot cycles.

The *virtual* work which the external forces would carry out if the system were made to describe a reversible cycle changes sign without changing its absolute value according as the cycle is described in one direction or the other. In order to fix our ideas, we suppose it to be positive when the cycle is described in the direction (1), (2), (3), (4), and designate it by Θ.

The work done by the external forces in the course of traversing one of the cycles in the series C(1,2,3,4) tends towards Θ when the cycle tends towards the reversible cycle. One can therefore be certain, when considering only those cycles which are quite close to the reversible cycle, that all the external work is positive.

The work done by the external forces in the course of traversing one of the cycles in the series C(4,3,2,1) tends towards $-\Theta$ when the cycle tends towards the reversible cycle. One can therefore be certain, when considering only those cycles which are quite close to the reversible cycle, that all the external work is negative.

It follows that, for all the cycles in the series C(1,2,3,4), that

$$\rho = \frac{Q + Q'}{Q} > \mathrm{A}'$$

and, for all the cycles in the series C(4,3,2,1), that

$$\rho = \frac{Q + Q'}{Q} < \mathrm{A},$$

with

$$\mathrm{A}' \geq \mathrm{A}.$$

But if we consider the value of ρ for all the cycles in the series C(1,2,3,4), it is clear that it has in the limit the value of ρ for the reversible cycle described in the direction (1), (2), (3), (4). And if we consider the value of ρ for all the cycles in the series C(4,3,2,1), it is clear that it has in the limit the value of ρ for the reversible cycle described in the direction (4), (3), (2), (1). Referring to the definition of the amount of heat released in the course of a reversible change, Q and Q' change signs without [137] changing their absolute value when changing the direction in which the reversible cycle is described. Consequently, for the reversible cycle, the value of ρ is independent of the direction in which the cycle is traversed.

From this it follows that the value of ρ for all the cycles in the series C(1,2,3,4) and the value of ρ for all the cycles in the series C(4,3,2,1) have a common limit. Consequently, we have, as stated above,

$$\mathrm{A}' = \mathrm{A}.$$

The common value of the quantities A' and A is the value of the quantity ρ for any reversible cycle between the temperatures ϑ and ϑ'. This quantity is necessarily a function of the two temperatures ϑ and ϑ' alone. Designating this by $f(\vartheta, \vartheta')$, we arrive at the following result:

There exists a function $f(\vartheta, \vartheta')$ of the two temperatures ϑ and ϑ', negative when ϑ' is greater than ϑ, such that, for all Carnot cycles described between the temperatures ϑ and ϑ', and corresponding to a positive or zero external work,

$$\frac{Q + Q'}{Q} > f(\vartheta, \vartheta'),$$

and for all Carnot cycles described between the temperatures ϑ and ϑ', and corresponding to a negative external work,

$$\frac{Q + Q'}{Q} < f(\vartheta, \vartheta').$$

We put

$$\psi(\vartheta', \vartheta) = f(\vartheta, \vartheta') - 1$$

The quantity $\psi(\vartheta', \vartheta)$ will be negative and greater than 1 in absolute value if ϑ' is greater than ϑ. Accordingly, for the first class of Carnot cycles,

$$\frac{Q'}{Q} > \psi(\vartheta', \vartheta), \tag{3}$$

and for the second,

$$\frac{Q'}{Q} < \psi(\vartheta', \vartheta). \tag{4}$$

It [138] remains, in order to demonstrate Carnot's theorem, to show that

$$\psi(\vartheta'', \vartheta) = \psi(\vartheta'', \vartheta)\psi(\vartheta', \vartheta), \tag{5}$$

ϑ, ϑ', ϑ'' being any three temperatures.

In order to establish this proposition, it suffices to observe, by means of a reversible Carnot cycle functioning between temperatures ϑ and ϑ' bringing into play at these two temperatures the amounts of heat Q and Q', and a reversible Carnot cycle functioning between temperatures ϑ' and ϑ'' bringing into play at these two temperatures the amounts of heat Q' and Q'', that it is possible to form a reversible Carnot cycle functioning between temperatures ϑ and ϑ'' bringing into play at these two temperatures the amounts of heat Q and Q'', The deduction is too simple to delay us.

Designating a function of ϑ, always positive and increasing with ϑ, by $F(\vartheta)$, it follows from the equality (5) that we can put

$$\psi(\vartheta', \vartheta) = -\frac{F(\vartheta')}{F(\vartheta)}. \tag{6}$$

The function $F(\vartheta)$ is evidently determined only up to a positive constant factor. It can be designated by the name *absolute temperature*.[14]

By means of this equality (6) and the inequalities (3) and (4), we arrive at the following proposition:

> *All Carnot cycles described between temperatures ϑ and ϑ', ϑ' being higher than ϑ, are divided into two classes.*
>
> *The first class is formed from those cycles corresponding to a positive or zero work done by the external forces. For all these cycles, it holds that*
>
> $$\frac{Q'}{Q} > -\frac{F(\vartheta')}{F(\vartheta)}.$$
>
> *The* [139] *second class is formed from those cycles corresponding to a negative work done by the external forces. For all these cycles, it holds that*
>
> $$\frac{Q'}{Q} < -\frac{F(\vartheta')}{F(\vartheta)}.$$

These two propositions can be united in a single statement. Recalling the classification of Carnot cycles introduced at the beginning of this section, it can be seen that, *for all possible Carnot cycles, it holds that*

$$\frac{Q}{F(\vartheta)} + \frac{Q'}{F(\vartheta')} > 0. \tag{7}$$

This is the inequality to which we will give the name *Carnot's Theorem*.

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[14] It will be noticed that the absolute temperature is presented here by a definition analogous to that given by G. Lippmann (G. Lippmann, *Journal de Physique théorique et appliquée*, 2nd. series, vol. III, pp. 52 and 277; 1884. *Cours de Thermodyamique*: 1886).

1.5 Entropy

We consider two arbitrary states of the same system, designated by (1) and (2), and we suppose that, in each of these two states, the *system has the same temperature at all of its points*. This temperature needn't necessarily be the same in state (1) and in state (2). We will suppose, at the same time, once and for all, that it is the same in all the states that we might have to consider.

Suppose that we can pass from state (1) to state (2) in infinitely many ways. Each of these manners of transformation is constituted by an infinite linear series S_1^2 of states of the system, the system being, in each of these states, subject to the action of certain external forces, constrained by certain connections and endowed with a certain kinetic energy. Further, we suppose that among the series S_1^2, we consider only those which satisfy the following condition: *The system, being without initial kinetic energy in any one of the states constituting* S_1^2 *and remaining subject to the same external forces, can pass into any one of the states which follow it in the series* S_1^2; *and, with the addition of certain appropriately chosen connections, we can arrange that its kinetic energy, zero in the first state, will remain zero in the second*. This is a fundamental restriction which we will suppose is always fulfilled in what follows.

Suppose, [140] in the same way, that we can pass from state (2) to state (1) in infinitely many ways, each of these manners of transformation being constituted by a linear series S_2^1 of states of the system, satisfying restrictions analogous to those imposed on the series S_1^2.

The states through which the system passes, either when it goes from state (1) to state (2) or when it goes from state (2) to state (1), are not in general states of equilibrium for the system subject to external forces really acting on it when it passes through each of these states. But we will assume that, for each of these states, it is possible to imagine external forces and connections such that the states become the equilibrium states for the system. It will then be possible to suppose that there exist reversible modifications leading from any one of these states to any one of the others.

In order to simplify the following demonstrations, we will assume that, in each of the series S_1^2 and in each of the series S_2^1 the system never passes more than once through the same state. We will easily be able to show later that the results obtained do not depend on this simplifying assumption.

Next we will assume that, given any series S_1^2 and any series S_2^1, it is possible to establish a unique correspondence between the states composing the one series with the states composing the other series, this correspondence satisfying the following conditions:

1. Two states infinitesimally close in the series S_1^2 correspond to two states infinitesimally close in the series S_2^1.
2. If, in the series S_1^2 the state A precedes the state B, then in the series S_2^1 the state A′ corresponding to A follows the state B′ corresponding to B.

3. Given two corresponding states, it is possible to pass from the one to the other by a reversible adiabatic change.

These are the rather numerous restrictions that we will assume realised by the changes that we will study. Only after it is assured that they are fulfilled in a particular case do we have the right to apply to that case the theorems we are going to demonstrate. Should their large number be alarming, we can only say that this large number of restrictions to which [141] the theorems of thermodynamics are subjected makes it all the more necessary to state these restrictions precisely, because each of these restrictions becomes a source of errors when it is ignored, just as we ordinarily do, under the veil of false evidence.

Let A and B be two infinitesimally close states in the series S_1^2. When the system passes from the state A to the state B, it releases an amount of heat dQ. Its kinetic energy[15] increases by $d\sum mv^2/2$. Let ϑ be the temperature of the system in the state A. We form the quotient

$$\frac{1}{F(\vartheta)}\left(dQ + A\,d\sum\frac{mv^2}{2}\right),$$

and designate by

$$J_1^2 = \int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ + A\,d\sum\frac{mv^2}{2}\right) \tag{8}$$

the sum of analogous quotients for all the elements of the series S_1^2.

Similarly, let A′ and B′ be two infinitesimally close states in the series S_2^1. When the system passes from the state B′ to the state A′, it releases an amount of heat dQ'.[16] Its kinetic energy[17] increases by $d\sum mv'^2/2$. Let ϑ' be the temperature of the system in the state A′. We form the quotient

$$\frac{1}{F(\vartheta')}\left(dQ' + A\,d\sum\frac{mv'^2}{2}\right),$$

and designate by

$$J_2^1 = \int_{(2)}^{(1)} \frac{1}{F(\vartheta')}\left(dQ' + A\,d\sum\frac{mv'^2}{2}\right) \tag{8a}$$

the sum of analogous quotients for all the elements of the series S_2^1.

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[15] *demi-force vive*.

[16] [dQ in the original.]

[17] *demi-force vive*.

We will demonstrate that it always holds that

$$J_2^1 + J_2^1 > 0. \tag{9}$$

Since it can always be supposed that the two elements AB, A′B′ are two corresponding elements of the series S_1^2 and S_2^1, it suffices to demonstrate that, for two such corresponding elements, [142] it holds that

$$\frac{dQ + A\,d\sum\frac{mv^2}{2}}{F(\vartheta)} + \frac{dQ' + A\,d\sum\frac{mv'^2}{2}}{F(\vartheta')} > 0. \tag{10}$$

This is quite easily done in the following way.

We have supposed that we can make the system begin in the state A without kinetic energy and arrive in state B without kinetic energy, while allowing the external forces applied during the transformation AB to act, but introducing certain connections where necessary. We designate this new change by A_1B_1. During the change AB and the change A_1B_1, the external forces perform the same work and the internal energy undergoes the same variation. Therefore, designating by dQ_1 the amount of heat released by the system during the change A_1B_1, we have

$$dQ_1 = dQ + A\,d\sum\frac{mv^2}{2}. \tag{11}$$

Similarly, it is possible for the system to pass from state B′ to state A′ with the kinetic energy equal to 0 in both of these two states, by preserving the external forces acting during the transformation B′A′, but introducing certain connections. Designating this new change by $B'_1A'_1$, and the amount of heat released during the change $B'_1A'_1$ by dQ'_1, we have

$$dQ'_1 = dQ' + A\,d\sum\frac{mv'^2}{2}. \tag{11a}$$

In view of the equalities (11) and (11a), the inequality to be demonstrated, (10), becomes

$$\frac{dQ_1}{F(\vartheta)} + \frac{dQ'_1}{F(\vartheta')} > 0. \tag{12}$$

It is possible, in accordance with what has been assumed, to pass from state A to the state A′ by a reversible adiabatic series, which we will designate by AA′. Similarly, it is possible to pass from state B to the state B′ by a reversible adiabatic series, which we will designate by BB′.

This being the case, we note that there exists either a state B_2 in the series BB′ infinitesimally close to B in which the system has the same [143] temperature ϑ as in the state A, or else a state A_2 in the series AA′ infinitesimally close to A in which the system has the same [143] temperature $(\vartheta + d\vartheta)$ as in the state B. In order to fix our ideas, we suppose that the first case obtains.

Similarly, there exists either a state A'_2 in the series AA' infinitesimally close to A' in which the system has the same temperature $\left(\vartheta + d\vartheta'\right)$ as in the state B', or else a state B'_2 in the series BB' infinitesimally close to B' in which the system has the same [143] temperature ϑ' as in the state A'. In order to fix our ideas, we suppose that the first case obtains.

Here we introduce a new hypothesis implicitly accepted by all the treatises on thermodynamics but which must be verified in each particular case. This hypothesis can be formulated in the following way.

When the system is subject to the action of external forces acting during the transformation AB or A_1B_1, it is possible to find connections which force the system, departing without kinetic energy from state A, to arrive also without kinetic energy in state B_2 by an infinitesimal *isothermal* transformation A_1B_2 performed at the temperature ϑ. Further, it is possible to find connections such that the system, leaving state B_2 without initial kinetic energy, arrives also without kinetic energy in the state B by an infinitesimal *adiabatic* transformation B_2B_1.

If such a hypothesis is satisfied, it follows from the remark made in Section 1.1 in connection with the first law of thermodynamics that the collection of the two infinitesimal changes A_1B_2 and B_2B_1 release the same amount of heat as does the infinitesimal change A_1B_1. Moreover, since the change B_2B_1 is adiabatic, the two changes A_1B_2 and B_2B_1 give rise to the same release of heat dQ_1.

Similarly, if such a hypothesis is satisfied for the states B', A' and A'_2, the change $B'_1A'_1$ gives rise to the release of the same heat dQ'_1 as an isothermal change $B'_1A'_2$, carried out at the temperature $(\vartheta' + d\vartheta')$, and takes the system from the state B' without initial kinetic energy to the final state A'_2 without final kinetic energy.

Given that the state B_2 is within the reversible adiabatic change BB', the change B_2B' is itself adiabatic and reversible. Consequently, [144] it is possible to take the system in state B_2 without kinetic energy in infinitely many ways, and make it reach B' without kinetic energy by an adiabatic change. We designate one such change by $B_2B'_1$.

Similarly, we designate by A'_2A_1 one of the adiabatic changes by which it is possible to take the system without kinetic energy in the state A'_2 and carry it without kinetic energy into the state A.

The series of four changes A_1B_1, $B_2B'_1$, $B'_1A'_2$, A'_2A_1 constitutes a Carnot cycle described by the system. If we now apply the inequality (7), true of all Carnot cycles, to this cycle, we have

$$\frac{dQ_1}{F(\vartheta)} + \frac{dQ'_1}{F(\vartheta' + d\vartheta')} > 0$$

or simply

$$\frac{dQ_1}{F(\vartheta)} + \frac{dQ'_1}{F(\vartheta')} > 0.$$

This inequality is precisely the inequality (12) that was to be demonstrated.

We have seen that the inequality (12) is equivalent to (10), and that this entails the inequality (9). We therefore have, in virtue of the equalities (8) and (8a),

$$\int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ + A\,d\sum\frac{mv^2}{2}\right) + \int_{(2)}^{(1)} \frac{1}{F(\vartheta')}\left(dQ' + A\,d\sum\frac{mv'^2}{2}\right) > 0. \tag{13}$$

This inequality is easily transformed.

The symbol

$$\int_{(1)}^{(2)} \frac{1}{F(\vartheta')}\left(dQ' + A\,d\sum\frac{mv'^2}{2}\right)$$

for a transformation such as S_2^1 which begins in the state (2) and ends in state (1) has not, as yet, been given any sense. It is convenient to attribute to it the same sense as

$$-\int_{(2)}^{(1)} \frac{1}{F(\vartheta')}\left(dQ' + A\,d\sum\frac{mv'^2}{2}\right).$$

The [145] inequality (13) becomes

$$\int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ + A\,d\sum\frac{mv^2}{2}\right) > \int_{(1)}^{(2)} \frac{1}{F(\vartheta')}\left(dQ' + A\,d\sum\frac{mv'^2}{2}\right) \tag{13a}$$

and can be formulated in the following way:

The sum

$$\int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ + A\,d\sum\frac{mv^2}{2}\right)$$

is greater for any transformation in which the system passes from state (1) *to state* (2) *than for any transformation in which the system passes from state* (2) *to state* (1).

Now let us suppose that there exists a reversible transformation $\sum$ from state (1) to state (2), which is the common limit of an infinity of transformations S_1^2 and an infinity of transformations S_2^1. It will then be quite easy for us to demonstrate the following proposition, which is the fundamental proposition of this part of thermodynamics:

There exists a quantity F(1, 2) *uniquely dependent on the state of the system in* (1) *and the state of the system in* (2) *such that, for all transformations by which the system passes from* (1) *to* (2), *we have*

$$\int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ + A\,d\sum\frac{mv^2}{2}\right) - \mathrm{F}(1,2) > 0,$$

and for each transformation by which the system passes from (2) *to* (1), *we have*

$$\int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ \,+\, A\,d\sum\frac{mv^2}{2}\right) - \mathrm{F}(1,2) < 0.$$

This quantity F(1, 2) *is the value of the integral*

$$\int_{(1)}^{(2)} \frac{dQ}{F(\vartheta)},$$

for [146] *any reversible transformation whatsoever which connects the states* (1) *and* (2).

By very simple considerations which are unnecessary to present here, we arrive at the following proposition:

There exists a function S of the parameters defining the state of the system such that, if S_1 and S_2 designate the values of S relative to the states (1) and (2), we have

$$\mathrm{F}(1,2) = \mathrm{S}_1 - \mathrm{S}_2$$

It is this function S, completely defined up to an additive constant as above, that Clausius has proposed to call the *entropy* of the system. This name is now adopted by all physicists. If, for any change whatsoever transporting the system from state (1) to state (2), we give with Clausius the name *uncompensated transformation* to the quantity

$$\mathrm{P} = \int_{(1)}^{(2)} \frac{1}{F(\vartheta)}\left(dQ \,+\, A\,d\sum\frac{mv^2}{2}\right) + \mathrm{S}_2 - \mathrm{S}_1, \tag{14}$$

then the preceding proposition becomes:

All changes correspond to a positive uncompensated transformation.

This is the great law for which thermodynamics is indebted to Clausius. Having brought it to the fore, we will have no more than a word to say in deducing the fundamental theorem on which Gibbs' work rests.

1.6 Uncompensated Work, Thermodynamic Potential and Gibbs' Theorem

Clausius' law gives us the means of determining the equilibrium states of the system. If, from a state of the system, all the virtual changes that can be imagined would engender a zero or negative uncompensated transformation, the system is certainly at equilibrium. But this proposition leads above all to interesting results when applied to systems whose temperature ϑ is maintained constant. In that case, we call [147] the product

$$\Theta = E\,F(\vartheta)\,\mathrm{P}. \tag{15}$$

the *uncompensated work.*

We will be able to state the preceding proposition in a form like this:

A system will certainly be at equilibrium in a definite state if all virtual changes from this state imposed on the system correspond to a zero or negative uncompensated work.

This theorem is analogous, in its statement, to the principle of virtual velocities that Gauss has formulated. Far from being a simple coincidence, this analogy arises from the very nature of things, for it would be easy to prove that, if the restrictive hypotheses to which mechanics subjects all the systems that it studies were introduced into thermodynamics, this proposition would reduce to the statement of the principle of virtual velocities. Despite this important analogy, the preceding proposition would be of little use if the uncompensated work performed in an isothermal change were not susceptible to a remarkable expression as we are going to show.

When the temperature is maintained constant, the equalities (14) and (15) give us

$$\Theta = E\int_1^2 \left(dQ + Ad\sum \frac{mv^2}{2}\right) + E\,F(\vartheta)\,(S_2 - S_1).$$

But on the other hand, if we designate the work done by the external forces during the change under consideration by W, equality (1) gives us

$$E\int_1^2 \left(dQ + Ad\sum \frac{mv^2}{2}\right) = E(U_2 - U_1) + W.$$

Summarising, we have the expression

$$\Theta = E[U_1 - F(\vartheta)S_1] - E[U_2 - F(\vartheta)S_2] + W. \tag{16}$$

This expression is particularly remarkable in the case where the external forces allow, either by themselves or in virtue of the connections imposed on the system, what is called in mechanics a *potential*. [148] In this case, if the potential is designated by V,[18] whose values are V_1 and V_2 in state (1) and state (2), then

$$W = V_1 - V_2. \tag{17}$$

Then, putting

$$\Phi = E[U - F(\vartheta)S] + V, \tag{18}$$

the equality (16) becomes

$$\Theta = \Phi_1 - \Phi_2. \tag{19}$$

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[18] [Duhem uses the symbol "W" for the potential.]

The uncompensated work will be determined by means of the quantity Φ just as external work W is determined by means of the potential V. The quantity Φ can therefore, with some justification, be called the *thermodynamic potential*.

This name will be even more appropriate when the form taken by the rule just indicated for the determination of stable equilibrium states is noted. This rule can in fact be stated thus:

> *A state of a system will be a stable equilibrium state if it corresponds to a minimum of the thermodynamic potential.*

This is the fundamental theorem discovered by Gibbs. It is the analogue in thermodynamics of the proposition on the stability of equilibrium discovered by Lagrange and demonstrated by Lejeune-Dirichlet. Suffice it to say that it constitutes the origin of one of the greatest steps forward that have been made in this science, whether in the clarification of its principles or enriching the number of its applications.

Chapter 2
Historical Background and Principal Applications of Gibbs' Theory

2.1 Historical Background of Gibbs' Theory

We have seen how the fundamental postulates of thermodynamics lead to Clausius' ideas about Carnot's principle, [160]* perhaps the most important to have been introduced into natural philosophy during the second half of our century. We will not retrace here the history of the research which has led physicists from the work of Sadi Carnot to these ideas. Clausius has himself taken the trouble to record the principal points of this history,[1] and it would be rash to rival his competence and impartiality. We will therefore restrict ourselves to following the path which leads from the ideas of Clausius to the beautiful and fruitful method of Gibbs.

This path will be concerned with studies of chemical mechanics involving thermodynamics. The discovery of the phenomena of dissociation by H. Sainte-Claire Deville instigated numerous important works in the domain of chemical mechanics revealing the existence of equilibrium states closely related to those whose laws physics traces by studying vaporisation and fusion. But they are rendered more complex by the large number of substances[2] among which such an equilibrium is established, and by the large number of variables which can influence the state of these substances. It was difficult to apply synthetic methods to these complex phenomena, based exclusively on the employment of closed cycles, which have led to such important propositions in the study of vaporisation and fusion.

These methods have not, however, been condemned to futility before the new order of just discovered phenomena. J. Moutier,[3] who made the first applications of thermodynamics to dissociation phenomena, has shown that synthetic reasoning can lead to important consequences in the domain of chemical mechanics. Applying first

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*[The second part of the article continues later on in the journal, beginning on p. 159.]

[1] R. Clausius, *Zur Geschichte der mechanischen Wärmetheorie* (*Poggendorff's Annalen der Physik und Chemie*, Bd. CXLV, p. 496; 1872). *See* also R. Clausius, *Die mechanische Wärmetheorie*. Zweitte Auflage, t. I, Abschnitt XIII.

[2] *substances*.

[3] J. Moutier, *Sur quelques relations entre la Physique et la Chimie* (*Encyclopedie chimique* de Fremy, *Introduction*, t. II).

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
DOI 10.1007/978-94-007-0311-7_2,

the general propositions of Clausius to isothermal cycles, he gave a [161] complete and elegant solution to the problem of the vapour pressure of the same substance[4] in two different states—a problem about which Regnault and J. Thomson had, in the one case, only an inkling, and in the other, merely hinted at a solution.

But these applications remained limited to those phenomena of chemical mechanics most directly analogous to the phenomena of fusion and vaporisation. Physicists limited themselves with difficulty to the consideration of closed cycles, which had on several occasions furnished demonstrations which, though full of elegance, required the theorist's ingenuity to invent an appropriate cycle for each new investigation. They felt the need to replace this approach by analytic methods leading by a sure and uniform road to the equations on which the solution of each problem in thermodynamics depends.

One method, it is true, stands out immediately from Clausius' propositions. For any elementary reversible transformation, the excess of heat equivalent to the work of the external forces over the heat released is the total differential of the internal energy. The ratio of the amount of heat and the absolute temperature is, except for sign, the total differential of the entropy. Consequently, expressing these two combinations by means of the independent variables and writing the conditions of integration of the expressions thus obtained is a reliable method of obtaining the conditions of equilibrium of a system. Since 1854, in the memoir where he extended the second law of thermodynamics to all closed cycles, Clausius[5] has made use of this method. In 1858, G. Kirchhoff [6] showed how fruitful this was by magnificent applications to the study of changes of states—first-rate applications which it is fitting to place alongside the discovery of the relation obtaining between the heat of [162] dilution of a solution and vapour pressure that this solution sustains. Finally, in 1863, Clausius[7] wrote a memoir especially concerned with showing how all the equations of thermodynamics could be established by this unique method, defying the attempts of those who sought, 20 years later, to lay claim to this method and put their name on it.

The analytic precision of this method is beyond question. But, despite the advantages of using it in certain cases, it doesn't entirely satisfy the need physicists have felt since the creation of thermodynamics for something like the methods that mechanics offers where there is an analogy between the objects studied by the two sciences.

Two centuries of exertions, crowned by the work of Lagrange, have condensed statics in its entirety into a single principle of virtual velocities, complemented, for systems sustaining a potential, by the criterion of stability that Lagrange stated

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[4] *corps*.

[5] R. Clausius, *Sur un autre forme du second principe de la théorie mécanique de la chaleur* (*Théorie mécanique de la chaleur*, trans. Folie, t. I, p. 154).

[6] G. Kirchoff, *Ueber einen Satz der mechanischen Wärmetheorie und einige Anwendungen desselben* (*Poggendorff's Annalen der Physik und Chemie*, Bd. CIII; 1858).

[7] R. Clausius, *Sur diverses formes des équations fondamentales de la théorie mécanique de la chaleur, qui sont commodes dans l'application* (*Théorie mécanique de la chaleur*, trans. Folie, Memoir IX).

and Lejeune-Dirichlet demonstrated. Which proposition in thermodynamics should replace the principle of virtual velocities and the theorem about the stability of equilibrium? What function should play the role of the potential? This is the statement of the question that physicists had been led to put.

The first to have clearly posed the problem and tried to provide a solution is Berthelot. The rule he proposed, under the name of the principle of maximum work, is formulated as follows: All chemical reactions accompanied without the intervention of external energy tend towards the production of the system which releases most heat. This principle entails the following consequence: of two conceivable reactions, the one the inverse of the other, such that the one releases heat while the other absorbs heat, only the first is possible.

The heat released by a reaction which brings about no external work is the reduction undergone, as a result of this [163] change, of the internal energy. Consequently, in accordance with the rule proposed by Berthelot, the possibility of a reaction presupposes that this reaction results in a reduction in energy. The stability of a chemical equilibrium is thereby assured if this equilibrium corresponds to the least value which the energy of the system can take. Energy plays the role in chemical statics that the potential plays in statics proper.

The rule put forward by Berthelot is easy to apply: its consequences can be immediately subjected to experimental control and, in an immense number of cases, they accord most satisfactorily with the rule. But however useful the principle of maximum work is in the study of chemical reactions, it is subject to numerous exceptions, both among changes of physical state, and among the phenomena of solution or allotropic change which unite physics and chemistry. Most chemists too have been led to wish for a rule based on thermodynamics which would at the same time account for the numerous agreements which make the principle of maximum work so useful as well as the exceptions which prevent it being accorded an absolute generality.

Hortsmann[8] was the first to have the idea of turning to Clausius' views on Carnot's principle for the solution to the problem of chemical mechanics. According to Hortsmann, the role that thermochemistry attributed to internal energy fell upon entropy.

"Clausius", says Hortsmann, "by giving a mathematical form to certain ideas of W. Thomson, has defined a quantity, the entropy, which, in all changes in nature, always increases and which, on the contrary, cannot by any known natural force, be reduced. Phenomena in which the entropy remains constant are possible, such as stationary movements that we attribute to atoms of bodies of constant temperature.

According to me, in the phenomena of dissociation, the cause of the limit is the same; it results when the entropy has [164] become as large as possible, with all the changes that could occur. The problem is therefore resolved if it is known under what circumstances and in what way the entropy is changed in the phenomena concerned".

Such is the point of departure for Hortsmann. More recently, in a Note communicated to the Royal Institution on 5th March, 1875, Lord Rayleigh presented

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[8] Hortsmann, *Annalen der Chemie und Pharmacie*, t. CLXX, 20 Nov. 1873.

similar thoughts. According to Lord Rayleigh, it is not the sign of the amount of heat brought into play which determines the direction of chemical reactions; a chemical reaction is possible only if it corresponds to an increase in entropy.

This theory cannot be accepted without restriction. Clausius has demonstrated, it is true, that it is not possible to decrease the entropy of a system, but this demonstration is subject to a restriction. It applies only to a system which cannot borrow from the environment, or give up to it, heat, kinetic energy or work. If account is not taken of this restriction, it is possible to deduce erroneous consequences from the theorem. It is quite certain, for example, that the entropy of a mass of water decreases when it is vaporised at constant temperature. Nevertheless, the principle stated by Hortsmann can, when applied in the circumstances under which it can be demonstrated, lead to consequences which are in accord with experiment. It was in this way that Hortsmann, by studying the dissociation of ammonium carbamate, obtained the statement of an important law which applies to all analogous dissociation phenomena.[9]

Energy cannot, therefore, play the role of potential in chemical mechanics. Entropy cannot play the role of a function of forces. Physicists were led to look for a function which can serve to characterise equilibria amongst other quantities studied in thermodynamics.

In an important memoir, extracts of which appeared in [165] 1869,[10] but which were unfortunately not published in their entirety until 1876,[11] Massieu published the following result:

All the coefficients that determine the mechanical and physical properties of a body, the internal energy, entropy, specific heat, coefficients of expansion, compressibility, etc., are known when a certain function of the parameters defining the state of the body are known. Massieu called this function the *characteristic function*.

The characteristic function changes according as one system or another of independent variables determining the body is chosen. Massieu considered in particular two cases: that in which the proper variables determining the state of the body are taken to be the volume and the temperature, and that in which the pressure and the temperature are taken as variables.

In the first case, if T designates the absolute temperature, S the entropy of the body and U the internal energy, the body has as its characteristic function the quantity[12]

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[9] The theory of Hortsmann now rejected has just been revived without essential modification, at least in its principles, by Max Planck in a memoir entitled *Ueber das Princip der Vermehrung der Entropie* (*Wiedemann's Annalen der Physik und Chemie*, vol. XXX, p. 562; 1887).

[10] F. Massieu, *Sur les fonctions caractéristiques* (*Comptes rendus des séances de l'Académie des Sciences*, t. LXIX, pp. 858 and 1057; 1869).

[11] F. Massieu, *Mémoire sur les fonctions caractéristiques des divers fluides et sur la théorie des vapeurs* (*Mémoires des Savants étrangers*, t. XXII, year 1876; *Journal de Physique*, 1st. series, vol. VI, p. 216; 1877).

[12] [Modern notation uses A rather than Duhem's H.]

$$H = T S - U.$$

In the second case, retaining the preceding notation, and in addition designating the calorific equivalent of work by A, the volume of the body by v and the pressure it supports by p, the body has as its characteristic function the quantity[13]

$$H' = T S - U - A p v.$$

Massieu established several properties of these functions H and H', and showed how all the equations of thermodynamics could be written in terms of just these functions and their partial derivatives. With this, he singularly advanced and perfected the application of purely analytic methods to thermodynamics. He brought to light new functions, more important than the internal energy and the entropy, [166] since the expression of the latter two can be deduced from knowledge of the former.

These are the new functions whose use, thanks to J. Willard Gibbs, was to give to thermodynamics a new and fruitful impetus.

The ideas which guided Gibbs are quite like those which Hortsmann wanted for the laws of chemical equilibria. But more happily than his predecessor, Gibbs avoided the errors into which he had fallen and finally succeeded in obtaining the fundamental theory.

> "*The energy of the universe is constant*".
> "*The entropy of the universe tends towards a maximum*".

These are Clausius' two propositions which Gibbs, like Hortsmann, takes as the point of departure for his investigations and as the most important epigraph of his memoirs. These are the propositions which lead him to the equilibrium conditions of a system—conditions which he states, without demonstration, in two equivalent forms as follows[14]:

> *For the equilibrium of an isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.*
> *For the equilibrium of an isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.*

The first of these two conditions is nothing other than the condition of equilibrium given by Hortsmann, but modified with the precaution restricting its application to changes in which the energy doesn't vary. Nevertheless, on the subject of the exactitude of these statements, a reservation should be made. The conditions of equilibrium stated by Gibbs are sufficient; they [167] are not necessary. From what, thanks to Clausius, we know about all possible changes, we can deduce that

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[13] [Modern notation uses G rather than Duhem's H'.]

[14] *On the equilibrium, etc*. (*Transactions of the Connecticut Academy,* vol. III, 1st part, p. 109).

it is not possible to produce change corresponding to a negative sum of the uncompensated transformations. But from the fact that a change produces a positive sum of the uncompensated transformations, we cannot conclude that it will necessarily take place. Gibbs[15] has already indicated several considerations which relate to this principle. But it is Moutier[16] we owe for having precisely stated this and in several cases shown the necessity.

I would add that the equilibrium conditions suggested by Gibbs necessitate another correction. They are only exact for changes which entail neither external work nor variation in temperature. Given this restriction, it is easy to convince oneself of their exactitude by referring back to our Equation (16) in Chapter 1. Assuming an infinitesimal isothermal change and designating the uncompensated work by $d\Theta$ and the external work by dW, we have

$$d\Theta = E\,dU - E\,T\,dS + dW,$$

and this quantity should be positive. Restricting attention to changes in which $dW = 0$, clearly dU will be positive for all of these changes for which dS equals 0 and dS will be negative for all those changes for which dU equals 0. But these conclusions no longer hold when the change under consideration involves a positive or negative external work.

The restrictions just indicated should also be applied to the following theorem, stated by Gibbs as a consequence of the conditions of equilibrium[17]:

> *If the temperature of a system is maintained constant, it is necessary and sufficient for the system to be at equilibrium that the* [168] *function*
>
> $$\mathcal{F} = E(U - T\,S),$$
>
> *is a minimum.*[18]

But only the first of the two restrictions that we have indicated applies to another theorem of Gibbs.[19]

> *When the temperature and pressure of a system are maintained uniform and constant, it is necessary and sufficient for equilibrium of the system that the quantity*
>
> $$\Phi = E(U - T\ S) + pv,$$
>
> *in which p designates the pressure and v the volume of the system, is a minimum.*

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[15] Gibbs, loc. cit., p. 111.

[16] J. Moutier, *Sur quelques relations entre la Physique et la Chimie* (*Encyclopedie chimique* de Fremy, Introduction, vol. II).

[17] Gibbs, loc. cit., p. 145.

[18] [As Donald Miller points out, this requires the volume to be constant.]

[19] Gibbs, loc. cit., p. 147.

These two propositions of Gibbs, with the restrictions that we have introduced, are just the statement, in two particular cases—that where the external forces do no work, and that where the external forces amount to a uniform and constant normal pressure—of the general theorem that we have stated in Section 1.6 in the first chapter. It is therefore quite appropriate to name this Gibbs' theorem.

On 2 February, 1882, Hermann von Helmholtz communicated to the Berlin Academy of Sciences a memoir *On the thermodynamics of chemical phenomena*,[20] soon followed by two other memoirs devoted to applications of the theory developed in the first.

This theory contains nothing not already found in the works of Massieu and Gibbs. It suffices to quote, in this regard, the acknowledgement Helmholtz gives of his predecessors at the beginning of his third memoir.

> The employment of partial derivatives of a single integral function to represent the energy and the entropy of a system of bodies, introduced [169] a great simplification into thermodynamics. This simplification was discovered before me, as early as the year 1877,[21] by Massieu. He has fully developed their consequences, at least in the case where the state of the body depends on a single parameter apart from temperature, but he has not deduced any conclusions relating to chemical phenomena. He calls the integral function that he considers the *characteristic function of the body*. This function, which he designates by the letter H, corresponds to my function $(-\mathfrak{F})$. I propose to retain the name *free energy* which I chose for the function $\mathfrak{F}$. It seems to me that this name captures very well the true physical significance of this quantity.
>
> The form in which Massieu presented the theorems concerned is a little more general than that on which I have settled. It is at the same time more convenient for the execution of certain calculations . . . .
>
> In 1878,[22] J.-W. Gibbs developed analytically and considerably extended and generalised the thermodynamic relations concerning changes of physical state or chemical state of a material system which can be composed of as many substances as you might wish either contiguous or mixed. Gibbs recovered from this Massieu's *characteristic function* and called it the *force function at constant temperature* . . . .

Thus, by his own account, Helmholtz has not introduced anything new in the theories of Massieu and Gibbs except for the name *free energy* for the quantity

$$\mathfrak{F} = E(U - T\,S)$$

and *binding energy* for the quantity

$$Z = E\,T\,S.$$

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[20] H. von Helmholtz, *Zur Thermodynamik chemischer Vorgänge* I Abhandl. (*Sitzungsberichte der Akademie der Wissenschaften zu Berlin*, vol. I, p. 23; 1882). II. Abhandl., *Untersuchungen uber* [sic] *Chlorzink-Kalomel Elemente* (ibid., vol. II, p. 825; 1882). III. Abhandl., *Folgerungen über galvanische Polarisation* (ibid., vol. I, p. 647; 1883).

[21] The works of Massieu date from 1869, as we have pointed out above.

[22] The investigations of Gibbs date from 1875 and not 1878.

This leads us to examine the names which have been [170] proposed to designate the various quantities figuring in this theory.

Massieu gave the name *characteristic functions* to the quantities

$$H = TS - U$$

and

$$H' = TS - U - A\,p\,v.$$

This name admirably describes the role which he discovered for these functions, because knowledge of them for a definite body yields knowledge of all the properties of this body and thus *characterises* the body. This name left more to be desired as soon as it was discovered what role the functions studied by Massieu play in the determination of equilibrium, when a name alluding to their mechanical analogues was wanted. It was therefore with good reason that Gibbs carried over from mechanics to thermodynamics the names of *force function* and *potential* to designate the various functions figuring in his equations. And it is with a view to maintaining this usage, introduced by the inventor of the theory we are now occupied with, that we have called the function Φ, defined by Equation (18) in Chapter 1, the *thermodynamic potential of the system*.

For the names just mentioned, which have the double advantage of not introducing a term unfamiliar to physicists, and of nicely recalling the role of the quantities employed, Helmholtz has suggested substituting the names *free energy* and *binding energy* as we have just mentioned above. These names are open to more than one criticism; but, applying Gauss' slogan: *Simus faciles in verbis*,[23] we will not delay matters by taking up these criticisms but continue to a swift exposition of the principal applications of Gibbs' theory.

2.2 Applications of Gibbs' Theory to Dissociation Phenomena

A certain number of dissociation phenomena show a direct analogy with vaporisation phenomena. Everyone knows of Debray's experiments which brought this analogy to the fore by the study of the [171] dissociation of the carbonate of chalk. Thermodynamics didn't delay in seizing upon these phenomena and extending to them considerations analogous to those it has applied quite successfully to the study of vaporisation. But many dissociation phenomena are distinguished from those by a circumstance which singularly complicates the study of them. The system whose equilibrium is to be studied contains not just a single gaseous body, but two or more which mix with one another. To this category of phenomena belong the dissociation of water vapour, carbonic acid, sulphurous acid, the oxide of carbon and hydrochloric acid—the study of which led H. Sainte-Claire Deville to the conception of dissociation phenomena—and the dissociation of sal ammoniac, which has

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[23] [Let's not quibble over words.]

recently been studied with the same care by Naumann, Hortsmann and Isambert. It is clearly of great interest to apply the considerations of thermodynamics to such phenomena.

Further interest in this study was aroused by the following circumstance.

In 1840, Cahours observed that the density of acetic acid vapour decreased in relation to that of air in a remarkable way when the temperature at which this density was determined was increased. Similar facts were indicated in the study of a certain number of gaseous bodies. H. Sainte-Claire Deville and Troost studied with great care the density variations of hyponitrous acid and sulphur vapour. In the latter case, they found that the density increased threefold when the temperature fell from 1,000 to 500°. Crafts and Meier have more recently shown that the density of iodine vapour varies twofold when the temperature falls from 1,600 to 800°.

Many physicists have thought that such variations should not be simply attributed to errors which the gases under consideration show in relation to the laws of Mariotte and Gay-Lussac. They have sought an explanation of a chemical kind. They have thought that the variations of density were due to the splitting of polymers, a splitting which becomes accentuated when the temperature increases. They have in that way reconciled [172] the variations of density with the apparent variations in the density of gaseous phosphorus perchloride, because of the gradual decomposition of this body into phosphorous chloride and chlorine. It is of the first importance to develop the theory of dissociation of gaseous compounds that split into gaseous elements, to be sure that this theory can furnish an explanation of the observed phenomena.

It is this theory which constitutes one of the principal applications of Gibbs' method.[24]

Gibbs supposes that the gases under study are brought to the ideal state where they follow exactly the laws of Mariotte and Gay-Lussac. He can then obtain the complete expression of their thermodynamic potential and establish the laws of their decomposition. What is obtained is, it is true, only an approximate theory. But however approximate are the laws of Mariotte and Gay-Lussac in the study of the physical properties of gases, they have an incontestable utility. Shouldn't the same hold for a theory of dissociation of gaseous compounds subject to the same approximations?

We do not wish to detail Gibbs' theory here. Suffice it to say that its author has compared the numerical results of experimental observations of phosphorous perchloride[25] and that this comparison has shown that the theory agrees with experiment as well as could be hoped. An analogous comparison has shown that the hypothesis of the dissociation of a polymer satisfactorily explained the variations of density of the vapour of nitrogen peroxide[26] and acetic acid.

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[24] Gibbs, *On the equilibrium of heterogeneous substances* (*Transactions of the Connecticut Academy of Arts and Sciences*, vol. III, p. 210).

[25] Gibbs, *On the density of vapours, etc.* (*American Journal of Sciences and Arts*, vol. XVIII; 1879).

[26] *l'acide hypo-azotique*.

2.3 Application of Gibbs' Theory to the Voltaic Cell

Gibbs has not restricted the application of the fruitful theory which he has developed to the study of dissociation. He has also applied it to the study of capillarity and shown that [173] thermodynamics can give a new significance to the theory under which Gauss had subsumed this branch of physics. But is it above all in the study of the electromotive force of a voltaic cell that Gibbs has been led, by his method, to new and fruitful results. Let us give an idea of the problem which had to be solved and the solution which Gibbs has put forward.

Edmond Becquerel had the first idea of relating the value of the electromotive force of a voltaic cell to the magnitude of the thermal phenomena accompanying the reaction taking place in the cell. Here is the law that he has thus been led to state:

> *When an electric charge, equal to unity, traverses a cell, this cell is the location of a certain chemical reaction. If this chemical reaction produces no current, it releases a quantity of heat* Q. *If the electromotive force of the cell is designated by* $\mathcal{E}$, *and* E *is the mechanical equivalent of heat, then we have*

$$E\,\mathrm{Q} = \mathcal{E}.$$

Unfortunately, it was not long before this simple law was contradicted by experiment. Favre showed first, in 1858, that there frequently existes a quite considerable positive or negative difference between the *chemical heat* Q and what he has since called the *voltaic heat*, $\mathcal{E}/\mathrm{E}$. Raoult (1864–1865), Edlund (1869–1883) and F. Braun (1878) have shown in a considerable number of experiments that the vast majority of voltaic couples deviate from the rule proposed by Edmond Becquerel, and that those that do follow this law are exceptions.

This discrepancy between experiment and Becquerel's theory seemed inexplicable. For as several, amongst others, Favre, have indicated, they believed that Becquerel's formula was a rigorous consequence of the principles of thermodynamics. Braun had the idea that the reason for this discrepancy should be sought in Carnot's theorem, which would lead to the substitution of Becquerel's rule by a more exact rule. But the [174] rule that he proposed lacked precision and several of his conclusions are now unacceptable. The true rule, which should be substituted for Edmond Becquerel's rule, was given by Gibbs, at the very moment that Braun published his ideas, in the second part of *On the equilibrium of heterogeneous substances.*[27] This is how this fundamental rule might be formulated:

> *When a unit electric charge traverses a cell, a certain chemical reaction takes place in the cell. If this chemical reaction didn't produce any current, it would produce a variation* $(\Phi_2 - \Phi_1)$ *of the thermodynamic potential of the system such that*

$$\mathcal{E} = \Phi_1 - \Phi_2.$$

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[27] *On the equilibrium of heterogeneous substances* (*Transactions of the Connecticut Academy of Arts and Sciences*, vol. III, part II, p. 503).

This fundamental postulate became the point of departure for an entirely new theory of the galvanic cell—a theory which experiment had already given important confirmation. As we have said, the postulate is due to Gibbs. However, the theory at issue usually goes under the name of *Helmholtz' theory*. A work that we have published on this question, at a time when, unfortunately, we had only an incomplete knowledge of Gibbs' works, might, perhaps, have had some influence in the introduction of this misleading name. It therefore obliges us to rectify this injustice here and proclaim Gibbs' incontestable priority.

In a hydro-electric couple, the electromotive force depends on the greater or lesser concentration of the liquids in which the electrodes are immersed. In order to make precise the influence that the concentration of liquids exerts on the electromotive force, James Moser[28] undertook the study of cells in which the reaction produced at one [175] pole is reversed at the other pole. The electromotive force then depends solely on the concentration of the liquids. Two vessels, put in communication by a siphon, contained unequal concentrations of a single metallic salt. Two electrodes, formed from the metal of this salt, were immersed in these vessels. This is the kind of cell in which Moser measured the electromotive force.

At the same time as Moser published the results of his experimental investigations performed in Helmholtz' laboratory, Helmholtz[29] applied the propositions of thermodynamics to the phenomena studied by Moser.

The solutions, enclosed in the two vessels each containing cells studied by Moser, had different vapour pressures. Helmholtz showed that, from the variations undergone by the vapour pressure of these solutions when their concentrations varied, it was possible to deduce the value of their electromotive force. Comparison of the values thus calculated with the value determined experimentally was satisfactorily in agreement.

In this theoretical study, it is true that Helmholtz made use of Carnot's theorem; but for all that, he had not renounced the law of Edmond Becquerel, as can be concluded from the following passage[30]: "... By virtue of the law which regulates the other phenomena of electrolysis, the work produced in this case by the chemical forces should act as the electromotive force. This work can be calculated by means of the mechanical theory of heat ...". Thus, Gibbs became the true founder of the new theory of the cell when he formulated the fundamental postulate which we have just stated precisely in the same year (1878) that Helmholtz' memoir appeared in the *Annalen der Physik und Chemie*. The beautiful consequences that, several years later, [176] Helmholtz deduced from this theory should not allow us to forget the name of the man who created it and who proclaimed its rigour and generality, thus

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[28] J. Moser, *Galvanische Ströme zwischen verschieden concentrirten Lösungen desselben Körpers und Spannungsreihen* (*Monatsber. der Berl. Akad.*, 8 Nov. 1877: *Wiedemann's Annalen der Physik und Chemie*, vol. III, p. 216; 1878).

[29] H. Helmholtz, *Ueber galvanische Ströme verursacht durch Concentrationsunterschiede. Folgerungen aus der mechanischen Wärmetheorie* (*Monatsber. der Berl. Akad.*, 26 Nov. 1877, *Wiedemann's Annalen der Physik und Chemie*, vol. III, p. 201; 1878).

[30] *Wiedemann's Annalen der Physik und Chemie*, vol. III, p. 203.

drawing a consequence of the first order from the new method which he introduced into thermodynamics.

This is the point to which the method and its principal applications has reached after the work of Gibbs and Helmholtz. The path had been traced out and was known to be reliable. It remained to show that the principle of the new method could be simply deduced from the postulates of thermodynamics, to develop the theory of dissociation to which it led, to relate the proposition on which the theory of the cell is based to the elementary laws of electricity, and finally, to extend the consequences of the new doctrine into all the branches of physics. What has been the fruit of the efforts in these various directions since the works of Gibbs and Helmholtz? It is not for us to say.

Part II
Commentary on the Principles of Thermodynamics: The Principle of the Conservation of Energy (1892)*

Introduction

Science always advances by a series of oscillations.

During some periods, the principles of science are discussed. An examination of the hypotheses which they presuppose and the restrictions by which they are constrained is undertaken. Then, for a time, when the principles seem well-established, the efforts of the theorists are directed towards the deduction of consequences; applications multiply and experimental verifications become numerous and precise.

But this development, at first rapid and easy, eventually becomes slower and more arduous. The over-cultivated ground loses its fertility. Obstacles emerge which the established principles cannot surmount, contradictions which they do not succeed in resolving and problems with which they cannot grapple. At such a time, it becomes necessary to return to the foundations on which the science is based, to examine anew their degree of soundness, to assess exactly what they can support without giving way. Once this work is done, it will be possible to build up the new consequences of the theory.

The applications of thermodynamics during the last thirty years have been numerous. And by common agreement of all those who are interested in this science, a revision of its principles has become necessary. It is the attempt at such a revision that we now submit to the readers of the *Journal de Mathémathiques*.

All [270] physical theory rests on a certain number of definitions and hypotheses which are, to a certain extent, arbitrary. It is therefore possible to seek to expound such a theory in a logical order; but to claim to have given it the only logical order to which it is susceptible would be an unjustifiable claim. We will be careful to make no such claim. We are convinced that the principles of thermodynamics can be connected together in a different, but equally—perhaps more—satisfactory, manner from that we have adopted. We dare not even hope that no lacuna exists in the organisation that we have sought to establish.

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*"Commentaire aux principes de la Thermodynamique. Première Partie: Le principe de la conservation de l'énergie", *Journal de Mathématiques Pure et Appliquées*, 8 (1892), 269–330.

If the question that we have examined appears more philosophical than mathematical, then we may be allowed to invoke, by way of justifying its introduction in this Journal, the interest manifested quite recently by an illustrious analyst in research into the principles of thermodynamics. This will be our excuse to the mathematicians.

Chapter 3
Preliminary Definitions

3.1 On Absolute Motion

We will take for granted geometry and kinematics. We will borrow from these sciences any results that we need.

Experience allows us to conclude whether one of two portions of matter is displaced in relation to the other, so that the notion of *relative motion* is an experimental concept. This is the concept that kinematics deals with.

But [271] this concept is not sufficient for the object that we propose to treat. The hypotheses which we will state, and the laws which we will formulate, will involve not only the relative movement of various quantities of matter in relation to one another. They will involve the movements of various quantities of matter in relation to a certain ideal triad of coordinate axes which we suppose traced somewhere. It will frequently happen that propositions concerning movements relative to this particular coordinate system, and which we regard as exact, become manifestly false if the movements are supposed to be relative to some other coordinate system which is in motion relative to the first.

We will call this particular coordinate system, to which all the motions we will speak of are referred, the *absolutely fixed coordinate system*. The axes of this coordinate system will be *absolutely fixed axes*. A movement relative to this particular coordinate system is called an *absolute motion*. A portion of matter whose various points are not kept in motion by any movement relative to this coordinate system will be said to be at *absolute rest*. In particular, a coordinate system which is immobile in relation to the absolutely fixed coordinate system will define a new absolutely fixed coordinate system.

We are not able to judge whether a given coordinate system is indisputably fixed or not. Any judgement of this kind is subordinated to the belief in the legitimacy of some hypothesis. If we regard a certain hypothesis involving consideration of absolute movements as exact, and if this hypothesis, applied to the relative movements of a certain coordinate system, leads to inexact results, we say that this coordinate system is not absolutely fixed. But this conclusion is only obligatory in so far as we are bent on upholding the hypothesis which has served us as a criterion. We will be right to regard as fixed the coordinate system at issue if we agree to reject the hypothesis.

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
DOI 10.1007/978-94-007-0311-7_3,

3.2 On Bodies and Mixtures or Combinations

We will understand a body to be a linearly connected space filled, *in a continuous manner*, by a certain quantity of matter.

We will not discuss the question whether bodies are really [272] continuous or formed from very small, discontinuous quantities separated by equally small empty intervals.

In physics, it is both impossible and useless for us to know the real constitution of matter. We seek simply to conceive an abstract system which furnishes us with an image of the properties of bodies. In order to construct this system, we are free to represent a body which seems to us to be continuous either as a continuous distribution of matter in a certain space, or as a discontinuous ensemble of very small atoms. Since the first mode of representation is conducive, in all the branches of physics, to more simple, clear and elegant theories, we adopt it in preference to the second.

Consider two bodies A, B which, at a certain instant t, occupy spaces a, b having no part in common. These two bodies are not always and necessarily distinct; the quantities of matter which constitute them might, at an instant t', distinct from t, and earlier or later than t, make up a single body C, occupying a space c, in such a way that any element dw of the space c encloses, at instant t', a quantity of matter which, at instant t, constituted body A, and also a quantity of matter which, at instant t, constituted body B, the first quantity occupying, at instant t, a certain volume element dv of the space a and the second quantity occupying, at instant t, a certain volume element dv' of the space b.

In the case just mentioned, the body C results either from the *mixture* or the *combination* of two bodies A and B.

Many physicists do not accept the possibility of a combination or mixture of the kind we have just defined. They regard as impossible this intimate penetration by which the matter filling each volume element of the continuous body C results from the union between the matter enclosed by a volume element of the continuous body A and the matter enclosed by a volume element of the continuous body B. It is this impossibility that they call the *impenetrability of matter*.

For these physicists, the words *mixture* and *combination* do not represent appearances. When we believe we see the two bodies [273] unite to form a new body C, the extremely small parts whose discontinuous collection constitutes each of these two bodies remain, in reality, distinct. The small parts of body A are simply interposed between the small parts of body B, without the space occupied by any one of these parts of body A having anything in common with the space occupied by any of the parts of body B.

Reasons analogous to those which led us to regard the matter which constitutes a body as continuous lead us to resist this way of conceiving mixture or combination and to adopt the definition just given.

Let us consider a body C formed by the mixing of two bodies A and B. The matter which, at the instant t, fills the volume element dw of the body C is composed of a part p of the matter which forms body A and a part q of the matter which forms body B. At a different time t', these two parts p and q are not necessarily united with one another in the same volume element; the matter constituting the part p might fill a volume element dw' where it is either free or unified with a part q', different from q, of the matter of body B. At the same time, the matter which constitutes the part q might fill another volume element dw'' where it is either free or unified with a part p'', different from p, of the matter of body A.

Thus, when a body C is a mixture of two bodies, the matter filling each volume element of this body is formed by the union of two different quantities, and *these two quantities may be kept in motion by different movements*. In that case, at each point of the mixture there might be occasion to consider two different velocities, each of these velocities being relative to one of the parts of the mixture.

All that we have said about a mixture of two bodies applies equally well to a mixture of any number of bodies.

3.3 On Bodies Isolated in Space

Experience shows us that we can remove all the bodies which surround a given body at a given instant. The existence of such bodies therefore seems to us to have no necessary connection with the existence of the given body. We thus come to conceive of the possibility of [274] the existence of this body isolated in space unbounded in every sense and absolutely empty.

This conception of bodies isolated in unbounded and absolutely empty space is a pure abstraction. Experience never offers us a body without any parts contiguous with other bodies, and physics leads us to accept that even if we were to succeed in removing all the solid, liquid and gaseous bodies that we can directly or indirectly lay hold on, so as to make a *physical vacuum* in the space surrounding a given body, this space would still be filled with a certain matter that has been called *ether*. It is therefore, I repeat, in virtue of a pure abstraction that we can conceive of a body as existing alone in space. But I don't believe that it is possible to build up physics without making use of this abstraction.

3.4 On the Variables Which Define the State and Movement of a System

Let us consider a collection of bodies isolated in space. This collection of bodies may, from one instant to another, change position, shape, state, etc. Let us consider it as it is at the instant t, disregarding what it was at all instants earlier than t and what it will be at all instants later than t. At this instant t, it possesses certain properties. In order to represent these properties, theoretical physics defines certain algebraic and geometric magnitudes and then establishes relations between these magnitudes which symbolise physical laws to which the system is subjected.

The magnitudes may be defined in very different ways. Geometry, for example, tells us in what way it is possible, by the definition of certain magnitudes, be they limited or unlimited in number, to determine the shape and position of each of the material particles composing the system. Other magnitudes which represent physical and chemical properties are defined within various theories of which physics is composed. In this chapter, we will show how physics defines one of these magnitudes which is particularly important, *temperature*. In the following chapter, we will deal with another, *mass*.

In the study of a system, it might be of interest to consider [275] at the same time several magnitudes whose definitions are interrelated. Thus, it is necessary to speak of the mass[1] of a body, of its density and its volume, even though by *definition*, the density of a body is the ratio of its mass and its volume. Magnitudes connected to one another by their definition are not independent.

Magnitudes representing the properties of a system at a given instant are *independent* if the definition of each implies no relation between its value at the instant t and the value of each of the others at the same instant t. Thus, the volume and mass of a body will be two independent magnitudes. Similarly, the components of the electric current at each point of a conductor and the electric density at each point of the same conductor are independent magnitudes. Without contradicting either the definition of the current density or the definition of electric current, it is possible, at the instant t, to attribute arbitrary values to the former and to the three components of the latter.

We have said that several magnitudes are independent if the definition of each of them implies no relation between its value *at the instant t* and the value of each of the others *at the same instant t*. But while the values of independent variables may all be chosen arbitrarily at an isolated instant t, in certain cases it would not be permissible to arbitrarily choose their values at all the instants during a certain interval of time. Thus, for the instant t, *considered in isolation*, it is possible to choose arbitrarily the electric density and the components of the electric current at each point of a conductor. But it is not possible, without absurdity, to do this at *all the instants* of the interval of time $(t_1 - t_0)$. In fact, the very definition of electric current shows that if, at each point of the conductor, (i) the components of electric current at every instant of the interval of time $(t_1 - t_0)$ are known, as well as (ii) the electric density at a particular instant of the interval of time $(t_1 - t_0)$, then the value of [276] the electric density is determined at every instant of the interval $(t_1 - t_0)$, so that this value cannot be chosen arbitrarily.

In all that we have just said, it should be noted that when we speak of the *dependence* between various magnitudes, we intended to speak only of a dependence resulting from the definition of these magnitudes and not of a dependence resulting from a physical law. So *logically* independent magnitudes need not be *physically* independent. Giving them arbitrary values is an operation which, without being absurd, may be contrary to the laws of nature.

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[1] *In order to give examples* we are, of course, obliged to anticipate, since no other magnitude representing a physical property has been defined in the foregoing.

Among the magnitudes, independent or not, which serve to represent a system at an isolated instant *t*, the definition of some of them constrains them to have the same value for a given system whatever the isolated instant considered. This is the case, for example, with the mass of the system, or again with the total electric charge. There are others which can, for the same system, have different values at different instants. The former are said to define the *nature* of the system and the latter to define the *state*.

Let us consider the independent magnitudes that suffice to represent *completely* the properties of a system at an isolated instant *t*. Some, A, B, ..., L, define the nature of the system; others, $\alpha, \beta, \ldots, \lambda$, define its state.

If the quantities A, B, ..., L conserve their values and if the variables $\alpha, \beta, \ldots, \lambda$ are given different values $\alpha', \beta', \ldots, \lambda'$, this would represent a different state of the same system.

If the quantities A, B, ..., L conserve their values and if the variables $\alpha, \beta, \ldots, \lambda$ are given different values $\alpha', \beta', \ldots, \lambda'$, this would represent a different state of the same system.

Let us therefore imagine a continuous series of different states of the system, that is to say, a continuous series of groups of values of the quantities $\alpha, \beta, \ldots, \lambda$. Let us successively fix our attention on these various states, in an order which allows continuous passage from one state to another. By designating this a *purely intellectual operation*, we are saying that we impose a *virtual change* on the system.

All changes realisable by a system correspond to variations of the quantities $\alpha, \beta, \ldots, \lambda$ compatible with the definitions of these quantities. The sequence of states through which the system passes therefore constitutes a virtual change of the system.

Conversely, [277] can a virtual change always be regarded as the sequence of states that a system traverses during a real change? Remembering that the variables $\alpha, \beta, \ldots, \lambda$ which can, by their definitions, take arbitrary values, may be connected to one another by physical laws, it can be seen that a virtual change may be compatible with the definitions of the variables appropriate for representing the various states of the system but conflict with certain physical laws, and, consequently, not be physically realisable.

Moreover, the values it is possible to attribute to the variables $\alpha, \beta, \ldots, \lambda$ at an isolated instant *t* are arbitrary. But such is not always the case with the values that can be attributed to these variables at various instants of a certain temporal interval. Thus, regarding the sequence of groups of values of $\alpha, \beta, \ldots, \lambda$, representing the various states of the system during a virtual change as a sequence of states *which succeed one another* during a certain interval of time soon leads to a contradiction with the definition of the variables $\alpha, \beta, \ldots, \lambda$. If, for example, in the virtual change considered, it is supposed that non-uniform currents run through a conductor, and if, on the other hand, the charge density at each point is taken to be invariable, a continuous sequence of states is obtained whose succession in time would be in contradiction with the definition of electric current. Thus, the definitions of the variables $\alpha, \beta, \ldots, \lambda$ can suffice to render certain virtual changes unrealisable.

We have said that the constants A, B, . . ., L and the variables $\alpha, \beta, \ldots, \lambda$ represent the physical properties of the system considered at the instant *t*, disregarding the properties of the system at instants preceding and following *t*. Now considering a system at an isolated instant, disregarding the properties of the system at instants preceding and following it, does not allow for a distinction between the body at rest and in motion. The word *motion* only has meaning for the system in so far as it can be envisaged during a certain lapse of time, however short. Consequently, the values of the quantities $\alpha, \beta, \ldots, \lambda$, necessary and sufficient for representing the properties of the system at the isolated instant *t*, do not in general suffice to tell us whether the system is in motion and what the motion is.

We [278] say that *the motion* of the system at the instant *t is defined* if not only the state of the system at this instant is known, but also the magnitude and direction of the speed with which the material filling each of the elements of volume of the system moves. In the case where a volume element is filled with a mixture of several substances, it is necessary to know the velocity with which each of the parts of the material which compose the mixture moves.

Consider an infinitesimal part of the material which forms a system. The coordinates *x, y, z,* which indicate the position of one of its points at the instant *t* in relation to an absolutely fixed co-ordinate system, are known when the values of the variables $\alpha, \beta, \ldots, \lambda$ are known at this instant. In fact, if these variables are known, then the shape, position and properties possessed by all the parts of the system at the instant *t* should be known. In order to determine *x, y, z,* we should therefore have equations of the form

$$\begin{cases} x = \varphi(\alpha, \beta, \ldots, \lambda), \\ y = \psi(\alpha, \beta, \ldots, \lambda), \\ z = \chi(\alpha, \beta, \ldots, \lambda). \end{cases} \tag{1}$$

φ, ψ and χ are three functions whose form depends on the nature of the system and also on the particular material considered. These relations do not depend explicitly on the time *t*, because if, at two different instants *t* and t', the variables $\alpha, \beta, \ldots, \lambda$ again take on the same values, as variables sufficient to determine the state of the system, the system will return identically to itself, and the coordinates *x, y, z* will take on the same values.

From Equations (1), the equations

$$\begin{cases} \dfrac{dx}{dt} = \dfrac{\partial\varphi}{\partial\alpha}\dfrac{d\alpha}{dt} + \dfrac{\partial\varphi}{\partial\beta}\dfrac{d\beta}{dt} + \ldots + \dfrac{\partial\varphi}{\partial\lambda}\dfrac{d\lambda}{dt}, \\ \dfrac{dy}{dt} = \dfrac{\partial\psi}{\partial\alpha}\dfrac{d\alpha}{dt} + \dfrac{\partial\psi}{\partial\beta}\dfrac{d\beta}{dt} + \ldots + \dfrac{\partial\psi}{\partial\lambda}\dfrac{d\lambda}{dt}, \\ \dfrac{dz}{dt} = \dfrac{\partial\chi}{\partial\alpha}\dfrac{d\alpha}{dt} + \dfrac{\partial\chi}{\partial\beta}\dfrac{d\beta}{dt} + \ldots + \dfrac{\partial\chi}{\partial\lambda}\dfrac{d\lambda}{dt}, \end{cases} \tag{2}$$

can be deduced. The Equations (2) show us that the components of the velocity [279] of any elementary part of the system are linear and homogeneous functions of $\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \ldots, \frac{d\lambda}{dt}$. These functions depend, moreover, in some way on the variables $\alpha, \beta, \ldots, \lambda$.

Thus, in order to define the motion of a system at the instant t, it is sufficient to add to the values of $\alpha, \beta, \ldots, \lambda$ the values of $\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \ldots, \frac{d\lambda}{dt}$. Is this also necessary?

In a large number of cases, not all the quantities $\alpha, \beta, \ldots, \lambda$ figure in the Equations (1), and consequently, not all the quantities $\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \ldots, \frac{d\lambda}{dt}$ in Equations (2). Sometimes we have to distinguish between those of the quantities $\alpha, \beta, \ldots, \lambda$ which figure in the Equations (1) from those which do not. We preserve for the former the letters $\alpha, \beta, \ldots, \lambda$ and for the latter, we adopt the letters $a, b, \ldots, l$.

We will say that an isolated system is *at rest* when the material which composes it is immobile, its state being, moreover, able to undergo the variations with time which allow each of the parts composing it to be in the same position. For such a system, the quantities $\alpha, \beta, \ldots, \lambda$ retain their values independently of time, whereas the quantities $a, b, \ldots, l$ are able to undergo any variation with time.

We will say that an isolated system is *at equilibrium* if its state does not vary with time. For such a system at equilibrium, the quantities $a, b, \ldots, l$ as well as the quantities $\alpha, \beta, \ldots, \lambda$ have their values independently of time.

Imagine that a system departs from a certain state characterised by certain determinate values of the variables $\alpha, \beta, \ldots, \lambda$ and by a certain velocity clearly determined for each infinitesimal material part in which it might be supposed to be divided. Further, suppose that the system might undergo a series of greater or lesser changes, and finally, that, after a certain time, it is brought to a state identical to the initial state, that is to say, to a state where the variables $\alpha, \beta, \ldots, \lambda$ have the same values as in the initial state, where the velocity of each elementary part is the same as that in the initial state. The series of transformations [280] undergone by the system is called a *closed cycle*. We will often have occasion to consider such transformations in the course of this work.

It is understood that when a system undergoes any transformation, the velocity of each of the elementary parts in which it may be supposed to be divided varies with time in continuous fashion.

In most of the preceding considerations, we have supposed that the state of the system is defined by the values of a limited number of variable parameters. It is easily seen that this hypothesis has merely the aim of simplifying the language, but that everything that we have said can be extended without difficulty to a system whose definition requires knowledge of an infinity of variable parameters.

3.5 On Independent Systems

Consider a system of bodies S isolated in space where $\alpha, \beta, \ldots, \lambda$ are the variables which, at each isolated instant t, completely determine its state.

Suppose that the bodies forming the system can be divided into two groups, S_1, S_2.

Suppose further that the variables $\alpha, \beta, \ldots, \lambda$ can be divided into two groups, $\alpha_1, \beta_1, \ldots, \lambda_1$ and $\alpha_2, \beta_2, \ldots, \lambda_2$ with the following properties:

1. Nothing in the definition of the variables $\alpha_1, \beta_1, \ldots, \lambda_1$ presupposes the existence or properties of the group of bodies S_2 or the variables $\alpha_2, \beta_2, \ldots, \lambda_2$;
2. Nothing in the definition of the variables $\alpha_2, \beta_2, \ldots, \lambda_2$ presupposes the existence or properties of the group of bodies S_1 or the variables $\alpha_1, \beta_1, \ldots, \lambda_1$.

If these conditions are realised, it may be supposed that the group of bodies S_1 is isolated in space, and that, at each instant of a certain interval of time, the variables $\alpha_1, \beta_1, \ldots, \lambda_1$ have, for the isolated group, values identical to those they would have, at the corresponding instant of an equal interval of time within the system S. This hypothesis contradicts nothing in the definition of the variables $\alpha_1, \beta_1, \ldots, \lambda_1$.

Similarly, it can be supposed that the group of bodies S_2 is isolated in space, and that, at each instant of a certain interval of time, that the variables $\alpha_2, \beta_2, \ldots, \lambda_2$ have, for the isolated group, values identical [281] to those they would have at the corresponding instant of an equal interval of time within the system S. This hypothesis contradicts nothing in the definition of the variables $\alpha_2, \beta_2, \ldots, \lambda_2$.

Further, the two hypotheses that we have just presented, while not contradicting the definition of the groups of variables $\alpha_1, \beta_1, \ldots, \lambda_1$ and $\alpha_2, \beta_2, \ldots, \lambda_2$, may be at odds with certain experimental laws.

When two groups of bodies, S_1 and S_2, satisfy the conditions just enumerated, we say that these two groups constitute *two material systems able to exist independently of one another*, or, more concisely, *two independent systems*.

Note that in this case, the variables $\alpha_1, \beta_1, \ldots, \lambda_1$ evidently suffice to fix the state of the system S_1 without saying anything with regard to the state of system S_2. Conversely, the variables $\alpha_2, \beta_2, \ldots, \lambda_2$ evidently suffice to fix the state of the system S_1 without saying anything with regard to the state of system S_1. Thus, *when two systems are independent of one another, it is possible to isolate each them from the other without changing its state*. To repeat, in this statement, the word *possible* designates an operation which is not in contradiction with the definitions, but is not necessarily an operation conforming to the laws of physics.

We will illuminate what we have just said with some examples:

(1) The system S is a body whose state we regard as defined when we know the position, density and temperature of each of the infinitesimal materiel parts which compose it.

Without contradicting the definitions of temperature and density, we can, after having divided the body into two parts, S_1 and S_2, ignore part S_2 and consider part S_1 isolated in space while preserving for each of the infinitesimal material parts which compose it the position, density and temperature which it would have had, at the same instant, in the system S. We can also ignore the part S_1 and retain the part S_2 isolated in space while preserving for each of the infinitesimal material parts [282] which compose it the position, density and temperature which it would have had, at the same instant, in the system S.

In this case, which is of great importance, the two systems S_1 and S_2 are independent.

(2) The system S is a conductor which carries certain electric charges. The definition of these charges requires that the sum of the charges distributed over the conductor S remains constant during the period considered. But if this conductor is regarded as comprising two contiguous parts, S_1 and S_2, the sum of the charges distributed over the portion S_1 might well vary from one moment to another, as may the sum of charges distributed over the part S_2.

Suppose now that, during a certain period of time, we consider the part S_2 to be suppressed and the part S_1 to be isolated in space. Can we entertain the idea, at each instant of this period, of a distribution of electricity over this part S_1 identical to that which it would carry at the same instant, if it were incorporated in the system S? No, because as just remarked, this distribution will, in general, have a variable value for the total quantity of electricity carried by S_1 from one instant to another. When isolated in space, the conductor S_1 should have an invariable total electric charge in accordance with the definition of electric charge.

Thus, in the case that we have just analysed, the two bodies S_1, S_2 do not form two independent systems.

(3) The system S is a conductor carrying a certain electric charge through which certain currents flow. In order to fix our ideas, we will suppose that these currents are uniform. The charge distribution is then invariable, both on the surface of the conductor S and in the interior, during the period considered.

We cut the conductor S into two parts, S_1, S_2 by a surface σ. Can we ignore part S_2 and regard part S_1 as isolated in space while preserving, during the period considered, a distribution of currents and charges identical to that which would obtain in this part S_1 when [283] it is incorporated in the conductor S? Clearly not, because in the conductor S, the various points of the surface σ carry an invariable electrification whereas if the part S_1 were isolated in space, the currents running through it would make the electrification of the surface σ vary from one instant to another.

In this case too, the two bodies S_1, S_2 are not independent systems.

It is as well to note that in saying that two bodies S_1, S_2 do not constitute two independent systems, we do not wish to say that each of these two bodies cannot be conceived as isolated in space. On the contrary, we allow that a body may always be thought of as isolated in space (see Example 3). What we mean is that it is not possible to accept that each of them, isolated in space, preserves, at each instant of an interval of time, the state which it would have at the same instant as if it were incorporated into the entire system.

Thus, in the last two examples, the body S_1 can be conceived as isolated in space. But what is contradictory is to attribute to it, during a certain time, the distribution of electrical charges and currents that it would carry during the same time if were united with the body S_2 to form the system S.

Physics cannot decide, without exceeding the domain or its methods of legitimate application, whether the universe is bounded or not. But in all questions of physics, it is possible to reason as if the universe were formed of a certain number of bodies enclosed within a surface of closed extension. In fact, it is allowed that, when studying a group of bodies, it is possible, without detectable error, to consider as non-existent all bodies which lie beyond a certain bounded distance.

We consider, then, the very large, though bounded, part of the universe that it is necessary to take into account when we wish to study a definite group of bodies S_1. Let S be this part of the universe, and let S_2 be what remains of S when S_1 has been removed. If the two groups of bodies S_1, S_2 constitute two independent systems, we will say that the group S_1 forms a *material system*. It is always in this well-defined sense that we will employ the word *material system*.

We can extend to such a system the words *rest* and *equilibrium* without changing the [284] definitions that we have given them at the end of Section 3.4 for an isolated system.

3.6 On Temperature

Among the variables serving to define the state of a system, there is one which plays a particularly important role in the course of the present work, the *temperature*. We will now show how this variable can be defined. This study will, moreover, have the advantage of showing us how a physicist brings certain magnitudes into correspondence with physical properties of a system.

Our organs give us the sensation of *warm* bodies and *cold* bodies, and of bodies warmer or colder than other bodies. This sensation of warmth or cold, of greater or lesser warmth or of more or less intense cold, we regard as the sign of a certain property possessed by bodies that they possess to a greater or lesser degree. We accept that that a body is warm, if it is more or less warm than another, that it is cold if it is less warm than our own body.

Our faculty of abstraction soon attributes to bodies aspects of this property which we characterise by the words *being warm, being cold, being more or less warm* that go unnoticed in sensation.

We cannot compare the degree of warmth of bodies if the bodies are too cold or too warm. Outside certain limits, for any of the senses, our organs will be injured or destroyed. Nevertheless, we conceive that outside these limits bodies continue to be more or less warm than other bodies.

In comparing our sensations with those of our fellow-creatures, we see that we sometimes find two bodies unequally warm whereas someone else finds them equally warm, or conversely. We are thus led to accept that the sensibility of our organs is limited and that, without being identical, the degrees of warmth of two bodies may be so alike that we are not able to distinguish them.

A warm body can only influence our organs by the part of [285] its surface in contact with these organs, and this surface always has a certain extension. The time during which we touch this surface always has a certain duration. Nevertheless, we accept that the character of being warm holds as well of the parts in the interior of the body as of those parts at the surface, that it holds of each of the infinitesimal parts of which the body can be considered to be decomposed and at each infinitesimal moment of duration, that at such an instant it varies from one point to another, and that at such a point it varies from one instant to another.

Observations of the most ordinary kind show us that, in most cases, when a warm body is in the presence of a cold body, the cold body is warmed and the warm body is cooled. Generalising this observation, we accept as exact the following law:

> *In order that an isolated*[2] *system be at equilibrium, it is necessary that all the material parts composing the system are equally warm.*

This law again leads us to correct the evidence of our sensations. Experience teaches us, in fact, that in certain systems that we regard as being at equilibrium, various parts can appear to us as being far from equally warm. For example, a piece of steel and a piece of wood, the combination of which is in equilibrium [286], give us very different sensations of warmth. We continue, however, to regard them as being in reality equally warm, and we admit that our sensations do not always inform us exactly about the degree of warmth of bodies.

The words *being warm* therefore correspond to a property of each of the infinitesimal parts into which a body can be considered to be divided. What is this property in itself? Is it reducible, by virtue of its own nature, to quantitative elements? These are questions which physics cannot resolve. *As we conceive it*, this property is not quantitative. It seems to us that it is susceptible of being reproduced identically with itself, of being augmented and diminished, *but not susceptible of addition*.

But we can put this non-quantitative property into correspondence with an algebraic magnitude which, *without standing in any relation to its nature*, will be a representation of it.

We can, in fact, conceive of the existence of a magnitude which satisfies the following conditions:

1. This magnitude has a determinate value at each point of any body.
2. It has the same value at two points which are equally warm.
3. It has different values at two unequally warm points, the greater value corresponding to the warmer point.
4. If two points tend to become equally warm, the values of the magnitude considered which corresponds to them tends towards the same limit.

Evidently, if the values taken by such a magnitude at various points of a collection of bodies are known, then it will always be known exactly whether the degree of

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[2] It should be noted that this law is only exact in so far as the system to which it applies is *isolated*. A metallic bar with one end immersed in steam and the other in melting ice is in equilibrium when a constant heat flux is established. However, the various points of this bar are not equally warm. But this bar does not constitute an isolated system. If it were to be incorporated in an isolated system, that would contain, at the same time, the boiling water and the melting ice which are not in equilibrium. An analogous observation is applicable to the state of equilibrium achieved by a thermo-electric chain when constancy is established, both for the heat flux and the electric flux.

warmth varies from one part to another of the collection, and in which sense it varies.

This magnitude, for which the various values serve, not to *measure* (that would, after the foregoing, make no sense), but to *represent* the various degrees of warmth, will be called *temperature*.

The definition of temperature leaves a high degree of arbitrariness in the choice of this magnitude. Let us imagine that the temperature of all points has, in fact, been determined in a first way. Let ϑ be this temperature. The magnitude $\Theta = f(\vartheta)$ could evidently be, in [287] turn, taken as temperature if the function $f(\vartheta)$ possesses the following three characteristics;

1. For each value that the variable ϑ can take, the function $f(\vartheta)$ takes one and only one value;
2. The function $f(\vartheta)$ varies in continuous fashion with continuous variations in ϑ;
3. The function $f(\vartheta)$ always varies in the same sense as ϑ.

The operation by which, at a given instant, it would be known how the various parts of a body would be classed if all the elements of the same class were equally warm, and if all the elements in any class were warmer than the elements in the preceding and less warm than the elements in the following class—this operation, I say, seems logically possible to us, although our senses do not allow us to realise it except within restricted limits and in a grossly approximate fashion.

We therefore conceive that a temperature, constant for all the elements found in the same class and increasing from one class to another, can be chosen, although our sensations do not furnish us with the means of realising such a choice with any precision. That suffices for this temperature to figure in our arguments without risk of employing words with no sense. As a matter of fact, it is this temperature exclusively, conceived in abstract fashion, that will be at issue in our theories.

But if we wish to apply to concrete systems the results to which we are led by the abstract arguments in which temperature figures, it doesn't suffice to know that it is possible to construct a magnitude, called *temperature*, taking a determinate value at each point of these systems. It is necessary to have an exact or approximate means of actually constructing such a magnitude to obtain its numerical value; that is to say, to class the parts of bodies according to their increasing degree of warmth. We have seen that our senses, employed directly, are not adequate for this purpose.

The method employed to obtain an experimental determination of the temperature, or rather of *a* temperature, applies [288] only to a particular case, albeit a very extensive one. With various special hypotheses, which we will not examine here, it can be extended to certain other cases.

This experimental determination depends on the following law, the origin of which we have already spoken:

For equilibrium in an isolated system it is necessary that all its parts are equally warm.

If, as we have every right to, we use in our arguments a temperature ϑ, whose determination is conceived in abstract fashion, and not realisable in an effective manner, we can state the preceding law in the following form:

> *If an isolated system is at equilibrium, the temperature ϑ has the same value at all of its points.*

Given this law, suppose that we have a system S, isolated and at equilibrium; then it has the same temperature at all of its points.

The system S is itself formed of two *independent* systems T and U.

The system U, except for the property of being independent of T, may be any whatever.

On the other hand, it is supposed that the system T possesses, at least approximately, the following features[3]:

1. For a given value of the temperature ϑ which is the same at all its points, the system T can be at equilibrium in just one way, whatever the independent system U to which it is attached. The various properties exhibited by this system T at equilibrium therefore depend uniquely on the temperature. If there is among them one which is measurable (for example, a geometric property), the number which measures it is a function of the temperature ϑ alone.
2. [289] Among the measurable properties of the system T, there is at least one which always increases as the system T is warmed. However the temperature ϑ is chosen, the number Θ which measures this property will always vary in the same sense.

In accordance with what was said above, *the number Θ can be taken as an appropriate measure of the temperature* of system T, and consequently, of system U.

Therefore, every time the system T, chosen once and for all, can be attached to a certain system U independent of system T and forming with it an isolated system at equilibrium, the degree of warmth possessed by the system U under these conditions can effectively be put into correspondence with a value of the temperature.

When the system T and the property of the system whose measure Θ gives the numerical value of the temperature have been defined, a choice of *thermometer* has been made. When an indication of the numerical value of the temperature of the system U is given, the thermometer which has been chosen should evidently be mentioned in order that this indication makes sense.

We leave to the reader the task of explaining the above generalities in application to the various thermometers ordinarily employed.

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[3] These features are perceived by us in more or less gross experience, such as, for example, by allowing the direct use of our senses. Then, by way of hypotheses, we have accepted that the system T possesses them either rigorously or with an approximation superior to our first observations.

Chapter 4
The Principle of the Conservation of Energy

4.1 The Mechanical Work[1] and the Energy of a System

We can, by our efforts, produce, or assist in producing, a certain transformation in a system: we can displace a body, start it off with a certain velocity, break it, or deform it. On the other hand, we can employ our efforts to place an obstacle in the way of a transformation of the system, to impede the transformation: we can halt a moving body, slow it down, and prevent it being deformed. We [290] say then that we have performed a certain task, done a certain [amount of] *mechanical work*.

Daily experience teaches us that we can substitute for our personal action a body or a collection of bodies capable of producing, or contributing towards the change that we produce or to which we contribute, and of preventing the change that we prevent. The object of physics is, in practice, in a great number of cases precisely to know which bodies can be substituted for our personal activity in order to facilitate or hinder a certain change, which machines can replace labour in the accomplishment of a certain task. We regard the mechanical work that we would have performed if we had ourselves acted on the system which is transformed as performed by the body or collection of bodies that we have substituted for ourselves or our fellow men.

This notion of the mechanical work done by bodies external to a system while the system undergoes a certain change is one we carry over to the case where the change undergone by the system is of such a nature that our personal action can neither help nor hinder it. The mechanical work done by external bodies is considered to represent the mechanical work which an operator with a constitution unlike ours would perform, and which is capable of bringing to the transformation of the system the help or hindrance brought to bear by the external bodies.

Therefore, when a system is transformed in the presence of external bodies, we consider the external bodies as contributing to this transformation either by causing it or by aiding it or by impeding it. It is this contribution, whose nature remains

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[1] *oeuvre* [Duhem uses both *oeuvre* and *travail*, the latter introduced in Chapter 5 below with the sense of work as usually understood in thermodynamics.]

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
DOI 10.1007/978-94-007-0311-7_4,

obscure to us, that we call the *mechanical work done during a transformation of a system by the bodies external to the system*.

Without seeking to penetrate the nature of this contribution, which is not the object of physics, but of metaphysics, we will endeavour to create a mathematical expression appropriate for serving as a symbol of this contribution. To this end, we will determine the form of an expression subject to certain conventions. These conventions are not established by chance; we will choose them so that they reflect the most simple and salient characteristics [291] presented by the notion of mechanical work, or, at least, so that they easily accord with these characteristics.

Let us suppose that a system, subjected to the action of certain external bodies, undergoes a certain transformation. Let us then suppose that the same system undergoes the same transformation, now with different bodies external to the system. The mechanical work done in the first case and in the second case by the bodies external to the system is the same, although the bodies are different. This characteristic, that we must attribute to the notion of mechanical work, leads us to put forward the following convention:

> FIRST CONVENTION.—*The magnitude representing the mechanical work done during a transformation of a system by the bodies external to this system is determined when the nature of the system and the transformation to which it is subjected is known. It is independent of the bodies external to the system.*

A second convention follows that it is very natural to adopt:

> SECOND CONVENTION.—*Let us suppose that a system were to undergo various transformations* $1, 2, \ldots, \mathrm{n}$*, successively, while the bodies external to the system perform mechanical work represented, respectively, by the algebraic magnitudes* $G_1, G_2, \ldots, G_{\mathrm{n}}$. *The totality of transformations* $1, 2, \ldots, \mathrm{n}$ *can be considered as a single transformation. The mechanical work done by the bodies external to the system during this resultant transformation will be represented by the magnitude* $(G_1 + G_2 + \ldots + G_{\mathrm{n}})$.

Now that no confusion between the mathematical symbol and the notion that it represents need be feared, we can give the name *mechanical work done* during the transformation of a system by the bodies external to the system to the algebraic magnitude which represents this mechanical work.

Let us imagine that a system begins in a certain initial state with a certain initial motion, and that a series of modifications takes it, [192] at the end of a certain time, to a final state identical to its initial state, with a final motion identical to its initial motion. We will regard the mechanical work that the external bodies have performed during a part of this transformation as having been destroyed by the mechanical work done during the remainder of the transformation, so that the total mechanical work will be zero. We will thus be led to put forward the following convention:

> THIRD CONVENTION.—*When a system traverses a closed cycle, the mechanical work done during the course of the cycle by the bodies external to the system is equal to* 0.

This convention suggests, in the first place, that the magnitude representing the mechanical work done will not have the same sign for every change in a system.

Some of the various changes constituting a closed cycle must correspond to positive mechanical work, and the others negative, so that the sum of positive mechanical work is exactly compensated by the sum of negative mechanical work.

But in addition, this convention furnishes much more precise information on the form of the magnitude G representing the mechanical work done during the change of a system by bodies external to the system.

Consider two different states of the same system. In one of these states, which we designate with the symbol 1, the variables defining the properties of the system take the values $\alpha_1, \beta_1, \ldots, \lambda_1$ and the velocities of the various particles composing the system have the components $u_1, v_1, w_1; u'_1, v'_1, w'_1; \ldots$. In the other state, which we designate with the symbol 2, the variables defining the properties of the system take the values $\alpha_2, \beta_2, \ldots, \lambda_2$, and the velocities of the various particles composing the system have the components $u_2, v_2, w_2; u'_2, v'_2, w'_2; \ldots$.

Imagine a certain number of distinct changes $M_1^2, M_1'^2, M_1''^2, \ldots$, all of which take the system from state 1 to state 2, and let M_2^1 be a change in which the system goes from state 2 to state 1.

Let

$$G_1^2, \quad G_1'^2, \quad G_1''^2, \ldots, \; G_2^1$$

be [293] the mechanical work done by the bodies external to the system during the changes

$$M_1^2, \quad M_1'^2, \quad M_1''^2, \ldots, \; M_2^1.$$

The two changes M_1^2, M_2^1, imposed on the system one after the other, take it in a closed cycle. The same holds for the two changes $M_1'^2, M_2^1$, and again the two changes $M_1''^2, M_2^1, \ldots$.

The preceding convention then yields

$$\begin{aligned} G_1^2 + G_2^1 \quad &= 0, \\ G_1'^2 + G_2^1 \; &= 0, \\ G_1''^2 + G_2^1 &= 0, \\ \ldots\ldots\ldots&\ldots\ldots\ldots \end{aligned}$$

or

$$G_1^2 = G_1'^2 = G_1''^2 = \ldots.$$

The result that this equation expresses may be stated thus:

> *The mechanical work accomplished by external bodies on a system during a change of the system depends on the state and the motion of the system at the beginning and at the end of the change, but not on any other details characterising this change.*

In compliance with this statement, we will from now on put

$$G_1^2 = \psi(\alpha_1, \dots;\, u_1, v_1,\, w_1 \dots |\alpha_2, \dots;\, u_2, v_2,\, w_2 \dots)$$

We will now give the function ψ a more explicit form.

We consider the system that we are studying to be in a certain state, *determined once and for all*, that we will designate by the index 0. In this state, $\alpha_0, \beta_0, \dots, \lambda_0$ are the values of the variables which define the properties of the system, and $u_0, v_0, w_0; u_0', v_0', w_0', \dots$ are the components of the velocities with which the material particles composing it move.

If the system passes from the state 0 to the state 1, the external bodies perform the mechanical work

$$G_0^1 = \psi(\alpha_0, \dots;\, u_0, v_0,\, w_0 \dots |\alpha_1, \dots;\, u_1, v_1,\, w_1 \dots)$$

If [294] the system passes from the state 1 to the state 2, the external bodies perform the mechanical work

$$G_1^2 = \psi(\alpha_1, \dots;\, u_1, v_1,\, w_1 \dots |\alpha_2, \dots;\, u_2, v_2,\, w_2 \dots)$$

These two transformations, effected one after the other, constitute a transformation carrying the system from the state 0 to the state 2. During such a transformation, the external bodies perform the mechanical work

$$G_0^2 = \psi(\alpha_0, \dots;\, u_0, v_0,\, w_0 \dots | \dots \alpha_2, \dots;\, u_2, v_2,\, w_2 \dots).$$

But on the other hand, the mechanical work done by the external bodies during this last transformation should, by the second convention, have the value $\left(G_0^1 + G_1^2\right)$. Accordingly,

$$G_0^2 = \left(G_0^1 + G_1^2\right)$$

or

$$\left\{\begin{aligned} &\ \psi(\alpha_0, \dots;\, u_0, v_0,\, w_0 \dots |\alpha_2, \dots;\, u_2, v_2,\, w_2 \dots) \\ &= \psi(\alpha_0, \dots;\, u_0, v_0,\, w_0 \dots |\alpha_1, \dots;\, u_1, v_1,\, w_1 \dots) \\ &\qquad + \psi(\alpha_1, \dots;\, u_1, v_1,\, w_1 \dots |\alpha_2, \dots;\, u_2, v_2,\, w_2 \dots). \end{aligned}\right. \tag{1}$$

This identity (1) will determine the form of the function ψ.

Since the state 0 has been determined once and for all, the quantities

$$\alpha_0, \quad \beta, \dots, \lambda_0, \quad u_0, \quad v_0, \quad w_0, \quad u_0', \quad v_0', \quad w_0', \quad \dots$$

are not variables, but constants, and the quantity

$$\psi(\alpha_0, \dots;\, u_0, v_0,\, w_0 \dots |\alpha, \dots;\, u, v,\, w \dots)$$

is a function of the variables

$$\alpha,\quad \beta,\ldots,\lambda,\quad u,\quad v,\quad w,\quad u',\quad v',\quad w',\quad \ldots$$

alone.

We [295] can therefore put

$$\begin{cases} \psi(\alpha_0,\ldots;\, u_0, v_0,\, w_0\ldots|\alpha,\ldots;\, u, v,\, w\ldots) \\ \quad = \zeta(\alpha,\ldots;\, u, v,\, w\ldots) \end{cases} \tag{2}$$

and Equation (1) gives us

$$\begin{cases} \psi(\alpha_1,\ldots;\, u_1, v_1,\, w_1\ldots|\alpha_2,\ldots;\, u_2, v_2,\, w_2\ldots) \\ \quad = \zeta(\alpha_2,\ldots;\, u_2, v_2,\, w_2\ldots) - \zeta(\alpha_1,\ldots;\, u_1, v_1,\, w_1\ldots). \end{cases} \tag{3}$$

The mechanical work done by the external bodies during any change of a system is equal to the increase, by the effect of this change, of a certain magnitude which is determined without ambiguity when the state of the system and its motion is known.

This magnitude, defined by Equation (2), is called the *energy of the system*.

In order to define the energy of the system, we must chose a certain state of the system once and for all, which we have designated the state 0. But this choice was arbitrary. We could have argued in the same way having chosen once and for all the state ω, different from the state 0. If we designate by $\alpha_\omega, \beta_\omega, \ldots, \lambda_\omega$ the values of the variables determining the properties of the system in the state ω, and by $u_\omega, v_\omega, w_\omega; u'_\omega, v'_\omega, w'_\omega$ the components of the velocities moving the various parts of the system in this state, we would obtain a new determination of the energy of the system, defined by the equation

$$\begin{cases} \psi(\alpha_\omega,\ldots;\, u_\omega, v_\omega,\, w_\omega\ldots|\alpha,\ldots;\, u, v,\, w\ldots) \\ \quad = \varepsilon(\alpha,\ldots;\, u, v,\, w\ldots). \end{cases} \tag{2a}$$

Let us evaluate the difference between the corresponding values of these two determinations of energy.

The Equations (2) and (2a) yield

$$\begin{aligned} &\varepsilon(\alpha,\ldots;\, u, v,\, w\ldots) - \zeta(\alpha,\ldots;\, u, v,\, w\ldots) \\ &\quad = \psi(\alpha_\omega,\ldots;\, u_\omega, v_\omega,\, w_\omega\ldots|\alpha,\ldots;\, u, v,\, w\ldots) - \\ &\qquad \psi(\alpha_0,\ldots;\, u_0, v_0,\, w_0\ldots|\alpha,\ldots;\, u, v,\, w\ldots). \end{aligned}$$

But [296] Equation (3) shows that we have

$$\begin{aligned} &\psi(\alpha_0,\ldots;\, u_0, v_0,\, w_0\ldots|\alpha,\ldots;\, u, v,\, w\ldots) = \\ &\quad - \psi(\alpha,\ldots;\, u, v,\, w\ldots|\alpha_0,\ldots;\, u_0, v_0,\, w_0\ldots). \end{aligned}$$

Accordingly,

$$\begin{aligned}&\varepsilon(\alpha,\ldots;\, u, v,\, w\ldots) - \zeta(\alpha,\ldots;\, u, v,\, w\ldots)\\ &\quad = \psi(\alpha_\omega,\ldots;\, u_\omega, v_\omega,\, w_\omega\ldots|\alpha,\ldots;\, u, v,\, w\ldots) +\\ &\qquad \psi(\alpha,\ldots;\, u, v,\, w\ldots|\alpha_0,\ldots;\, u_0, v_0,\, w_0\ldots),\end{aligned}$$

or, in virtue of Equation (1)[2]

$$\begin{aligned}&\varepsilon(\alpha,\ldots;\, u, v,\, w\ldots) - \zeta(\alpha,\ldots;\, u, v,\, w\ldots) =\\ &\quad \psi(\alpha_\omega,\ldots;\, u_\omega, v_\omega,\, w_\omega\ldots|\alpha_0,\ldots;\, u_0, v_0,\, w_0\ldots).\end{aligned}$$

The right-hand side of this equation is a constant.

Therefore, *the values of two determinations of the energy for the same state of the system differ by a constant*. This can be stated by saying that *the energy is determined up to a constant*.

4.2 The Kinetic Energy[3] and the Internal Energy

Every transformation undergone by a system can be decomposed into two elements. First, there is a *change of state*: the variables defining the state of the system pass from the values $\alpha_1, \beta_1, \ldots, \lambda_1$ to the values $\alpha_2, \beta_2, \ldots, \lambda_2$. Second, there is a *change of motion*: the components of the velocities with which the elementary parts of the material of the system move pass from the values $u_1, v_1, w_1, u'_1, v'_1, w'_1, \ldots$ to the values $u_2, v_2, w_2, u'_2, v'_2, w'_2, \ldots$. The following convention, as arbitrary as the preceding ones, rests on the distinction between these two elements of any transformation:

> FOURTH CONVENTION.—*The mechanical work done by the external bodies on a system during a transformation of the system is the sum of two terms: the one depends on the change of state of the system* [297] *and not on its movement, and the other depends on the change of movement of the system but not on its state.*

This convention is expressed by the identity:

$$\left\{\begin{aligned}&\psi(\alpha_1,\ldots;\, u_1, v_1,\, w_1\ldots|\alpha_2,\ldots;\, u_2, v_2,\, w_2\ldots)\\ &\quad = \varphi(\alpha_1,\ldots\lambda_1|\alpha_2,\ldots,\lambda_2) + \chi(u_1, v_1,\, w_1\ldots|\, u_2, v_2,\, w_2\ldots).\end{aligned}\right. \tag{4}$$

In virtue of this Equation (4), Equation (2) becomes

$$\left\{\begin{aligned}&\zeta(\alpha,\ldots;\, u, v,\, w\ldots) =\\ &\quad \varphi(\alpha_0,\ldots\lambda_0|\alpha,\ldots,\lambda) + \chi(u_0, v_0,\, w_0\ldots|\, u, v,\, w\ldots).\end{aligned}\right. \tag{5}$$

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[2] [Where ε as it stands in the following equation replaces ζ in the original.]

[3] force vivre.

The quantities $\alpha_0, \beta_0, \dots, \lambda_0$ are chosen once and for all, and the quantity

$$\varphi(\alpha_0, \dots \lambda_0 | \alpha, \dots, \lambda)$$

is therefore only a function of the variables $\alpha, \beta, \dots, \lambda$, so we can put

$$\varphi(\alpha_0, \dots \lambda_0 | \alpha, \dots, \lambda) = U\,(\alpha, \dots, \lambda) \tag{6}$$

Similarly, the quantities $u_0, v_0, w_0 \dots$ are chosen once and for all, and the quantity

$$\chi(u_0, v_0,\ w_0 \dots |\ u, v,\ w \dots)$$

is therefore a function of the variables $u, v, w, \dots$ only, so we can put

$$\chi(u_0, v_0,\ w_0 \dots |\ u, v,\ w \dots) = K\,(u, v,\ w \dots) \tag{7}$$

In virtue of Equations (6) and (7), Equation (5) becomes

$$\varepsilon(\alpha, \dots; u, v, w \dots) = U(\alpha, \beta, \dots, \lambda) + \frac{\mathfrak{T}}{E} \tag{8}$$

> *The energy of a system is the sum of two terms, the one that depends only on the state of the system and not at all on its motion, and* [298] *the other, independent of the state of the system, that is known when the velocity of each of the elementary parts of the system is known.*

The first term is called the *potential energy* or the *internal energy*; the second is called the *actual energy* or the *kineticenergy*. We will try to determine the form of the latter.

To begin with, we note that the velocities designated by $u_0, v_0, w_0, \dots$ are chosen arbitrarily. Henceforth we agree to take

$$u_0 = 0, v_0 = 0, w_0 = 0, \dots$$

Now, in accordance with Equation (7), the function $K(u, v, w, \dots)$ equals 0 if we have

$$u = u_0, \quad v = v_0, \quad w = w_0, \dots$$

Consequently, we are henceforth assured that *the function*

$$K(u, v, w, \dots)$$

equals 0 *when we have*

$$u = 0, \quad v = 0, \quad w = 0, \dots$$

Second, we will build on a convention that might be regarded as unavoidable, which we state as follows:

> FIFTH CONVENTION.—*When a system is formed from several parts which are independent of one another and infinitely distant from one another, the mechanical work accomplished during any change of the system by the bodies external to the system is the sum of the mechanical work accomplished during the change corresponding to each of the parts by the bodies external to these parts.*

From this statement the following consequences are easily deduced:

> *When a system is formed from several parts which are independent* [299] *of one another and infinitely distant from one another, the internal energy of the system is the sum of the internal energies of the isolated parts, and the kinetic energy of the system is the sum of the kinetic energy of the isolated parts.*

Since the kinetic energy does not depend on the state of the system, we can, in order to determine the form of this energy, mentally decompose the system into infinitesimal material parts, isolate these material parts from one another, and disperse them into space so that they become infinitely separated. This operation changes the state of the system, but not its kinetic energy, if care is taken to preserve for each material particle, after the operation, the velocity which it had before the operation.

But after this operation the kinetic energy of the system is the sum of the kinetic energies of the various parts which compose it. We are therefore reduced to determining the form of the kinetic energy of an infinitesimal portion of matter.

Let u, v, w be the components of the velocity of an infinitesimal portion of material. The kinetic energy will be a function, $k(u, v, w)$, of u, v, w, where the form of the function k depends on the nature of the material particle, but not on its state. For a given particle, the form of this function is invariable; it is this form that we wish to know.

> SIXTH CONVENTION.—*The bodies external to an infinitesimal system always perform the same mechanical work when, beginning at rest, they impart a velocity of the same magnitude, whatever the direction in space of this velocity.*

This convention, which amounts to saying that, in absolute space, all directions are equivalent, might be regarded as logically necessary. It immediately entails this consequence: *The function $k(u, v, w)$ does not depend separately on the three components u, v, w of the velocity V, but only on the magnitude of this latter velocity*. We can replace the symbol $k(u, v, w)$ by the symbol $k(V)$.

> SEVENTH CONVENTION.—[300] *The mechanical work done by the external bodies in imparting a certain velocity to a particle originally at rest is always mechanical work with the same sign.*

We will agree to count such mechanical work as *positive*. The function $k(V)$ will then be essentially positive.

> EIGHTH CONVENTION.—*Let P, P' be two material particles. If the bodies external to these two particles perform the same mechanical work to impart to both a certain velocity V_0,*

> *then they will also perform the same mechanical work when imparting to each the same velocity V, whatever this latter velocity might be.*

In other words, the equation

$$k(V) = k'(V)$$

cannot hold for a certain value V_0 of V without holding identically.

Given this convention, let us consider a particle to which a function $k(V)$ corresponds. Divide it into very small parts. These parts will have as their kinetic energy $x(V), x'(V), \ldots$, respectively. We know that the kinetic energy $k(V)$ of the particle[4] will have the value

$$k(V) = x(V) + x'(V) + \ldots. \tag{9}$$

Moreover, each of the quantities $x(V), x'(V), \ldots$ is positive, and each is therefore less than $k(V)$. Thus, *if a material element is a part of another material element, then for a given velocity it has less kinetic energy*. Moreover, it is evident that *the kinetic energy of a material element for a given velocity varies continuously if the amount of matter enclosing this element is continuously increased or decreased*. By appealing to these two propositions, the following proposition can be easily demonstrated: *Given a material particle* P, *it is always possible, for any integer* N, *to divide it into* N [301] *particles which, for a given value, have the same kinetic energy*. The preceding convention shows that *these* N *particles always have the same kinetic energy if they all move with the same velocity, whatever this velocity may be*. If this proposition is combined with Equation (9), it is easily seen that, *for a given velocity, the kinetic energy of each of these particles is an Nth part of the kinetic energy of the particle* P.

Take any two material elements P and P′ whose kinetic energies are represented by the functions $k(V)$ and $k'(V)$. Let V_0 be a particular value of V. Consider the ratio $k'(V_0)/k(V_0)$ and suppose first that the ratio is commensurable.

Suppose[5]

$$\frac{k'(V_0)}{k(V_0)} = \frac{N'}{N},$$

where N and N′ are integers having no common factor.

Let the particle P be divided into N elements $\varpi, \ldots$ having, for a given velocity, the kinetic energies $x(V), \ldots$ equal to one another and to $k(V)$/N.

Let the particle P′ be divided into N′ elements $\varpi', \ldots$ having, for a given velocity, the kinetic energies $x'(V)$,[6] … equal to one another and to $k'(V)/\mathrm{N}'$.

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[4] *la première partie*.

[5] [The original reads $\frac{N'}{N'}$ on the right-hand side.]

[6] [$x(V)$ in the original.]

We have

$$x\,(V_0) = \frac{k\,(V_0)}{N}, \quad x'\,(V_0) = \frac{k'\,(V_0)}{N'},$$

and consequently,

$$x\,(V_0) = x'\,(V_0)\,.$$

Then, given the preceding convention, whatever V may be,

$$x\,(V) = x'\,(V)\,,$$

so that the equations

$$k\,(V) = Nx\,(V)\,, \quad k'(V) = N'x'(V)$$

[302] yield

$$\frac{k\,(V)}{k'\,(V)} = \frac{N}{N'} = \frac{k\,(V_0)}{k'\,(V_0)}.$$

The kinetic energies which correspond to the same velocity for two different material elements stand in a ratio which is independent of this velocity.

We have just proved this proposition for the case where the ratio $k'(V_0)/k(V_0)$ is commensurable. But it is evidently general, because if the ratio $k'(V_0)/k(V_0)$ were to vary with V, it would be a continuous function of V. Therefore, for certain values of V, it would pass through commensurable values; the preceding argument would then show that the hypothesis according to which $k'(V)/k(V)$ varies with V is absurd.

Consider two bodies of any finite extension, C and C$'$, and suppose that all the points of these two bodies move at a certain velocity V. Let $K(V)$ and $K'(V)$ be their kinetic energies. Each of these kinetic energies is the sum of energies which, for the same velocity, the various material elements into which each of these two bodies might be supposed divided would have. Consequently, it is not difficult to deduce from the preceding proposition that *the ratio $K'(V)/K\,(V)$ is independent of the velocity V*; *it depends only on the nature of the two bodies* C *and* C$'$.

Take a definite body Γ, for example the standard kilogram in the Archives. Suppose that all the points of this body move at the same velocity V. Let $\chi(V)$ be the kinetic energy of the body in these circumstances.

Then let C be any other body, finite or infinitesimal. Suppose that all the points of this body move at the same velocity V.

Let $K(V)$ be the kinetic energy of the body C under these conditions, and put

$$K(V) = M\chi(V). \tag{10}$$

Regarding [303] the number M defined by this Equation (10), we can immediately affirm the following propositions:

1. *The number* M *does not depend on the velocity V; it only depends on the nature of the bodies* Γ *and* C;
2. *The number* M *is essentially positive*;
3. *The number* M *associated with an infinitesimal material element is infinitesimal like this element*;
4. *The number* M *connected with a collection of bodies is equal to the sum of the analogous numbers connected with each of the various bodies comprising this collection*;
5. *For the body* Γ, *the number* M *is equal to* 1.

The number M designates the *mass* of the body C. The body Γ is said to constitute the *standard mass* or the *unit of mass*.

It can be seen that the mass of a body is proportional to the mechanical work that must be done on it by the bodies external to it in order to take it from a state of rest to a state of motion in which all its points move at a given velocity.

Consider any system whose various elementary parts P, P′, P″, ... move at velocities $V, V', V'', \ldots$, whatever they may be. The kinetic energy of the system is the sum of the kinetic energies of the various parts. Now, if the masses of the elements P, P′, P″, ... are designated by $m, m', m'', \ldots$, then these partial kinetic energies would, in view of Equation (10), have the respective values

$$m\chi(V), m'\chi(V'), m''\chi(V''), \ldots$$

The kinetic energy of the system therefore has the value

$$K = m\chi(V) + m'\chi(V') + m''\chi(V'') + \ldots = \Sigma m\chi(V). \tag{11}$$

The form of this kinetic energy will therefore be completely known to us if we determine the form of the function $\chi(V)$. In order to do this, we appeal to a new convention.

> NINTH CONVENTION.—[304] *In order to impart a certain velocity in a certain direction D on all the points of a material element, the external bodies must perform the same mechanical work, whether the material element starts from rest or is already in motion with any velocity whatever in a direction D′, normal to D.*

We accept this convention which, however natural it might strike us, has by no means the character of a logical necessity.

Let *V* be a velocity and *u, v, w* its components along three rectangular coordinates O*x*, O*y*, O*z*. Suppose these three components are positive. Take a material element of mass *m* and give it a velocity *u* in the direction O*x*. We will perform mechanical work of magnitude

$$g_1 = m\chi(u)$$

Let us now impart to this element with velocity u in the direction Ox a velocity v in the direction Oy. In accordance with the preceding convention, the mechanical work done in this second change is the same as if we had imparted the velocity in the direction Oy to the moving body starting at rest, and therefore is of the magnitude

$$g_2 = m\chi(v).$$

To this element now moving with the two velocities u along Ox and v along Oy, we apply mechanical work capable of imparting to it a velocity w along Oz. This mechanical work, equal by the preceding convention to that which would impart a velocity along Oz to a body starting at rest, takes the value

$$g_3 = m\chi(w).$$

These three changes together take the moving body from rest to a velocity V. The mechanical work done in the three changes taken together, which has the value $(g_1 + g_2 + g_3)$, must be equal to $m\chi(V)$.

We [305] therefore have the identity

$$\chi(V) = \chi(u) + \chi(v) + \chi(w).$$

Differentiating this identity with respect to u, and using the equation

$$u^2 + v^2 + w^2 = V^2,$$

we find

$$\frac{d\chi(u)\big/du}{d\chi(V)\big/dV} = \frac{u}{V}.$$

The values of u and V are arbitrary. It can therefore be seen that $d\chi(V)\big/dV$ should be proportional to V. Noting, in addition, that $\chi(V)$ must go to zero with V yields the conclusion:

The function $\chi(V)$ is proportional to V^2.

We put

$$\chi(V) = \frac{V^2}{2E}, \tag{12}$$

where E is an *essentially positive* quantity independent of V.

Then, from Equation (11), the kineticenergy[7] of any system is given by the formula

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[7] *l'énergie cinétique.*

$$K = \frac{1}{E}\sum\frac{mV^2}{2}. \tag{13}$$

The quantity

$$\mathfrak{T} = \sum\frac{mV^2}{2} \tag{14}$$

is [also] called the *kinetic energy*[8] *of the system.*

The constant E is called the *mechanical equivalent of heat;* we will see the reason for this later. The value of [306] this constant depends on the units of length, time, mass and mechanical work. Equation (12) shows, in fact, that if the standard mass Γ at rest is given a velocity which makes it traverse a unit of length during a unit of time, the mechanical work done should be numerically equal to $\frac{1}{2}E$.

From the Equations (8), (13) and (14), the energy of any system is given by the formula

$$\varepsilon(\alpha, \ldots; u, v, w \ldots) = U(\alpha, \beta, \ldots, \lambda) + \frac{\mathfrak{T}}{E}. \tag{15}$$

It remains to state one last convention concerning the internal energy $U(\alpha, \beta, \ldots, \lambda)$.

> TENTH CONVENTION[9].—*The value of the internal energy of a system does not change when its position in absolute space alone changes, without changing any other properties of the system.*

Thus, among the variables $\alpha, \beta, \ldots, \lambda$ there are none figuring in the expression $U(\alpha, \beta, \ldots, \lambda)$ which serve solely to fix the absolute position of the system in space.

4.3 The Principle of the Conservation of Energy

The conventions enumerated above have led us to define the form of a certain algebraic quantity appropriate to serve as the symbol for the notion of the mechanical work done during a transformation of a system by the bodies external to the system. This algebraic quantity is equal to the increase in the total energy of the system brought about by the transformation.

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[8] *force vivre.* [Since (14) is how the term "kinetic energy" is now standardly used, Duhem's archaic term is not preserved in this translation. Of the terms introduced by (13) and (14), $\mathfrak{T}$ is the one Duhem uses most frequently, dividing by E as appropriate (see e.g. (15) below).]

[9] This convention might seem *evident* to some minds. If, however, it is noted that the internal energy of the system depends on the *absolute* movement of the system, it can be seen that it would be by no means *absurd* to regard it as dependent on its *absolute* position in space.

But in the case where no external body interacts with the system, the mechanical work done by the external bodies during a change [307] should evidently be equal to 0. We are therefore led to state the following proposition:

> *When a material system, isolated in space, undergoes any transformation, the total energy of the system remains unchanged by the effect of this transformation.*

This proposition, expressed by the equation

$$U(\alpha, \beta, \ldots, \lambda) + \frac{\mathfrak{T}}{E} = const., \tag{16}$$

constitutes the *principle of the conservation of energy*.

It differs from everything that has been said so far, which has been of an arbitrary character. In the final analysis, we are absolutely free to consider the quantity[10]

$$G = U(\alpha_2, \beta_2, \ldots, \lambda_2) + \frac{\mathfrak{T}_2}{E} - U(\alpha_1, \beta_1, \ldots, \lambda_1) - \frac{\mathfrak{T}_1}{E},$$

and give it whatever name we like, for example the name *mechanical work done* by the bodies external to the system. But when we state that, in every transformation of an isolated system, there exists a quantity of the form

$$U(\alpha, \beta, \ldots, \lambda) + \frac{\mathfrak{T}}{E},$$

which remains invariable, we state a proposition whose consequences may confirm or be contrary to experience. It is a proposition that we cannot accept or reject as the fancy takes us. In a word, it is a *physical hypothesis*, the first that we have encountered so far. The purpose of the considerations in Sections 4.1 and 4.2 was to introduce this hypothesis, which we have been led to formulate; they do not prove it. It is for experience to verify its immediate and more distant consequences. [308]

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[10] [The third term on the right is $U(\alpha_1, \beta_3, \ldots, \lambda_1)$ in the original followed by the sign +.]

Chapter 5
Work and Quantity of Heat

5.1 The Establishment of a Fundamental Equation

Consider a system $\sum$, isolated in space, which can be divided into two independent systems, S and S$'$.

Let $\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$ be the variables determining the position of the system S, isolated in space, and its state. Of these variables, $\alpha, \beta, \ldots, \lambda$ are those which, relative to system S, figure in the Equations (1) of Chapter 3, whilst $a, b, \ldots, l$ do not figure there.

Similarly, let $\alpha', \beta', \ldots, \lambda', a', b', \ldots, l'$ be the variables determining the position and state of the system S$'$, isolated in space.

If the system S is isolated in space, its internal energy will be a certain function of $\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$, which we will designate by

$$U(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l).$$

Its kinetic energy will be a quadratic form of the variables

$$u = \frac{d\alpha}{dt}, \quad v = \frac{d\beta}{dt}, \ \ldots, \ w = \frac{d\lambda}{dt}$$

which may depend on the variables $\alpha, \beta, \ldots, \lambda$ in some way, but not on the variables $a, b, \ldots, l$. Let $\mathfrak{T}$ be this kinetic energy.

If the system S$'$ is isolated in space, its internal energy will be a certain function of $\alpha', \beta', \ldots, \lambda', a', b', \ldots, l'$ which we will designate by

$$U'(\alpha', \beta', \ldots, \lambda', a', b', \ldots, l').$$

Its kinetic energy will be a quadratic form of the variables

$$u' = \frac{d\alpha'}{dt}, \quad v' = \frac{d\beta'}{dt}, \ \ldots, \ w' = \frac{d\lambda'}{dt}$$

which [309] may depend on the variables $\alpha', \beta', \ldots, \lambda'$ in some way, but not on the variables $a', b', \ldots, l'$. Let $\mathfrak{T}'$ be this kinetic energy.

Let us consider the system $\sum$.

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
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If the variables

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l,$$

$$\alpha', \beta', \ldots, \lambda', a', b', \ldots, l',$$

are known, then the position and the state of each of the two systems S and S′ which compose it are known. The state of the system $\sum$ is therefore known. The internal energy of the system $\sum$ will be a function of these variables. We designate it by

$$\Upsilon(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, \alpha', \beta', \ldots, \lambda', a', b', \ldots, l').$$

Clearly, we can write

$$\begin{aligned} \Upsilon = {} & U(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l) + U'(\alpha', \beta', \ldots, \lambda', a', b', \ldots, l') \\ & + \Psi(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, \alpha', \beta', \ldots, \lambda', a', b', \ldots, l'). \end{aligned} \tag{1}$$

The kinetic energy of the system $\sum$ is clearly equal to $(\mathfrak{T} + \mathfrak{T}')$.

The total energy of the system $\sum$ will have the value

$$\varepsilon = \Upsilon + \frac{1}{E}(\mathfrak{T} + \mathfrak{T}'). \tag{2}$$

Let us write that the infinitesimally small change undergone by the system $\sum$ during the time *dt* leaves the value of this energy ε invariable.

Put

$$\begin{aligned} \varphi &= \frac{da}{dt}, \quad \chi = \frac{db}{dt}, \ \ldots, \ \psi = \frac{dl}{dt}, \\ \varphi' &= \frac{da'}{dt}, \quad \chi' = \frac{db'}{dt}, \ \ldots, \ \psi' = \frac{dl'}{dt}. \end{aligned}$$

In [310] accordance with Equation (1), Υ undergoes, during *dt*, a variation

$$\begin{aligned} \delta\Upsilon = \Bigg[& \left(\frac{\partial U}{\partial \alpha} + \frac{\partial \Psi}{\partial \alpha}\right) u + \left(\frac{\partial U}{\partial \beta} + \frac{\partial \Psi}{\partial \beta}\right) v + \ldots + \left(\frac{\partial U}{\partial \lambda} + \frac{\partial \Psi}{\partial \lambda}\right) w \\ & \left(\frac{\partial U}{\partial a} + \frac{\partial \Psi}{\partial a}\right) \varphi + \left(\frac{\partial U}{\partial b} + \frac{\partial \Psi}{\partial b}\right) \chi + \ldots + \left(\frac{\partial U}{\partial l} + \frac{\partial \Psi}{\partial l}\right) \psi \\ & \left(\frac{\partial U'}{\partial \alpha'} + \frac{\partial \Psi}{\partial \alpha'}\right) u' + \left(\frac{\partial U'}{\partial \beta'} + \frac{\partial \Psi}{\partial \beta'}\right) v' + \ldots + \left(\frac{\partial U'}{\partial \lambda'} + \frac{\partial \Psi}{\partial \lambda'}\right) w' \\ & \left(\frac{\partial U'}{\partial a'} + \frac{\partial \Psi}{\partial a'}\right) \varphi' + \left(\frac{\partial U'}{\partial b'} + \frac{\partial \Psi}{\partial b'}\right) \chi' + \ldots + \left(\frac{\partial U'}{\partial l'} + \frac{\partial \Psi}{\partial l'}\right) \psi' \Bigg] \end{aligned}$$

As for the variation undergone by the kinetic energy during the same time, a known method allows this to be put in the form

$$\begin{aligned}\delta\left(\mathfrak{T}+\mathfrak{T}'\right) = -\Bigg[&\left(\frac{\partial\mathfrak{T}}{\partial\alpha} - \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u}\right)u + \left(\frac{\partial\mathfrak{T}}{\partial\beta} - \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial v}\right)v + \dots \\ &+ \left(\frac{\partial\mathfrak{T}}{\partial\lambda} - \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial w}\right)w + \left(\frac{\partial\mathfrak{T}'}{\partial\alpha'} + \frac{d}{dt}\frac{\partial\mathfrak{T}'}{\partial u'}\right)u' \\ &+ \left(\frac{\partial\mathfrak{T}'}{\partial\beta'} + \frac{d}{dt}\frac{\partial\mathfrak{T}'}{\partial v'}\right)v' + \dots + \left(\frac{\mathfrak{T}'}{\partial\lambda'} + \frac{d}{dt}\frac{\partial\mathfrak{T}'}{\partial w'}\right)w'\Bigg]\,dt.\end{aligned}$$

If we say that the total energy, ε, given by Equation (2), remains invariable, we find the following equation:

$$\left\{\begin{aligned}&\left[\frac{\partial U}{\partial\alpha} + \frac{\partial\Psi}{\partial\alpha} - \frac{1}{E}\left(\frac{\partial\mathfrak{T}}{\partial\alpha} - \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u}\right)\right]u + \dots \\ &+ \left[\frac{\partial U}{\partial\lambda} + \frac{\partial\Psi}{\partial\lambda} - \frac{1}{E}\left(\frac{\partial\mathfrak{T}}{\partial\lambda} - \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial w}\right)\right]w \\ &+ \left(\frac{\partial U}{\partial\alpha} + \frac{\partial\Psi}{\partial\alpha}\right)\varphi + \dots + \left(\frac{\partial U}{\partial l} + \frac{\partial\Psi}{\partial l}\right)\psi \\ &+ \left[\frac{\partial U'}{\partial\alpha'} + \frac{\partial\Psi}{\partial\alpha'} - \frac{1}{E}\left(\frac{\partial\mathfrak{T}'}{\partial\alpha'} - \frac{d}{dt}\frac{\partial\mathfrak{T}'}{\partial u'}\right)\right]u' + \dots \\ &+ \left[\frac{\partial U'}{\partial\lambda'} + \frac{\partial\Psi}{\partial\lambda'} - \frac{1}{E}\left(\frac{\partial\mathfrak{T}'}{\partial\lambda'} - \frac{d}{dt}\frac{\partial\mathfrak{T}'}{\partial w'}\right)\right]w' \\ &+ \left(\frac{\partial U'}{\partial a'} + \frac{\partial\Psi}{\partial a'}\right)\varphi' + \dots + \left(\frac{\partial U'}{\partial l'} + \frac{\partial\Psi}{\partial l'}\right)\psi' = 0.\end{aligned}\right. \tag{3}$$

This [311] fundamental equation will serve as our point of departure for the considerations which are the object of the present chapter.

5.2 On Work[1]

Let us put

$$\left\{\begin{array}{ll} E\dfrac{\partial\Psi}{\partial\alpha} = -A, & E\dfrac{\partial\Psi}{\partial a} = -\mathscr{A}, \\ E\dfrac{\partial\Psi}{\partial\beta} = -B, & E\dfrac{\partial\Psi}{\partial b} = -\mathscr{B}, \\ \dots\dots\dots\dots, & \dots\dots\dots\dots, \\ E\dfrac{\partial\Psi}{\partial\lambda} = -L, & E\dfrac{\partial\Psi}{\partial l} = -\mathscr{L}, \end{array}\right. \tag{4}$$

---

[1] *travail.*

We will say that the quantities $A, B, \ldots, L$ represent the *forces* exerted by the system S′ on the system S, and that the quantities $\mathcal{A}, \mathcal{B}, \ldots, \mathcal{L}$ represent the *influences* exerted by the system S′ on the system S. The totality of forces and influences exerted by the system S′ on the system S are called the *actions* of the system S′ on the system S.

The quantity

$$(Au + Bv + \ldots + Lw)dt$$

is the *work* done during the time dt by the *forces* that the system S′ exerts on the system S. The quantity

$$(\mathcal{A}\varphi + \mathcal{B}\chi + \ldots + \mathcal{L}\psi)dt$$

is the *work* done during the time dt by the *influences* that the system S′ exerts on the system S. The sum of these two quantities is the *work* done during the time dt by the *actions* of the system S′ on the system S.

Consider a virtual change of the system S; let

$$\delta\alpha, \delta\beta, \ldots, \delta\lambda, \delta a, \delta b, \ldots, \delta l$$

be the variations undergone as a result of this change by the variables

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l.$$

The [312] expressions

$$A\delta\alpha + B\delta\beta + \ldots + L\delta\lambda,$$

$$\mathcal{A}\delta a + \mathcal{B}\delta b + \ldots + \mathcal{L}\delta l,$$

$$A\delta\alpha + B\delta\beta + \ldots + L\delta\lambda + \mathcal{A}\delta a + \mathcal{B}\delta b + \ldots + \mathcal{L}\delta l,$$

are called, respectively,

The *virtual work of the forces* done by the system S′ on the system S;

The *virtual work of the influences* exerted by the system S′ on the system S;

The *virtual work of the actions* done by the system S′ on the system S.

The work (real or virtual) of the actions of the system S′ on the system S has, in accordance with Equations (4), the value

$$-E\left(\frac{\partial\Psi}{\partial\alpha}\delta\alpha + \ldots + \frac{\partial\Psi}{\partial\lambda}\delta\lambda + \frac{\partial\Psi}{\partial a}\delta a + \ldots + \frac{\partial\Psi}{\partial l}\delta l\right).$$

This is not, in general, the total differential of a uniform function of the variables $\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$ determining the system S. In order to transform this expression into a total differential, it is necessary to add the term

$$-E\left(\frac{\partial\Psi}{\partial\alpha'}\delta\alpha' + \ldots + \frac{\partial\Psi}{\partial\lambda'}\delta\lambda' + \frac{\partial\Psi}{\partial a'}\delta a' + \ldots + \frac{\partial\Psi}{\partial l'}\delta l'\right),$$

that is to say, the work of the actions of the system S on the system S′.

Thus, the work of actions of the system S′ on the system S is not, in general, a total differential, but *the work of the mutual actions of the two systems* S *and* S′ *is always the total differential of a function which is defined in a uniform way when the state of the system* $\sum$ *constituted by the aggregate of the two systems* S *and* S′ *is known.*

The function $E\Psi$ whose total differential, changed in sign, [313] gives the work of the mutual actions of the two systems S and S′ is called the *potential* of these actions.

Like the function Υ, this potential depends on the properties of the two systems S and S′ and on their relative position, *but not on the absolute position that the system* $\sum$ *occupies in space;* the same holds for the mutual actions of the two systems S and S′.

This theorem can be generalised and extended to a system $\sum$ formed from n independent systems S_1, S_2, ... , S_n. In order not to complicate the notation, but without seriously infringing on generality, we will suppose that the system $\sum$ is formed of just three partial systems S_1, S_2, S_3.

Let

$$\alpha_1, \ldots, \lambda_1, a_1, \ldots, l_1,$$

$$\alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2,$$

$$\alpha_3, \ldots, \lambda_3, a_3, \ldots, l_3$$

be the three systems of variables defining, respectively, the state of each of the three systems S_1, S_2, S_3.

Let

$$U_1(\alpha_1, \ldots, \lambda_1, \alpha_1, \ldots, l_1),$$

$$U_2(\alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2),$$

$$U_3(\alpha_3, \ldots, \lambda_3, a_3, \ldots, l_3)$$

be the internal energies of these systems considered in isolation.

The internal energy of the system $\sum$ can evidently be put in the following form:

$$\begin{aligned} &\Upsilon = U_1 + U_2 + U_3 + \\ &\Psi(\alpha_1, \ldots, \lambda_1, a_1, \ldots, l_1, \alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2, \alpha_3, \ldots, \lambda_3, a_3, \ldots, l_3). \end{aligned} \tag{5}$$

In order to construct the function Ψ, we can proceed in the following way. We envisage first the system $\sum_{23}$ formed from the composition of the two systems S_2 and S_3, whose internal energy will have the [314] form

$$\Upsilon_{23} = U_2 + U_3 + \Psi_{23}(\alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2, \alpha_3, \ldots, \lambda_3, a_3, \ldots, l_3). \tag{6}$$

Then we combine the system $\sum_{23}$ with the system S_1 in such a way as to form system $\sum$. The internal energy of this system will be of the form

$$\begin{aligned}&\Upsilon = U_1 + \Upsilon_{23} + \\ &X_1(\alpha_1,\ldots,\lambda_1,a_1,\ldots,l_1,\alpha_2,\ldots,\lambda_2,a_2,\ldots,l_2,\alpha_3,\ldots,\lambda_3,a_3,\ldots,l_3).\end{aligned} \tag{7}$$

Comparison of formulas (5), (6) and (7) yields the equation

$$\begin{aligned}&\Psi = \Psi_{23}(\alpha_2,\ldots,\lambda_2,a_2,\ldots,l_2,\alpha_3,\ldots,\lambda_3,a_3,\ldots,l_3) + \\ &X_1(\alpha_1,\ldots,\lambda_1,a_1,\ldots,l_1,\alpha_2,\ldots,\lambda_2,a_2,\ldots,l_2,\alpha_3,\ldots,\lambda_3,a_3,\ldots,l_3).\end{aligned} \tag{8}$$

The definitions put forward above show us that the actions exerted by the system S_1 on the system $\sum_{23}$, that is, the composite of systems S_2, S_3, are determined by the equations

$$\begin{cases} A_1 = -E\dfrac{\partial X_1}{\partial \alpha_1}, & \mathcal{a}_1 = -E\dfrac{\partial X_1}{\partial a_1}, \\ \ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots, \\ L_1 = -E\dfrac{\partial X_1}{\partial \lambda_1}, & \mathcal{L}_1 = -E\dfrac{\partial X_1}{\partial l_1}, \end{cases} \tag{4a}$$

which allows us to write, in virtue of Equation (8),

$$\begin{cases} A_1 = -E\dfrac{\partial \Psi_1}{\partial \alpha_1}, & \mathcal{a}_1 = -E\dfrac{\partial \psi_1}{\partial a_1}, \\ \ldots\ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots, \\ L_1 = -E\dfrac{\partial \Psi_1}{\partial \lambda_1}, & \mathcal{L}_1 = -E\dfrac{\partial \psi_1}{\partial l_1}. \end{cases} \tag{4b}$$

The actions that the system S_2 undergoes on the part of the aggregate of systems S_3 and S_1, and the actions that the system S_3 undergoes on the part of the aggregate [315] of systems S_1 and S_2 are determined analogously. The following proposition is easily deduced:

> *In a complex system formed from several independent systems, each of the latter undergo certain actions by the others in conjunction. All these actions, taken together, support a potential.*
>
> *This potential $E\Psi$ depends on the properties of the various independent systems composing the complex system, and on their relative position. It does not depend on the absolute position that the complex system occupies in space.*

Demonstrations analogous to those furnishing the Equation (8) allow us to write, using similar notations, the equations

$$\begin{aligned}\Psi &= \Psi_{31}(\alpha_3,\dots,\lambda_3,a_3,\dots,l_3,\alpha_1,\dots,\lambda_1,a_1,\dots,l_1)\\ &\quad + \mathrm{X}_2(\alpha_2,\dots,\lambda_2,a_2,\dots,l_2,\alpha_3,\dots,\lambda_3,a_3,\dots,l_3,\alpha_1,\dots,\lambda_1,a_1,\dots,l_1).\\ \Psi &= \Psi_{12}(\alpha_1,\dots,\lambda_1,a_1,\dots,l_1,\alpha_2,\dots,\lambda_2,a_2,\dots,l_2)\\ &\quad + \mathrm{X}_3(\alpha_3,\dots,\lambda_3,a_3,\dots,l_3,\alpha_1,\dots,\lambda_1,a_1,\dots,l_1,\alpha_2,\dots,\lambda_2,a_2,\dots,l_2).\end{aligned} \tag{8a}$$

The Equations (8) and (8a) will clearly be verified by putting

$$\begin{cases} X_1 = \Psi_{31} + \Psi_{12},\\ X_2 = \Psi_{12} + \Psi_{23},\\ X_3 = \Psi_{23} + \Psi_{31},\end{cases} \tag{9}$$

which entail

$$\Psi = \Psi_{23} + \Psi_{31} + \Psi_{12},$$

but they do not necessarily entail the Equations (9).

Let us see to which consequences the Equations (9) lead.

The actions that the system S_2 would exert on system S_1, were these [316] two systems to exist alone, would be given by the equations

$$\begin{cases} A_{12} = -E\dfrac{\partial\Psi_{12}}{\partial\alpha_1}, & \boldsymbol{a}_{12} = -E\dfrac{\partial\Psi_{12}}{\partial a_1},\\ \dots\dots\dots\dots\dots, & \dots\dots\dots\dots\dots\dots,\\ L_{12} = -E\dfrac{\partial\Psi_{12}}{\partial\lambda_1}, & \boldsymbol{\mathcal{L}}_{12} = -E\dfrac{\partial\Psi_{12}}{\partial l_1}.\end{cases}$$

The actions that the system S_2 would exert on system S_2, were these [316] two systems to exist alone, would be given by the equations

$$\begin{cases} A_{13} = -E\dfrac{\partial\Psi_{13}}{\partial\alpha_1}, & \boldsymbol{a}_{13} = -E\dfrac{\partial\Psi_{13}}{\partial a_1},\\ \dots\dots\dots\dots\dots, & \dots\dots\dots\dots\dots\dots,\\ L_{13} = -E\dfrac{\partial\Psi_{13}}{\partial\lambda_1}, & \boldsymbol{\mathcal{L}}_{13} = -E\dfrac{\partial\Psi_{13}}{\partial l_1}.\end{cases}$$

These equations, together with Equations (4a) and (9), yield

$$\begin{array}{ll} A_1 = A_{12} + A_{13}, & \boldsymbol{a}_1 = \boldsymbol{a}_{12} + \boldsymbol{a}_{13},\\ \dots\dots\dots\dots\dots, & \dots\dots\dots\dots\dots\dots,\\ L_1 = L_{12} + L_{13}, & \boldsymbol{\mathcal{L}}_1 = \boldsymbol{\mathcal{L}}_{12} + \boldsymbol{\mathcal{L}}_{13}.\end{array}$$

From these and other analogous equations which can be demonstrated in the same way, the following theorem can be deduced:

> *In a complex system formed from several independent systems, the actions on each of the latter by all of the others is obtained by superposing the actions to which it would be subjected by each of the others if each of these others were alone placed in its presence.*

It can be seen that *this theorem, although compatible with the definition of mutual actions exerted between various systems, is not, however, a necessary consequence of it*. Whenever its exactitude is accepted in a particular theory, a hypothesis is thereby introduced.

Returning to the general study of a system $\sum$ composed of *n* independent systems [317] S_1, S_2, ... , S_n, suppose that these *n* systems are *n* bodies each one of which occupies a variable position in space but remains in the same state. We will then say that *any change of the system is a displacement without change of state*.

When the system S_i alone is displaced in space, without changing its properties, the internal energy U_i of this system remains the same. Consequently, in a displacement without change of state, each of the quantities $U_1, U_2, \ldots, U_\mathrm{n}$ remains the same. In accordance with Equation (5), the internal energy Υ of the system $\sum$ differs only by a constant from the function Ψ. Accordingly, we have the following theorem:

> *When a complex system formed from several independent systems is subjected only to displacements without change of state, the totality of the actions exerted between the various partial systems has as its potential the product of the internal energy of the complex system and the mechanical equivalent of heat.*

This theorem is used frequently in the applications of thermodynamics.

From this theorem unfolds another:

Let $\mathfrak{T}$ be the kinetic energy of the system $\sum$. The total energy of this system will have the value $\left(\Upsilon + \frac{1}{E}\mathfrak{T}\right)$. If the system $\sum$ is isolated, this total energy cannot vary. The equation

$$\Upsilon + \frac{1}{E}\mathfrak{T} = \text{const.}$$

should be upheld in any change of the system. If the system $\sum$ is subject only to displacement without change of state, this equation can be replaced by the following

$$E\Psi + \mathfrak{T} = \text{const.}$$

or

$$Ed\Psi + d\mathfrak{T} = 0.$$

Now [318] ($-Ed\Psi$) represents the work done by the actions between the systems S_1, S_2, ... , S_n, while the kinetic energy of the system $\sum$ is augmented by $d\mathfrak{T}$. We can therefore state the following theorem:

> *Consider a complex system formed of independent, isolated systems and subject only to displacements without change of state. In all real changes undergone by such a system, the kinetic energy increases by an amount equal to the work accomplished by the actions exerted between the various partial systems of which it is composed.*

We note that we have defined the forces exerted and influences exerted on a material system by another system which is independent of it. We have not defined the forces or the influences obtaining between two parts of the same system when the two parts cannot be regarded as two independent systems. Such forces and influences are sometimes spoken of in physics. Thus, in electrodynamics one speaks of the actions exerted between the various parts of the same conductor through which currents flow. When such actions are considered, it is necessary to give a special definition, and it will not come as a surprise if the actions thus defined do not satisfy certain theorems to which actions exerted between independent systems, as we have just defined them, are necessarily subject. This observation has important applications in electrodynamics and electromagnetism.

5.3 On the Quantity of Heat

Return to the fundamental Equation (3).

Let

$$\left\{\begin{aligned} &\left[\left(A - E\frac{\partial U}{\partial \alpha} + \frac{\partial \mathfrak{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial u}\right) u + \ldots\right. \\ &\quad + \left(L - E\frac{\partial U}{\partial \lambda} + \frac{\partial \mathfrak{T}}{\partial \lambda} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial w}\right) w + \left(\boldsymbol{\mathcal{A}} - E\frac{\partial U}{\partial a}\right) \varphi + \ldots \\ &\quad \left. + \left(\boldsymbol{\mathcal{L}} - E\frac{\partial U}{\partial l}\right) \psi\right] dt = EdQ, \end{aligned}\right. \tag{10}$$

$$\left\{\begin{aligned} &\left[\left(A' - E\frac{\partial U'}{\partial \alpha'} + \frac{\partial \mathfrak{T}'}{\partial \alpha'} - \frac{d}{dt}\frac{\partial \mathfrak{T}'}{\partial u'}\right) u'\right. \\ &\quad + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ &\quad + \left(L' - E\frac{\partial U'}{\partial \lambda'} + \frac{\partial \mathfrak{T}'}{\partial \lambda'} - \frac{d}{dt}\frac{\partial \mathfrak{T}'}{\partial w'}\right) w' \\ &\quad \left. + \left(\boldsymbol{\mathcal{A}}' - E\frac{\partial U'}{\partial a'}\right) \varphi' + \ldots + \left(\boldsymbol{\mathcal{L}}' - E\frac{\partial U'}{\partial l'}\right) \psi'\right] dt = E\,dQ'. \end{aligned}\right. \tag{10a}$$[2]

[319]

Taking account of Equations (4) and the analogous equations relating to the actions of the system S on the system S′, Equation (3) becomes

$$dQ + dQ' = 0. \tag{11}$$

---

[2] [In original, $\frac{\partial U'}{\partial \alpha}$ instead of $\frac{\partial U'}{\partial \alpha'}$.]

We call the quantity dQ the *quantity of heat released by the system* S during the time dt. When this quantity is negative, we say that its absolute value is the *quantity of heat absorbed* by the system S during the same time. The quantity dQ' will similarly be called the *quantity of heat* released by the system S′ during the time dt.

Thus, Equation (11) tells us that *in all real changes of a complex isolated system* $\sum$ *comprising two independent systems* S *and* S′, *one of these systems* S, S′ *releases as much heat as the other absorbs*.

Consider the system S isolated in space. If the system S′ didn't exist, all the terms comprising the left-hand side of Equation (10a) would be identically zero. The same holds for dQ' and hence, in accordance with Equation (11), for dQ. From that we have the following theorem:

> *When a system which is isolated in space undergoes a real change, it neither absorbs nor releases heat.*

Several theories of physics lead us to regard a body as able to release or absorb heat even when this body seems to us to be isolated in space. This view is only compatible with the definition we have just given of the quantity of heat released by a system if we regard the space which seems empty to us as filled by a certain [320] body, the ether. This observation helps in grasping the importance of the preceding theorem.

Put

$$\left\{\begin{array}{l} E\dfrac{\partial U}{\partial \alpha} - \dfrac{\partial \mathfrak{T}}{\partial \alpha} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial u} - A = ER_{\alpha}, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ E\dfrac{\partial U}{\partial \lambda} - \dfrac{\partial \mathfrak{T}}{\partial \lambda} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial w} - L = ER_{\lambda}, \end{array}\right. \tag{12}$$

$$\left\{\begin{array}{l} E\dfrac{\partial U}{\partial a} - \boldsymbol{\mathcal{A}} = E\boldsymbol{\mathcal{R}}_{a}, \\ \dots\dots\dots\dots\dots\dots, \\ E\dfrac{\partial U}{\partial l} - \boldsymbol{\mathcal{L}} = E\boldsymbol{\mathcal{R}}_{l}. \end{array}\right. \tag{12a}$$

We call the quantities $R_{\alpha}, \dots, R_{\lambda}, \boldsymbol{\mathcal{R}}_{a}, \dots, \boldsymbol{\mathcal{R}}_{l}$ *calorific coefficients* of the system S, subject to the action of system S′ with its motion at the instant t. We see that these coefficients depend on

1. The properties of the system S;
2. The velocities and accelerations of the various points of the system;
3. The actions of the system S′ on S.

We envisage a virtual change $\delta\alpha, \ldots, \delta\lambda, \delta a, \ldots, \delta l$, of the system S. By definition, the quantity

$$dQ = -(R_\alpha \delta\alpha + \ldots + R_\lambda \delta\lambda + \boldsymbol{\mathcal{R}}_\alpha \delta a + \ldots + \boldsymbol{\mathcal{R}}_i \delta l) \tag{13}$$

is called the *quantity of heat released by the system* S *in the virtual change under consideration.*

In can be seen that this quantity is not, in general, the total differential of a function of $\alpha, \ldots, \lambda, a, \ldots, l$, because the coefficients of $\delta\alpha, \ldots, \delta\lambda, \delta a, \ldots, \delta l$ depend, in general, on other variables.

We know that the quantity[3]

$$dW = A\delta\alpha + \ldots + L\delta\lambda + \boldsymbol{\mathcal{A}}\delta\alpha + \ldots + \boldsymbol{\mathcal{L}}\delta l \tag{14}$$

represents the virtual work of the actions exerted on the system S. [321] We will call the quantity

$$d\tau = \left(\frac{\partial \mathfrak{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial u}\right)\delta\alpha + \ldots + \left(\frac{\partial \mathfrak{T}}{\partial \lambda} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial w}\right)\delta\lambda \tag{15}$$

the *virtual work of the inertial forces applied to the system* S.

Equations (12), (12a), (13), (14) and (15) then yield the following equation, applicable to all virtual transformations of the system S,

$$E\,(dQ + dU) = dW + d\tau. \tag{16}$$

> *Multiplying the sum of the quantity of heat released by a system during a virtual change and the variation undergone by the internal energy during the same change by the mechanical equivalent of heat yields a certain product; this product is equal to the virtual work of the exterior actions and the inertial forces applied to the system.*

This proposition constitutes the most general statement of the *law of equivalence of heat and work.*

When a real change, rather than any virtual change, is at issue, Equation (16) can be modified. In this case, in fact, the work dW of the inertial forces becomes equal to the variation of the kinetic energy, with sign changed, and we can write

$$dW - E\,dQ = \frac{d}{dt}\,(EU + \mathfrak{T})\,dt. \tag{17}$$

It can be seen that, *for any real change, the quantity*

$$dW - E\,dQ$$

is a total differential.

---

[3] [For typographical reasons, Duhem's original symbol has been replaced throughout by "W".]

Consider a system $\sum$ formed of two independent partial systems S_1, S_2; let σ be the system formed by the collection of bodies outside $\sum$.

Let [322]

$$U_1(\alpha_1, \ldots, \lambda_1, a_1, \ldots, l_1), \quad U_2(\alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2)$$

be the internal energies of the systems S_1, S_2 considered in isolation.

The system $\sum$ will have as its internal energy the quantity

$$\Upsilon = U_1 + U_2 + \Psi_{12}(\alpha_1, \ldots, \lambda_1, a_1, \ldots, l_1, \alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2).$$

Let u be the internal energy of the system σ considered in isolation. The internal energy of the system formed by the aggregate $\sum\sigma$ will be given by an expression

$$\Upsilon + u + X,$$

where X depends on the variables defining the position and the properties of each of the three systems S_1, S_2, σ.

Suppose that the system $\sum$ undergoes a virtual change

$$\delta\alpha_1, \ldots, \delta\lambda_1, \delta a_1, \ldots, \delta l_1, \delta\alpha_2, \ldots, \delta\lambda_2, \delta a_2, \ldots, \delta l_2,$$

and let us find the expression for the quantity of heat dQ released by the system $\sum$. We have

$$\begin{aligned} E\,dQ = -\Bigg[& \left(E\frac{\partial\Upsilon}{\partial\alpha_1} + E\frac{\partial X}{\partial\alpha_1} - \frac{\partial\mathfrak{T}}{\partial\alpha_1} + \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u_1} \right) \delta\alpha_1 + \ldots \\ & + \left(E\frac{\partial\Upsilon}{\partial\lambda_1} + E\frac{\partial X}{\partial\lambda_1} - \frac{\partial\mathfrak{T}}{\partial\lambda_1} + \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial w_1} \right) \delta\lambda_1 \\ & + \left(E\frac{\partial\Upsilon}{\partial a_1} + E\frac{\partial X}{\partial a_1} \right) \delta a_1 + \ldots + \left(E\frac{\partial\Upsilon}{\partial l_1} + E\frac{\partial X}{\partial l_1} \right) \delta l_1 \\ & + \left(E\frac{\partial\Upsilon}{\partial\alpha_2} + E\frac{\partial X}{\partial\alpha_2} - \frac{\partial\mathfrak{T}}{\partial\alpha_2} + \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u_2} \right) \delta\alpha_2 + \ldots \\ & + \left(E\frac{\partial\Upsilon}{\partial\lambda_2} + E\frac{\partial X}{\partial\lambda_2} - \frac{\partial\mathfrak{T}}{\partial\lambda_2} + \frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial w_2} \right) \delta\lambda_2 \\ & + \left(E\frac{\partial\Upsilon}{\partial a_2} + E\frac{\partial X}{\partial a_2} \right) \delta a_2 + \ldots + \left(E\frac{\partial\Upsilon}{\partial l_2} + E\frac{\partial X}{\partial l_2} \right) \delta l_2 \Bigg]. \end{aligned}$$

But [323] the kinetic energy $\mathfrak{T}$ of the system $\sum$ is the sum of the kinetic energies T_1, T_2 of the systems S_1, S_2. It is then easily seen that the preceding equation can be written[4]

$$\begin{aligned}
E\,dQ = -\Bigg\{&\left[E\frac{\partial}{\partial\alpha_1}(U_1+\Psi_{12}+X)-\frac{\partial\mathfrak{T}}{\partial\alpha_1}+\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u_1}\right]\delta\alpha_1+\ldots\\
&+\left[E\frac{\partial}{\partial\lambda_1}(U_1+\Psi_{12}+X)-\frac{\partial\mathfrak{T}}{\partial\lambda_1}+\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial w_1}\right]\delta\lambda_1\\
&+E\frac{\partial}{\partial a_1}(U_1+\Psi_{12}+X)\;\delta a_1+\ldots+E\frac{\partial}{\partial l_1}(U_1+\Psi_{12}+X)\,\delta l_1\\
&+\left[E\frac{\partial}{\partial\alpha_2}(U_2+\Psi_{12}+X)-\frac{\partial\mathfrak{T}}{\partial\alpha_2}+\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial u_2}\right]\delta\alpha_2+\ldots\\
&+\left[E\frac{\partial}{\partial\lambda_2}(U_2+\Psi_{12}+X)-\frac{\partial\mathfrak{T}}{\partial\lambda_2}+\frac{d}{dt}\frac{\partial\mathfrak{T}}{\partial w_2}\right]\delta\lambda_2\\
&+E\frac{\partial}{\partial a_2}(U_2+\Psi_{12}+X)\;\delta a_2+\ldots+E\frac{\partial}{\partial l_2}(U_2+\Psi_{12}+X)\,\delta l_2\Bigg\}\\
=\;&E\,(dQ_1+dQ_2)
\end{aligned}$$

where dQ_1, dQ_2 designate the quantities of heat released by the two systems S_1, S_2 during the same virtual change. This leads us to the following theorem:

> *When a system is formed from several independent parts, the quantity of heat which it releases during any virtual change is equal to the algebraic sum of the quantities of heat that the various parts release during the same change.*

This theorem will prove useful in what follows.

It would be natural to include here a reflection similar to that which suggested the definition of work: it is not possible to speak of the quantity of heat released by each part of a system except in so far as each of these parts can be considered as an independent system. When the various parts of a system are not independent of one another, the phrase ‘quantity of heat released by each of them’ has no meaning.

5.4 The Classical Problem of Dynamics

Suppose that, for a certain system, the calorific coefficients

$$R_\alpha,\ldots,R_\lambda,\mathscr{R}_\alpha,\ldots,\mathscr{R}_l$$

---

[4] [A – sign at the beginning of the 5th line has been changed to +, and a bracket “}” at the end of the immediately preceding line removed.]

are all identically equal to 0, or, in other words, that the quantity of heat released by the system in any real or virtual change is identically equal to 0. Equations (12) and (12a) become

$$\left\{\begin{array}{l} E\dfrac{\partial U}{\partial \alpha} - \dfrac{\partial \mathfrak{T}}{\partial \alpha} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial u} - A = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ E\dfrac{\partial U}{\partial \lambda} - \dfrac{\partial \mathfrak{T}}{\partial \lambda} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial w} - L = 0, \end{array}\right. \tag{18}$$

$$\left\{\begin{array}{l} E\dfrac{\partial U}{\partial a} - \boldsymbol{\mathfrak{a}} = 0, \\ \dots\dots\dots\dots\dots, \\ E\dfrac{\partial U}{\partial l} - \boldsymbol{\mathfrak{L}} = 0. \end{array}\right. \tag{18a}$$

The equations of motion of a system in which friction is zero are easily recognisable. In the case usually studied in mechanics, there are no variables other than those which figure in Equations (1) of Chapter 3. There is therefore no equation of type (18a). All the equations which govern the motion of the system have the form (18), given, as is known, by Lagrange.

Clearly, the laws of dynamics fall within the laws of thermodynamics as particular cases. They can be deduced from the latter by assuming all the calorific coefficients of the system are equal to 0. But in which case is this hypothesis verified? This is a question which remains to be examined, and nothing of what has so far been said resolves the issue. In most cases, it is only solved by way of hypothesis, directly or indirectly. Moreover, we will see later that there is another method, distinct from this, of deriving the equations of dynamics from the equations of thermodynamics.

5.5 Calorimetry

Imagine [325] an isolated system itself formed from three independent systems S_1, S_2, S_3, on which we will impose certain conditions.

Let U_1, U_2, U_3 be the internal energies of the systems S_1, S_2, S_3 considered in isolation. The internal energy of the complex system formed by their composition can be written

$$\Upsilon = U_1 + U_2 + U_3 + \Psi.$$

1. Regarding the function Ψ, we assume that it has the form

$$\Psi = \Psi_{23} + \Psi_{31} + \Psi_{12},$$

the function Ψ_{ij} depending only on the variables which characterise the state of the two systems S_i, S_j. This hypothesis entails the following consequence: The actions on any of the three systems S_1, S_2, S_3 by the composite of the remaining two are obtained by adding the actions to which it is subject from each of the other two taken in isolation.

2. The actions of system S_3 on system S_1 are zero, or are such that they do no work in the changes of the system S_1 that will be studied.
3. The actions of system S_2 on system S_1 are zero, and the same holds for the actions of system S_1 on system S_2.

The following consequences arise from these two hypotheses:

In the changes of the system S_1 to be studied, the work of the external actions applying to the system is always equal to 0.

The external actions applying to the system S_2 are just the actions exerted by system S_3.

4. The quantity of heat released or absorbed by the system S_3 is constant and equal to 0.

Since the quantity of heat released by the collection S_1, S_2, S_3, which forms an isolated system, must be equal to 0, and since, on the other hand, this quantity of heat must be equal to the sum of the quantities of heat released by each of the three systems S_1, S_2, S_3, the quantity of heat dQ_2 released during the time dt by the system S_2 will be equal and of opposite sign to the quantity of heat dQ_1 released [326] by the system S_1 during the same time,

$$dQ_1 + dQ_2 = 0. \tag{19}$$

Regarding the quantity dQ_1, we can write, in virtue of Equation (10) and noting that, in accordance with our hypotheses,

$$(A_1 u_1 + \ldots + L_1 w_1 + \boldsymbol{\mathcal{A}}_1 \varphi_1 + \ldots + \boldsymbol{\mathcal{L}}_1 \psi_1) dt = 0,$$

the following equation

$$\left[\left(E\frac{\partial U_1}{\partial \alpha_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial u_1} - \frac{\partial \mathfrak{T}}{\partial \alpha_1}\right) u_1 + \ldots + \left(E\frac{\partial U_1}{\partial \lambda_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial w_1} - \frac{\partial \mathfrak{T}}{\partial \lambda_1}\right) w_1 \right.$$
$$\left. + E\frac{\partial U_1}{\partial a_1}\,\varphi_1 + \ldots + E\frac{\partial U_1}{\partial l_1}\,\psi_1\right] dt = -E\,dQ_1.$$

In virtue of Equation (19), this becomes

$$E\,dQ_2 = \left[\left(E\frac{\partial U_1}{\partial \alpha_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial u_1} - \frac{\partial \mathfrak{T}}{\partial \alpha_1}\right) u_1 + \ldots \right.$$
$$\left. + \left(E\frac{\partial U_1}{\partial \lambda_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial w_1} - \frac{\partial \mathfrak{T}}{\partial \lambda_1}\right) w_1 + E\frac{\partial U_1}{\partial a_1}\,\varphi_1 + \ldots + E\frac{\partial U_1}{\partial l_1}\,\psi_1\right] dt\,.$$

This equation can be integrated immediately, yielding the following expression for the quantity of heat Q_2 released by the system S_2 during any finite change

$$EQ_2 = EU_1'' + \mathfrak{T}_1'' - EU_1' - \mathfrak{T}_1', \tag{20}$$

U_1', $\mathfrak{T}_1'$ represent the values of U_1, $\mathfrak{T}_1$ at the initial instant of the change, and U_1'', $\mathfrak{T}_1''$ represent the values of U_1, $\mathfrak{T}_1$ at the final instant of the same change.

The [327] equation of quantities of heat released by different changes produced within different systems can already be seen from Equation (20).

Suppose, in fact, that we retain system S_1 but replace the aggregate (S_2, S_3) by various aggregates ($\mathrm{S'}_2$, $\mathrm{S'}_3$), ($\mathrm{S''}_2$, $\mathrm{S''}_3$), ... while the hypotheses continue to hold. If, during various changes of these various systems, the system S_1 always starts from the same initial state with the same initial motion and ends in the same final state with the same final motion, the quantities of heat $Q_2, Q_2', Q_2'', \ldots$, released in these various changes by the systems S_2, $\mathrm{S'}_2$, $\mathrm{S''}_2$, ... , subject, respectively, to the actions of S_1, $\mathrm{S'}_1$, $\mathrm{S''}_1$, ... are equal to one another.

We now impose new restrictions on the system S_1:

5. System S_1 is at rest at the beginning and the end of each of these changes which we are studying, or, if it is in motion, its absolute motion is the same in both cases.
6. The state of system S_1 is fixed by knowledge of a single variable α_1.
7. In the changes being studied, the final value of this variable α''_1 differs little from its initial value α'_1.

The fifth hypothesis gives us

$$\mathfrak{T}_1'' - \mathfrak{T}_1' = 0.$$

The sixth and seventh allow us to write

$$U_1'' - U_1' = \varpi_1 \, (\alpha_1'' - \alpha_1'),$$

where ϖ_1 depends only on the initial state of the system S_1.

Equation (20) then becomes

$$Q_2 = \varpi_1 \, (\alpha_1'' - \alpha_1').$$

Therefore, if we take care to ensure that the system S_1 is in the same initial state, and if, in the various changes of the aggregates $(\mathrm{S}_1, \mathrm{S}_2), (\mathrm{S'}_1, \mathrm{S'}_2)$, $(\mathrm{S''}_1, \mathrm{S''}_2), \ldots$, we observe the variations [328] $(\alpha_1'' - \alpha_1')$, $(\alpha_1'' - \alpha_1')'$, $(\alpha_1'' - \alpha_1')''$, ... undergone by the variable defining the state of the system S_1, then we can determine the relative values of the quantities of heat $Q_2, Q'_2, Q''_2, \ldots$, released by the systems S_2, $\mathrm{S'}_2$, $\mathrm{S''}_2$, ... in these various changes.

The system S_1 just defined is called a *calorimeter*. The calorimeters used in practice only approximate to the ideal type of calorimeter. By various corrections, based either on direct hypotheses or on the consequences of various physical theories, discrepancies between their readings and those of the ideal calorimeter can be reduced. We leave it to the reader to consider by what set of ideas, in any particular case, a real calorimeter can be seen to reasonably verify the seven hypotheses that we have enumerated.[5]

The calorimeter determines the relation between two quantities of heat released by two different systems in two different circumstances. It therefore allows us to determine the value of a quantity of heat, measured absolutely, if the quantity taken as unity is known.

The definition given by Equations (10), (12), (12a) and (13) of the quantity of heat released during a real or virtual change of a system shows that a quantity of heat is a magnitude of the same kind as one of mechanical work.[6] The unit of the quantity of heat is therefore determined when the unit of mechanical work is known. Indeed, from Equation (10) it is easy to arrive at the following proposition:

> *If the mechanical work done during any change of the system by the bodies external to the system is equal to a unit of mechanical work, and if, during this change, the actions exerted on the system by the external bodies do not perform any work, the system* [329] *absorbs a quantity of heat equal to unity during this change.*

We have not as yet established any convention for the unit of mechanical work. Only a convention for the *sign* of mechanical work has been established. We have settled on this choice of sign so that the mechanical work done by putting a system into motion without changing its state is positive. We can therefore take any amount of mechanical work as the unit of mechanical work provided that it is positive.

We are going to prove that the work done by raising the temperature of a unit mass of water (whose state we suppose to be uniquely defined by the temperature) from a determinate initial temperature that we call the 0 of the centigrade scale to another determinate temperature that we call the +1 on the centigrade scale is positive. We can then take this mechanical work as the unit of mechanical work. The unit of the quantity of heat will be the quantity of heat absorbed by the unit of mass of water when, without external work, its temperature is raised from 0°C to +1°C.

To demonstrate this proposition, suppose that we have a complex and isolated system, itself formed of two independent systems S and S′. The system S is immobile and its state is assumed to be uniquely defined by its temperature. System S′ is a mobile body whose state is assumed invariable. These two systems S and S′ exert no action on one another. If the internal energy of system S, assumed isolated and with the temperature ϑ, is designated by $U(\vartheta)$, and the kinetic energy of system S′ by $\mathfrak{T}$, then the total energy of our complex system will have the very simple form

$$\varepsilon = U(\vartheta) + \frac{\mathfrak{T}}{E}.$$

---

[5] In practice, the system S_1 is always tied to the earth and doesn't, rigorously speaking, have the same absolute movement at the start as at the end of each change. But, given the accepted hypotheses regarding the absolute movement of the earth, the absolute movement of the calorimeter in the course of an operation undergoes variations which exert only a negligible influence on the results of experimental determinations.

[6] *oeuvre.*

At the beginning of the change the system S has temperature ϑ. System S′ is in motion, and its kinetic energy has the value $\mathfrak{T}$. System S′ collides with system S and rebounds. After the impact, it has a kinetic energy $\mathfrak{T}'$ and system S has a temperature ϑ'. Since the system [330] is assumed to be isolated, the total energy has not changed. It therefore follows that

$$U(\vartheta) + \frac{\mathfrak{T}}{E} = U(\vartheta') + \frac{\mathfrak{T}'}{E}$$

or

$$\frac{\mathfrak{T} - \mathfrak{T}'}{E} = U(\vartheta) - U(\vartheta') \tag{21}$$

Experiment shows that $\mathfrak{T}'$ is less than $\mathfrak{T}$*;* therefore

$$\left[U(\vartheta') - U(\vartheta)\right]$$

is positive.

When passing from the temperature ϑ to the temperature ϑ' without external work and without variation in the kinetic energy, the system S has absorbed a positive quantity of heat given by the equation

$$Q = U(\vartheta') - U(\vartheta). \tag{22}$$

We therefore know of a change which absorbs a positive quantity of heat. The calorimeter which gives us a magnitude and a sign for the ratio of the quantities of heat released in two changes therefore allows us to determine the sign of any quantities of heat and to prove *experimentally* the proposition formulated above.

Now that the unit of the quantity of heat has been determined, the calorimeter allows us to measure any quantity of heat, in particular the quantity of heat Q given by Equation (22). If, on the other hand, the variation in the kinetic energy ($\mathfrak{T} - \mathfrak{T}'$) is measured, an experimental determination of the mechanical equivalent of heat E can be deduced from Equation (21).

G.-A. Hirn has performed a real experiment closely related to the ideal experiment that we have just described.

Other methods have been employed, notably by Joule, to determine the value of E. The principles put forward here easily lead to the justification of these methods.

Part III

Commentary on the Principles of Thermodynamics: The Principle of Sadi Carnot and R. Clausius (1893)*

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*“Commentaire aux principes de la Thermodynamique. Deuxième Partie: Le principe de Sadi Carnot et de R. Clausius”, *Journal de Mathématiques Pure et Appliquées*, 9 (1893), 293–359. See vol. VIII, p. 269 [i.e. Part One.]

Chapter 6
The Carnot Cycle and Reversible Changes

6.1 Virtual Changes

We first recall the notion of virtual change with a view to making it more precise than was done in the course of the first part.

Consider a system found in a given state, as well as the bodies external to this system. The state of this system, its motion and the external actions acting on it are known if we know the values of the parameters

$$\alpha, \beta, \dots, \lambda, a, b, \dots, l$$

and of the quantities

$$\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \dots, \frac{d\lambda}{dt}.$$

In [294] order to know the inertial forces acting on the system and the calorific coefficients of the system, it is also necessary to know in addition the values of each of the quantities

$$\frac{d^2\alpha}{dt^2}, \frac{d^2\beta}{dt^2}, \dots, \frac{d^2\lambda}{dt^2}.$$

When change of a system is no longer real but virtual, the ordering of the various states of the system exists only in our understanding, and not in time. The quantities $\alpha, \beta, \dots, \lambda$ cannot be considered as functions of time. It is not, therefore, possible to speak of the quantities

$$\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \dots, \frac{d\lambda}{dt},$$

$$\frac{d^2\alpha}{dt^2}, \frac{d^2\beta}{dt^2}, \dots, \frac{d^2\lambda}{dt^2}.$$

It would thus seem, then, that it is not possible to speak of inertial forces or calorific coefficients for a system which undergoes a virtual change.

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In fact, these words do preserve a sense.

In the formulas which define the inertial forces and the calorific coefficients of a system for a real transformation, we replace the quantities

$$\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \dots, \frac{d\lambda}{dt},$$

$$\frac{d^2\alpha}{dt^2}, \frac{d^2\beta}{dt^2}, \dots, \frac{d^2\lambda}{dt^2}$$

by any magnitudes

$$u, v, \dots, w,$$

$$u', v', \dots, w',$$

subject only to restrictions that the same [295] definition of the system might impose on the quantities

$$\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \dots, \frac{d\lambda}{dt},$$

$$\frac{d^2\alpha}{dt^2}, \frac{d^2\beta}{dt^2}, \dots, \frac{d^2\lambda}{dt^2}.$$

We will have new expressions representing, by definition, the inertial forces and the calorific coefficients of the system during a virtual change. We can then speak of the *work effected by the inertial forces* and of the *quantity of heat released* by the system in the course of a virtual change.

The quantities $u, v, \dots, w$ must vary continuously in the course of a virtual transformation; on the other hand, the quantities $u', v', \dots, w'$ may display discontinuities.

6.2 Cycles

Recall the definition of a closed cycle, already given in the first part of this work (Section 4.1).[1]

Consider that a system starts from an initial state defined by the values

$$\alpha_0, \beta_0, \dots, \lambda_0, a_0, b_0, \dots, l_0$$

of the parameters

---

[1] [The definition is given in Chapter 3, towards the end of Section 3.4.]

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l,$$

and that its initial motion is defined by the values

$$u_0, v_0, \ldots, w_0$$

of the velocities

$$u, v, \ldots, w.$$

This system undergoes a series of *real* or *virtual* changes during which the parameters

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$$

and the velocities

$$u, v, \ldots, w$$

vary continuously.

It [296] reaches a state in which the variable quantities

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, u, v, \ldots, w$$

have the values

$$\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, u_1, v_1, \ldots, w_1.$$

If the quantities

$$\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, u_1, v_1, \ldots, w_1$$

are equal, respectively, to the quantities

$$\alpha_0, \beta_0, \ldots, \lambda_0, a_0, b_0, \ldots, l_0, u_0, v_0, \ldots, w_0,$$

then the system is said to have described a *closed cycle*, or simply a *cycle*.

If all the changes comprising the cycle are real changes, the cycle itself is *real*. If all the changes composing the cycle, or just a part of them, are virtual, then the cycle itself is *virtual*.

6.3 A Real Cycle Can Reproduce Itself Indefinitely

This is now the place to state a hypothesis which plays a fundamental role in the constitution of thermodynamics:

> HYPOTHESIS.—*Let S be a system and let $\sum$ be the collection of bodies external to this system. Consider two equal temporal intervals, one comprising the instants between t_0 and t_1,*

> *and the other comprising those between the instants* t_0' and t_1'. *Suppose that the following conditions are satisfied:*
>
> 1. *At any two corresponding instants of the intervals* (t_0, t_1) and (t_0', t_1'), *the system* $\sum$ *is in the same state.*
> 2. *At the instants* t_0 *and* t_0', *the system* S *is in the same state and moves at the same velocities.*
>
> *We accept that, under these conditions, at any two corresponding instants of the intervals* (t_0, t_1) *and* (t_0', t_1'), *the system* S *is in the same state.*

This [297] hypothesis can be stated in what is, perhaps, a less precise form, but more briefly, by saying that:

> *The change undergone by the system* S *in the temporal interval* (t_0, t_1) *is determined if:* 1. *the state of the external bodies* $\sum$ *at all instants of the interval* (t_0, t_1)*, and* 2. *the state and the velocities of the system* S *at the instant* t_0 *are known.*

We add that at the instant t_0 it is only possible to define the state of the systems $\sum$ and S close to the variables which fix the absolute position in space of the ensemble of the two systems.

Let us consider a real closed cycle, described by the system S. During the course of this closed cycle, the external bodies $\sum$ have passed through a succession of states. At the end of this cycle, the system S has returned to the same state with the same initial velocities. When this cycle has been completed, we see to it that the bodies $\sum$ once more follow the succession of states through which they passed during the course of the cycle. In accordance with the preceding hypothesis, the system S will describe the cycle once more.

We may therefore state the following proposition:

> *A real closed cycle can be exactly reproduced indefinitely* PROVIDED THAT IT IS POSSIBLE TO ARBITRARILY ARRANGE THE BODIES EXTERNAL TO THE SYSTEM.

6.4 Adiabatic, Exothermic and Endothermic Changes

Consider a system subject to an infinitesimal change, real or virtual, under the influence of certain other systems. As an effect of this transformation, the system releases a quantity of heat dQ, and the inertial forces (Section 5.3) perform work $d\tau$. If the quantity

$$d\mathfrak{Q} = dQ - \frac{1}{E} d\tau \tag{1}$$

is equal to 0, *the infinitesimal change under consideration is said to be adiabatic*.

A finite change is said to be adiabatic if all the infinitesimal changes which compose it are adiabatic.

Let [298]

$$\mathfrak{Q} = Q - \frac{\tau}{E}, \tag{2}$$

where Q is the quantity of heat released in a change and τ is the work of the inertial forces during the change.

We call $\mathfrak{Q}$[2] the *total calorific effect of the change*.

It is easily seen that the total calorific effect of an adiabatic change is always equal to 0. The converse of this proposition does not hold. The total calorific effect of a finite change may be equal to 0 without the calorific effect of each of the elementary changes composing this finite change being equal to 0, and consequently, without the finite change being adiabatic.

A change is said to be *exothermic, athermic* or *endothermic* depending on whether the total calorific effect of the change is *positive, zero* or *negative*.

What we have just said applies as well to virtual changes as to real changes. For an infinitesimal real change we have

$$d\tau = -d\mathfrak{T},$$

where $\mathfrak{T}$ is the kinetic energy of the system. The total calorific effect of a finite and *real* change is therefore defined by the equation

$$\mathfrak{Q} = Q + \frac{1}{E}(\mathfrak{T}_1 - \mathfrak{T}_0), \tag{2a}$$

where $\mathfrak{T}_0$ is the value of the kinetic energy of the system at the beginning of the change and $\mathfrak{T}_1$ the value of the same kinetic energy at the end of the change.

Consider a cycle.

The calorific effect of each of the elementary changes constituting the cycle is defined by the equation

$$d\mathfrak{Q} = dQ - \frac{1}{E}d\tau,$$

which [299] can also be written (Chapter 5, Equation (16))

$$E\,d\mathfrak{Q} = dW - E\,dU.$$

Integrating this equation for the whole cycle, and noting that the internal energy U of the system returns to the same value at the end of the cycle that it had at the beginning, we find

$$E\,\mathfrak{Q} = W. \tag{3}$$

---

[2] [Q in the original.]

> *The total calorific effect of a closed cycle, real or virtual, is equivalent to the total work done during the course of the cycle by all the external actions acting on the system.*

This theorem will be useful to us in the following chapter.

6.5 Isothermal Changes: The Carnot Cycle

One can well imagine a system which has, in each of the states it passes through in the course of a change, the same temperature ϑ, read on any thermometer, at all of its points. This temperature can, moreover, vary from one of the states traversed in this change to the following state.

When the temperature is the same not only at all the points of the system taken in each of the states constituting the real or virtual change, but also in all the states of this sequence, the change is said to be *isothermal.*

Consider a cycle subject to the following conditions:

1. The cycle is comprised exclusively of adiabatic and isothermal changes;
2. The isothermal changes figuring in the cycle occur at two different temperatures, ϑ and ϑ', where ϑ' is higher than ϑ.

Such a cycle is called a *Carnot cycle described between the temperatures ϑ and ϑ'.*

A Carnot cycle can, in accordance with this definition, be real or virtual.

If [300] the same system successively describes several Carnot cycles, identical or not, but between the same temperatures ϑ and ϑ', it is evident from the preceding definition that the collection of cycles can be regarded as a single Carnot cycle described between the temperatures ϑ and ϑ'.

Let these successive Carnot cycles be C_1, C_2, ... , C_n, and their ensemble be the Carnot cycle Γ.

Let $\mathcal{Q}_1, \mathcal{Q}_2, \ldots, \mathcal{Q}_\mathrm{n}$ be the total calorific effect of the changes produced at the temperature ϑ in each of these cycles C_1, C_2, ... , C_n, and let χ be the total calorific effect of the changes produced at the temperature ϑ in the cycle Γ.

Similarly, let $\mathcal{Q}'_1, \mathcal{Q}'_2, \ldots, \mathcal{Q}'_\mathrm{n}$ be the total calorific effect of the changes produced at the temperature ϑ' in each of these cycles C'_1, C'_2, ..., C'_n, and let χ' be the total calorific effect of the changes produced at the temperature ϑ' in the cycle Γ.

Clearly we have

$$\begin{cases} \chi = \mathcal{Q}_1 + \mathcal{Q}_2 + \cdots + \mathcal{Q}_n \\ \chi' = \mathcal{Q}'_1 + \mathcal{Q}'_2 + \cdots + \mathcal{Q}'_n . \end{cases} \tag{4}$$

6.6 Simultaneous Independent Changes: Generalisation of the Carnot Cycle

Let σ be a complex system formed from a certain system S and by the bodies $\sum$ external to this system. The system σ is isolated in space. During the time between the instants t_0, t_1, the system S undergoes a certain change M.

Similarly, let σ′ be a complex system formed from a certain system S′ and the bodies $\sum'$ external to this system. The system σ′ is isolated in space. During the time between the instants t'_0, t'_1, the system S′ undergoes a certain change M′.

Suppose that

$$t_1 - t_0 = t'_1 - t'_0.$$

Imagine now that at any instant τ_0, the system σ is placed in space in the state and with the velocities that it exhibited at the instant t_0, and the system σ′ in the state and with the velocities that it exhibited [301] at the instant t'_0,[3] the two systems σ and σ′ being infinitely far apart.

We accept the following hypothesis:

Hypothesis.—*Each of the two systems* σ, σ′ *will be changed as if it was isolated in space*.

If this hypothesis is combined with the hypothesis stated in §5, is it easily seen that, *in the interval of time*

$$\tau_1 - \tau_0 = t_1 - t_0 = t'_1 - t'_0,$$

the system S *will undergoe precisely the change* M *and the system* S′ *the change* M′.

We will then say that *the changes* M *and* M′ *are effected simultaneously and independently*.

It is easily seen, in virtue of the principles put forward in the first part of this work, that the quantity of heat released by the complex system (S, S′) during the interval of time (τ_0, τ_1) is the sum of the quantity of heat released by the system S undergoing the change M in the absence of the system σ′, and the quantity of heat released by the system S′ undergoing the change M′ in the absence of the system σ. Analogous propositions can be stated concerning the work done by the actions that the system (S, S′) undergoes on the part of the external bodies $\left(\sum, \sum'\right)$, the work of the inertial forces applied to the system (S, S′), and finally, the total calorific effect of the two changes M, M′ taken together.

If the two closed cycles C, C_1 are described simultaneously and independently by the systems S and S′, the system (S, S′) clearly describes a closed cycle.

Suppose that the two cycles C and C_1 are two Carnot cycles described between the same temperatures ϑ and ϑ'. If the isotherm described by the system S at the temperature ϑ and the isotherm described by the system S_1 at the same temperature ϑ are simultaneous, and similarly, if the isotherms described by the systems S and S_1 at the temperature ϑ' are simultaneous, the system (S, S_1) will also describe a

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[3] [t_0 in the original.]

Carnot cycle [302] between the temperatures ϑ and ϑ'. Otherwise, the closed cycle described by the system (S, S_1) will not, in general, be a Carnot cycle.

Nevertheless, *by an extension of the term Carnot cycle, it will be convenient to say that a complex system* (S, S_1) *describes a Carnot cycle* Γ *between the temperatures* ϑ *and* ϑ' *if the two infinitely separated systems* S, S_1 *composing it describe two simultaneous and independent Carnot cycles* C, C_1 *between the same temperatures* ϑ, ϑ'.

Let $\mathfrak{Q}, \mathfrak{Q}_1$ be the values of the total calorific effect of the changes described at the temperature ϑ in each of the two cycles C, C_1. Similarly, let $\mathfrak{Q}', \mathfrak{Q}_1'$ be the values of the total calorific effect of the changes described at the temperature ϑ' in each of the two cycles C, C_1.

By definition, we say that the quantity

$$\chi = \mathfrak{Q} + \mathfrak{Q}_1 \tag{5}$$

is the total calorific effect of the changes produced at the temperature ϑ in the cycle Γ, and the quantity

$$\chi' = \mathfrak{Q}' + \mathfrak{Q}_1' \tag{5a}$$

is the total calorific effect of the changes produced at the temperature ϑ' in the cycle Γ.

Of course, the term ‘Carnot cycle described between the temperatures ϑ, ϑ'’[4] can also be extended to n simultaneous, independent Carnot cycles described between the temperatures ϑ, ϑ'.

6.7 Changes Which Are a Sequence of Equilibrium States

When a system is at equilibrium in a certain state, it persists indefinitely in that state and is not transformed. It therefore seems that it is not possible to speak without contradiction of a *real change constituted by a sequence of equilibrium states*. But it is, in fact, possible to give these words a logical meaning.

A state of a system is defined, it will be recalled, from a knowledge of [303] the quantities

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$$

$$\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \ldots, \frac{d\lambda}{dt}.$$

Consider a system that undergoes a real change. At an instant t during this transformation, the system is in a well-defined state. The parameters analogous to $\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$ which define the properties of the external bodies acting on

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[4] [Duhem doesn’t distinguish use and mention.]

the system also have well-defined values. Imagine that, beginning at the instant t, the latter variables are maintained at the same values, so that *the properties of the bodies external to the system remain indefinitely as they were at the instant t.* If, following this operation, the system also persists in the state that it exhibited at the instant t, we say that at this instant t it was at equilibrium under the action of the external bodies in the presence of which it was found.

Now clearly it would be impossible that the values taken by the quantities

$$\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$$

$$\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \ldots, \frac{d\lambda}{dt},$$

at the instant t still agree at all later instants unless

$$\frac{d\alpha}{dt} = 0, \frac{d\beta}{dt} = 0, \ldots, \frac{d\lambda}{dt} = 0 .$$

Thus, in order that a certain state of a system undergoing a real transformation can be said to be a state of equilibrium of the system, it is necessary, but not sufficient, that the velocities of the various points of the system are all zero in this state.

From this proposition we can conclude another:

Consider a system undergoing a real change. Might it happen that the state exhibited by the system at each instant can be regarded as susceptible to becoming an equilibrium state of the system under the action of the external bodies in whose presence it is found, if [304] the latter preserve indefinitely the properties that they possess at that instant? For that, it is necessary, but not sufficient, that during the entire duration of the change,

$$\frac{d\alpha}{dt} = 0, \frac{d\beta}{dt} = 0, \ldots, \frac{d\lambda}{dt} = 0$$

or, in other words,

$$\alpha = \text{const.}, \beta = \text{const.}, \ldots, \lambda = \text{const.}$$

This proposition can be briefly stated in the following way:

> *In order that a real change be a succession of equilibrium states, it is necessary, but not sufficient, that all the points of the system remain at the same position in space during the entire course of the change.*

Now is it absurd to accept the existence of a change during which all the points of the system remain at the same position? Clearly not; in physics we are sometimes led to conceive of such changes. Take, for example, a container holding a mixture of hydrogen and chlorine. The combination occurs, and a transformation, a change of state takes place. It might well be held, however, that the matter filling each of the volume elements of the container at the beginning of the combination remains in the same volume element during the course of the change.

The reservations that we have just made only apply to *real* changes. In the course of a *virtual* change, the values of $\alpha, \beta, \dots, \lambda$ cannot be regarded as functions of time, in which case the preceding argument no longer applies. It is certainly true that if a virtual change is a sequence of equilibrium states, we should have, during the entire change,

$$u = 0, v = 0, \dots, w = 0;$$

but [305] since we do not have

$$u = \frac{d\alpha}{dt}, v = \frac{d\beta}{dt}, \dots, w = \frac{d\lambda}{dt},$$

these equalities do not prevent the quantities $\alpha, \beta, \dots, \lambda$ from changing value in the course of such a change.

Moreover, it is clear that any sequence of equilibrium states of a system, provided it is continuous, can always be envisaged as forming a virtual change of the system.

6.8 Reversible Changes

We now come to one of the most important notions which, at the same time, poses one of the most subtle problems of definition in thermodynamics: the notion of a *reversible transformation*.

Consider, for the same system, two real or virtual transformations S and[5] S_1 endowed with the following properties:

1. Each state E of the transformation S corresponds to a single state E_1 of the transformation S_1.
2. During the transformations S and S_1, the system traverses corresponding states in the same order; in particular, the initial state of transformation S corresponds to the initial state of transformation S_1, and the final state of change S corresponds to the final state of transformation S_1.
3. To two states E, E′, infinitesimally close in the change S, there correspond two states E_1, E'_1 infinitesimally close in the change S_1.
4. Two corresponding states E, E_1 exhibit the following properties:
    a. The parameters $\alpha, \beta, \dots, \lambda, a, b, \dots, l$ determining the properties of the system in the state S are infinitesimally close to the parameters

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[5] [In the original, the symbol following is S'_1.]

$\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1$ determining the properties of the system in the state E$_1$.

b. The quantities $\frac{d\alpha}{dt}, \frac{d\beta}{dt}, \ldots, \frac{d\lambda}{dt}$ (or $u, v, \ldots, w$) determining the real (or virtual) velocities of the system in the state E differ infinitesimally from the quantities $\frac{d\alpha_1}{dt}, \frac{d\beta_1}{dt}, \ldots, \frac{d\lambda_1}{dt}$ (or $u_1, v_1, \ldots, w_1$) [306] determining the real (or virtual) velocities of the system in the state E$_1$.
c. The quantities $\frac{d^2\alpha}{dt^2}, \frac{d^2\beta}{dt^2}, \ldots, \frac{d^2\lambda}{dt^2}$ (or $u', v', \ldots, w'$) determining the accelerations (real or virtual) of the system in the state E differ infinitesimally from the quantities $\frac{d^2\alpha_1}{dt^2}, \frac{d^2\beta_1}{dt^2}, \ldots, \frac{d^2\lambda_1}{dt^2}$ (or $u'_1, v'_1, \ldots, w'_1$)[6] determining the real (or virtual) accelerations of the system in the state E$_1$.
d. The parameters analogous to $\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$ determining the properties of the external bodies acting on the system while it is in state E differ infinitesimally from the parameters analogous to $\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1$ determining the properties of the external bodies acting on the system while it is in state E$_1$.

From these conditions on the two states E, E$_1$, it follows that the kinetic energy, the external actions, the inertial forces and the calorific coefficients have values differing infinitesimally for the system whether in state E or state E$_1$.

The two transformations S and S$_1$ whose properties we have just fixed constitute two *infinitesimally close transformations*. We call a sequence of transformations each of which is infinitesimally close to that which precedes it and that which follows it a *continuously variable transformation*.

Let $\sum$ be a real or virtual transformation of a system possessing the following properties:

1. In each of the states constituting it, the system is in equilibrium under the action of the external bodies in whose presence it finds itself.
2. If the change is virtual, the quantities $u, v, \ldots, w$ and $u', v', \ldots, w'$ are assumed to be zero throughout.
3. Let (A) be the initial state and (B) the final state of the transformation $\sum$; it is possible to pass from (A) to (B) by a continuously variable transformation, *realisable* under each of its forms, and having the transformation $\sum$, real or virtual, as its limiting form.
4. It is possible to pass from (B) to (A) by a continuously variable transformation S$'$, *realisable* under each of its forms, [307] and having as its limiting form the *real or virtual* transformation obtained by running through the equilibrium states $\sum$ in reverse order from (B) to (A).

Such a change $\sum$ is called a *reversible transformation*.

Is a reversible transformation realisable? Since a reversible transformation is a sequence of equilibrium states, we know that it will be impossible to realise it,

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[6] [In the original, (*ou* $u_1, v_1, \ldots, w_1$).]

except perhaps in the particular case specified in the preceding section. Thus, in general, a *reversible transformation is an entirely virtual change*.

The question might still be raised of whether the virtual changes which are reversible are possible. We respond to this question by accepting the following hypothesis:

> FUNDAMENTAL HYPOTHESIS.—*There are systems for which all changes, real or virtual, which are series of equilibrium states, are reversible changes.*

WE WILL ONLY STUDY SYSTEMS WHICH POSSESS THIS PROPERTY.

It shouldn't be thought that these systems alone exist in nature. It is easy to prove the contrary; cycles of *magnetic hysteresis*, for example, are irreversible changes although they are continuous sequences of equilibrium states.

We will establish some properties of reversible changes that will be of use in what follows.

If a reversible change is real, then, since it is a sequence of equilibrium states,

$$\frac{d\alpha}{dt}=0,\ \frac{d\beta}{dt}=0,\ldots,\ \frac{d\lambda}{dt}=0$$

during the entire duration of that change, and so also

$$\frac{d^2\alpha}{dt^2}=0,\ \frac{d^2\beta}{dt^2}=0,\ldots,\ \frac{d^2\lambda}{dt^2}=0\,.$$

If [308] a reversible change is virtual, then by definition, at each instant,

$$u=0, v=0,\ldots,w=0,$$

$$u'=0, v'=0,\ldots,w'=0.$$

Thus, *in a reversible change, whether real or virtual, the kinetic energy and the inertial forces are always zero*.

Let $A, B, \ldots, L, \mathfrak{A}, \mathfrak{B}, \ldots, \mathfrak{L}$ be the external actions to which the system is subject while it is in one of the states constituting the reversible change $\sum$. If the system undergoes this change from the state (A) to the state (B), the external actions perform work

$$\Theta=\int_{(A)}^{(B)}(A\delta\alpha+B\delta\beta+\cdots+L\delta\lambda+\mathfrak{A}\delta a+\mathfrak{B}\delta b+\cdots+\mathfrak{L}\delta l).$$

If the system undergoes the same change from (B) to (A), the external actions perform work

$$\Theta'=\int_{(B)}^{(A)}(A\delta\alpha+B\delta\beta+\cdots+L\delta\lambda+\mathfrak{A}\delta a+\mathfrak{B}\delta b+\cdots+\mathfrak{L}\delta l).$$

The two integrals are taken along the same path $\sum$, whence clearly

$$\Theta + \Theta' = 0.$$

Now, in accordance with the definition of a continuously variable change, the work W performed by the external actions while the system undergoes the real change S from the state (A) to the state (B) has the limit Θ when the change S tends towards the reversible change $\sum$. The work W' performed by the external actions while the system undergoes the real change S′ from the state (B) to the state (A) has the limit Θ' when the change S′ tends towards the reversible change $\sum$ reversed.

We therefore arrive at the following proposition:

> *If* S *and* S′ *are two continuously variable real changes,* [309] *the one the inverse of the other, which have as their common limit a certain reversible change* $\sum$*, the work* W *and* W' *performed by the external actions while the system undergoes these changes tends towards the same limit with opposite sign when the changes* S *and* S′ *tend towards the change* $\sum$*.*

It suffices to replace the external actions

$$A, B, \ldots, L, \mathcal{A}, \mathcal{B}, \ldots, \mathcal{L}$$

in the preceding argument by the calorific coefficients

$$R_\alpha, \ldots, R_\lambda, \mathcal{R}_a, \ldots, \mathcal{R}_l$$

and the words *external work* with the words *quantity of heat released by the system* in order to obtain the following proposition:

> *The quantities of heat* Q *and* Q′ *released by the system while it undergoes the changes* S *and* S′ *tend towards the same limit with opposite sign when the changes* S *and* S′ *tend towards the reversible change* $\sum$*.*

We complete these generalisations on reversible changes with the statement of two hypotheses which will be of much use in what follows.

> FIRST HYPOTHESIS.—*If a reversible change* $\sum$ *is isothermal, it can be regarded as the common limit of two continuously variable changes* S *and* S′*, the one the inverse of the other, which are always real and always isothermal.*

> SECOND HYPOTHESIS.—*If a reversible change* $\sum$ *is adiabatic, it can be regarded as the common limit of two continuously variable changes* S *and* S′*, the one the inverse of the other, which are always real and always adiabatic.*

Chapter 7
Carnot’s Theorem and Absolute Temperature

7.1 The Hypotheses of Clausius and Sir W. Thomson

Let $A, B, \ldots, L, \mathcal{A}, \mathcal{B}, \ldots, \mathcal{L}$ be the external forces and influences acting on a system taken in one of its states within a series constituting a Carnot cycle. During one of the elementary changes

$$d\alpha, d\beta, \ldots, d\lambda, da, db, \ldots, dl$$

into which the cycle can be decomposed, these actions perform work

$$dW = Ad\alpha + Bd\beta + \ldots + Ld\lambda + \mathcal{A}da + \mathcal{B}db + \ldots + \mathcal{L}dl,$$

and during the course of the whole cycle, they perform work

$$W = \int (Ad\alpha + Bd\beta + \ldots + Ld\lambda + \mathcal{A}da + \mathcal{B}db + \ldots + \mathcal{L}dl),$$

the integral extending over the whole cycle.

This work W can be positive, zero or negative.

The Carnot cycles for which W is zero and the Carnot cycles for which W is negative are the subject of two hypotheses, one due to Clausius and the other to Sir W. Thomson.

> CLAUSIUS’ HYPOTHESIS.—*If a system describes a* REAL *Carnot cycle between the temperatures* ϑ and ϑ' *(*ϑ' *being higher than* ϑ*), and if the external actions to which the system is subjected perform a total work equal to* 0 *during the course of the cycle, then it is not possible that an isothermal change occurring at the temperature* ϑ *should be endothermic, nor that an isothermal change occurring at the temperature* ϑ' *should be exothermic.*

> SIR W. THOMSON’S HYPOTHESIS.—*If a system describes a* [311] REAL *Carnot cycle between the temperatures* ϑ *and* ϑ' *(*ϑ' *being higher than* ϑ*), and if the external actions to which the system is subjected perform a total negative work during the course of the cycle, then it is impossible that the isothermal change occurring at the temperature* ϑ *be endothermic.*

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This is not the place to go into the way in which Clausius and Sir W. Thomson were led to state their hypotheses, nor to review the discussions undertaken by Clausius against the physicists who denied its correctness. In the classic treatises of thermodynamics, these two hypotheses are normally presented as equivalent and as equally capable of serving as the basis for Carnot's demonstration. For our part, we regard them as distinct and will employ both in our exposition.

7.2 Addition to the Hypotheses of Clausius and Sir W. Thomson

To these two hypotheses we will make an essential addition that we state in the following way:

> ADDITIONAL HYPOTHESIS.—*If a Carnot cycle described between the temperatures* ϑ and ϑ' *(*ϑ'*being higher than* ϑ*) is* REAL AND NOT REVERSIBLE *and if in the course of the cycle the external actions perform zero or negative work, then the isothermal change occurring at the temperature* ϑ *cannot be athermic.*

Combined with the hypotheses of Clausius and Sir W. Thomson, this additional hypothesis yields the following proposition:

> *Among all the Carnot cycles described between the temperatures* ϑ and ϑ' *(*ϑ' *being higher than* ϑ*) which are* REAL AND NOT REVERSIBLE, *consider those during the course of which the external actions perform zero or negative work; for all these cycles, the isothermal change occurring at the temperature* ϑ *is exothermic.*

The hypotheses that we have just stated cannot be *directly* verified by experiment. Combined with more or fewer other hypotheses, [312] they constitute the point of departure of theories whose distant consequences can alone be subjected to experimental control. An analogous remark applies, however, to nearly all the hypotheses that are encountered in physics.

7.3 Various Kinds of Carnot Cycles

Take all the Carnot cycles that can be conceived and try to distinguish among them all those whose properties are compatible, on the one hand, with the principle of the conservation of energy, and on the other, with the three hypotheses just mentioned.

Among all the Carnot cycles thus distinguished are surely all those which are realisable and irreversible. The properties which belong to all the cycles thus distinguished belong in particular to all the realisable and irreversible cycles.

> *Unless otherwise stated, we exclude from our investigations real, irreversible Carnot cycles, described between the temperatures* ϑ *and* ϑ'*, corresponding to a positive work of the external actions and for which the thermic effect produced at the temperature* ϑ *is equal to* 0.

Let ϑ and ϑ' always be the temperatures between which Carnot cycles are described, where ϑ' is higher than ϑ. Let $\mathcal{Q}$ be the total calorific effect of the isothermal change produced at the temperature ϑ, and $\mathcal{Q}'$ the total calorific effect of the isothermal change produced at the temperature ϑ'. Apart from these two, the changes comprising the cycle are adiabatic, so that the total calorific effect of the cycle is reduced to $(\mathcal{Q}+\mathcal{Q}')$.

The external actions to which the system is subjected during the course of the cycle perform the total work W.

The principle of the conservation of energy gives us (Chapter 6, Equation (3))

$$W = E(\mathcal{Q}+\mathcal{Q}'). \tag{1}$$

From [313] that, we have the following properties:

1. If the work W is zero, the two quantities $\mathcal{Q}$ and $\mathcal{Q}'$ are of opposite sign and have the same absolute value.
2. *If the work W is positive, at least one of the two quantities $\mathcal{Q}$ and $\mathcal{Q}'$ is positive, and if only one is, then it is the one of greatest absolute value.*
3. *If the work W is negative, at least one of the two quantities $\mathcal{Q}$ and $\mathcal{Q}'$ is negative, and if only one is, then it is the one of greatest absolute value.*

These propositions result from the application of the principle of the conservation of energy to the Carnot cycles considered.

We now apply to them the two hypotheses of Clausius and Sir W. Thomson stated in section 1 and the additional hypothesis stated in section 2. We are led to the following conclusion:

If the external work is zero or negative, the quantity $\mathcal{Q}$ is certainly positive; if the external work is positive, the quantity $\mathcal{Q}$ is positive or negative, but certainly not zero.

It is easy to conclude from these propositions that all realisable Carnot cycles which are not just a series of equilibrium states fall within one of the categories in the following classification:

1. The work W performed by the external actions is zero, $\mathcal{Q}$ is positive, $\mathcal{Q}'$ is negative and equal to $\mathcal{Q}$ in absolute value.
2. The work W performed by the external actions is negative, $\mathcal{Q}$ is positive, $\mathcal{Q}'$ is negative and greater than $\mathcal{Q}$ in absolute value.
3. The work W performed by the external actions is positive, and three cases can then be distinguished.
   a. $\mathcal{Q}$ is positive, $\mathcal{Q}'$ is positive or zero.
   b. $\mathcal{Q}$ is positive, $\mathcal{Q}'$ is negative and less than $\mathcal{Q}$ in absolute value.
   c. $\mathcal{Q}$ is negative, $\mathcal{Q}'$ is positive and greater than $\mathcal{Q}$ in absolute value.

This classification is summarised in the following Table[1]:

Cycles of the first kind	$W = 0$		$\mathcal{Q} > 0$	$\mathcal{Q}' < 0$	$\lvert\mathcal{Q}'\rvert = \lvert\mathcal{Q}\rvert$
Cycles of the second kind	$W < 0$		$\mathcal{Q} > 0$	$\mathcal{Q}' < 0$	$\lvert\mathcal{Q}'\rvert > \lvert\mathcal{Q}\rvert$
Cycles of the third kind	$W > 0$	Species *a*	$\mathcal{Q} > 0$	$\mathcal{Q}' \geq 0$	
		Species *b*	$\mathcal{Q} > 0$	$\mathcal{Q}' < 0$	$\lvert\mathcal{Q}'\rvert < \lvert\mathcal{Q}\rvert$
		Species *c*	$\mathcal{Q} < 0$	$\mathcal{Q}' > 0$	$\lvert\mathcal{Q}'\rvert > \lvert\mathcal{Q}\rvert$

We [314] now propose to compare the values taken for different cycles by the ratio

$$\rho = \frac{\mathcal{Q} + \mathcal{Q}'}{\mathcal{Q}}.$$

Since $(\mathcal{Q} + \mathcal{Q}')$ is zero for cycles of the first kind, negative for cycles of the second kind and positive for cycles of the third kind, as Equation (1)[2] shows, it can be seen that the ratio ρ has, for the various categories of cycles, the following sign:

Cycles of the first kind		$\rho = 0$
Cycles of the second kind		$\rho < 0$
Cycles of the third kind	Species *a*	$\rho > 0$
	Species *b*	$\rho > 0$
	Species *c*	$\rho < 0$

7.4 Carnot's Theorem

Inspection of the preceding Table shows us, first, that the ratio ρ is smaller for any cycle of species *c* of the third kind than for any cycle of the first kind, and also than for any cycle of species *a* or *b* of the third kind.

We will now demonstrate that *of two Carnot cycles described between the same temperatures ϑ and ϑ', one of species c of the third kind and the other of the second kind, the ratio ρ is certainly not greater for the former than it is for the latter*, it being assumed, of course, that these cycles obey the principle of the conservation of energy and the three hypotheses previously stated.

A rigorous demonstration of this theorem requires that we distinguish cases.

Let C_1 be the first cycle and C_2 the second. Let T_1, T_2 be the durations of these two cycles. We will begin by distinguishing two cases depending on whether the periods T_1, T_2 are or are not commensurable.

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[1] Last column added by PN.]

[2] [(2) in the original.]

1. *The ratio* $\frac{T_2}{T_1}$ *is commensurable.*
   We put

$$\frac{T_2}{T_1} = \frac{\mu_2}{\mu_1}, \tag{2}$$

where [315] μ_1, μ_2 are two integers with no common factor.

Let $W_1, \mathcal{Q}_1, \mathcal{Q}'_1, \rho_1$ be the quantities analogous to $W, \mathcal{Q}, \mathcal{Q}', \rho$ corresponding to the cycle C_1, and let $W_2, \mathcal{Q}_2, \mathcal{Q}'_2$ be the quantities analogous to $W, \mathcal{Q}, \mathcal{Q}', \rho$ corresponding to the cycle C_2. We know that

$$\mathrm{W}_1 > 0, \mathcal{Q}_1 < 0, \mathcal{Q}'_1 > 0,$$

$$\mathrm{W}_2 < 0, \mathcal{Q}_2 > 0, \mathcal{Q}'_2 < 0.$$

We distinguish two secondary cases, depending on whether the quantities W_1 and $|W_2|$ are commensurable or not.

A. *The ratio* $\frac{|W_2|}{W_1}$ *is commensurable.*
   We put

$$\frac{|W_2|}{W_1} = \frac{m_2}{m_1}, \tag{3}$$

where m_1, m_2 are two integers which we suppose have no common factor.
Put

$$\begin{cases} N_1 = m_2\,\mu_1, \\ N_2 = m_2\,\mu_2. \end{cases} \tag{4}$$

Consider N_1 cycles identical to the cycle C_1, described simultaneously and independently. Their collection will constitute a unique Carnot cycle γ_1, of duration T_1 and will be described between the temperatures ϑ and ϑ', for which the quantities analogous to W, $\mathcal{Q}$, $\mathcal{Q}'$ will have as values (Chapter 6, Equations (5) and (5a))

$$N_1 W_1, N_1 \mathcal{Q}_1, N_1 \mathcal{Q}'_1.$$

The cycle γ_1 can be reproduced μ_2 times in succession (Section 6.3).

These successive μ_2 cycles γ_1 can be considered as a unique Carnot cycle Γ_1, described between the temperatures ϑ and ϑ', of duration

$$\Theta_1 = \mu_2 T_1, \tag{5}$$

for [316] which the quantities analogous to W, $\mathcal{Q}$, $\mathcal{Q}'$ have as values

$$\mu_2 N_1 W_1, \mu_2 N_1 Q_1, \mu_2 N_1 Q'_1.$$

Consider, on the other hand, N_2 cycles identical to the cycle C_2, described simultaneously and independently. Their collection constitutes a unique Carnot cycle γ_2, described between the temperatures ϑ and ϑ' and of duration T_2, for which the quantities analogous to W, $\mathcal{Q}$, $\mathcal{Q}'$ have as values

$$N_2 W_2, N_2 \mathcal{Q}_2, N_2 \mathcal{Q}'_2.$$

The cycle γ_2 can be reproduced μ_1 times in succession. These successive μ_1 cycles γ_2 can be considered as a unique Carnot cycle Γ_2, described between the temperatures ϑ and ϑ', of duration

$$\Theta_2 = \mu_1 T_2, \tag{5a}$$

for which the quantities analogous to W, $\mathcal{Q}$, $\mathcal{Q}'$ have as values

$$\mu_1 N_2 W_2, \mu_1 N_2 Q_2, \mu_1 N_2 Q'_2.$$

Equations (2), (5) and (5a) show us that the duration Θ_1 of the cycle Γ_1 is equal to the duration Θ_2 of cycle Γ_2. It can thus be assumed that the two cycles are described simultaneously and independently. Their collection will form a new *real* Carnot cycle Γ, described between the temperatures ϑ and ϑ', for which the quantities analogous to W, $\mathcal{Q}$, $\mathcal{Q}'$ will have as values

$$\begin{aligned} W &= \mu_2 N_1 W_1, + \mu_1 N_2 W_2, \\ \mathcal{Q} &= \mu_2 N_1 \mathcal{Q}_1, + \mu_1 N_2 \mathcal{Q}_2, \\ \mathcal{Q}' &= \mu_2 N_1 \mathcal{Q}'_1, + \mu_1 N_2 \mathcal{Q}'_2, \end{aligned}$$

In virtue of Equations (4), these equalities can be written

$$\begin{cases} W = \mu_1 \mu_2 \left(m_2 W_1 + m_1 W_2 \right), \\ \mathcal{Q} = \mu_1 \mu_2 \left(m_2 \mathcal{Q}_1 + m_1 \mathcal{Q}_2 \right), \\ \mathcal{Q}' = \mu_1 \mu_2 \left(m_2 \mathcal{Q}'_1 + m_1 \mathcal{Q}'_2 \right). \end{cases} \tag{6}$$

In [317] virtue of Equation (3), the first of Equations (6) becomes

$$W = 0.$$

The cycle Γ is therefore a real, irreversible cycle of the first kind. In accordance with Clausius' hypothesis, presented in §1, and the complementary hypothesis stated in §2, the quantity $\mathcal{Q}$ must be positive. In virtue of the second Equation (6), this latter condition becomes

$$m_2 \mathcal{Q}_1 + m_1 \mathcal{Q}_2 > 0$$

or

$$\frac{m_1}{|\mathcal{Q}_1|} > \frac{m_2}{\mathcal{Q}_2}.$$

But in accordance with (3), we have,[3]

$$\frac{m_1}{m_2} = \frac{W_1}{|W_2|}.$$

Therefore,

$$\frac{W_1}{|\mathcal{Q}_1|} > \frac{|W_2|}{\mathcal{Q}_2}$$

or

$$\frac{W_1}{\mathcal{Q}_1} < \frac{W_2}{\mathcal{Q}_2}.$$

On the other hand, Equation (1) yields

$$W_1 = E(\mathcal{Q}_1 + \mathcal{Q}'_1),$$
$$W_2 = E(\mathcal{Q}_2 + \mathcal{Q}'_2).$$

The preceding inequality therefore becomes

$$\frac{\mathcal{Q}_1 + \mathcal{Q}'_1}{\mathcal{Q}_1} < \frac{\mathcal{Q}_2 + \mathcal{Q}'_2}{\mathcal{Q}_2}$$

or

$$\rho_1 < \rho_2. \qquad (7)$$

B. [318] *The ratio* $\frac{|W_2|}{W_1}$ *is incommensurable.*
Let m_1, m_2 be two integers with no common factor such that

$$\frac{m_2}{m_1} = \frac{|W_2|}{W_1} - \varepsilon, \qquad (8)$$

where ε is a positive quantity which can be taken to be as small as you like.

The cycle Γ is constructed as in the previous case.

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[3] [In the original, $\frac{W_2}{|W_2|}$. rather than $\frac{W_1}{|W_2|}$.]

Again, for this cycle we have

$$\begin{cases} W = \mu_1\mu_2\left(m_2W_1 + m_1W_2\right), \\ \mathcal{Q} = \mu_1\mu_2\left(m_2\mathcal{Q}_1 + m_1\mathcal{Q}_2\right), \\ \mathcal{Q}' = \mu_1\mu_2\left(m_2\mathcal{Q}'_1 + m_1\mathcal{Q}'_2\right). \end{cases} \tag{6}$$

The first Equation (6), together with Equation (8), gives

$$W = -\varepsilon m_1\mu_1\mu_2W_1.$$

Since W is negative, the cycle Γ is a *real, irreversible* Carnot cycle of the second kind. The Sir W. Thomson's hypothesis, stated in §1, together with the additional hypothesis, stated in §2, shows us that the quantity $\mathcal{Q}$ is necessarily positive, a condition which can be written, in virtue of the second Equation (6), as

$$m_2\mathcal{Q}_1 + m_1\mathcal{Q}_2 > 0$$

or

$$\frac{m_1}{|\mathcal{Q}_1|} > \frac{m_2}{\mathcal{Q}_2}$$

But Equation (8) yields

$$m_2W_1 = m_1\left|W_2\right| - \varepsilon m_1W_1,$$

so that

$$\frac{W_1}{|\mathcal{Q}_1|} > \frac{|W_2|}{\mathcal{Q}_2} - \varepsilon\,\frac{W_1}{\mathcal{Q}_2}.$$

ε is a positive quantity which can also be taken to be as small as you [319] like. The preceding inequality therefore requires that

$$\frac{W_1}{|\mathcal{Q}_1|} \geq \frac{|W_2|}{\mathcal{Q}_2}$$

or

$$\frac{W_1}{\mathcal{Q}_1} \leq \frac{W_2}{\mathcal{Q}_2}.$$

Equation (1) yields, moreover,

$$W_1 = E(\mathcal{Q}_1 + \mathcal{Q}'_1),$$
$$W_2 = E(\mathcal{Q}_2 + \mathcal{Q}'_2),$$

and it is clear that

$$\frac{\mathcal{Q}_1 + \mathcal{Q}'_1}{\mathcal{Q}_1} \leq \frac{\mathcal{Q}_2 + \mathcal{Q}'_2}{\mathcal{Q}_2}$$

or

$$\rho_1 \leq \rho_2. \tag{9}$$

2. *The ratio* $\frac{T_2}{T_1}$ *is incommensurable.*

Suppose that the cycle C_2 is one of a kind of Carnot cycle $\mathcal{C}_2$, continuously variable, always real and always described between the temperatures ϑ and ϑ'. Clearly, it is always correct to make this assumption.[4]

When the cycle $\mathcal{C}_2$ varies continuously, its duration T_2 remains constant or varies continuously. Clearly, it is always possible to choose the variations of the cycle $\mathcal{C}_2$ in such a way that its duration T_2 doesn't remain constant.

When the cycle $\mathcal{C}_2$ varies continuously, the quantities W_2, $\mathcal{Q}_2, \mathcal{Q}'_2$ vary continuously. Since in the case of the particular cycle C_2, none of these three quantities is equal to zero, we can always limit the variations of the cycle $\mathcal{C}_2$ on either side of the form C_2 in such a way that we always have

$$W_2 < 0, \mathcal{Q}_2 < 0, \mathcal{Q}'_2 < 0.$$

Then the cycle $\mathcal{C}_2$ will always be a cycle of the second kind. [320] Moreover, in so far as the cycle $\mathcal{C}_2$ varies continuously, the ratio ρ_2 varies continuously.

Now we know that if we consider one of the cycles $\mathcal{C}_2$ whose duration T_2 is commensurable with the duration T_1 of cycle C_1, we will have

$$\rho_2 \geq \rho_1.$$

What we have just said shows that for all the forms of cycle $\mathcal{C}_2$, and in particular for the form C_2,

$$\rho_2 \geq \rho_1. \tag{10}$$

If, therefore, two real and irreversible Carnot cycles are both described between the same temperatures, one of the third[5] *kind of species c and the other not of the third kind of species c, the ratio* ρ *for the former is less than or equal to the ratio* ρ *for the latter.*

This theorem can be restated in the following way:

Consider all the real, irreversible Carnot cycles described between the temperatures ϑ *and* ϑ'.

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[4] [It would seem that in this paragraph Duhem introduces the convention that $\mathcal{C}_2$ denotes a *kind* or *form* of Carnot cycle whereas C_2 stands for a particular Carnot cycle of form $\mathcal{C}_2$. The fact that this convention is not followed in the following paragraphs is perhaps best explained by printing errors in which the two styles of letter are confused, but I have not made any such corrections.—trans.]

[5] [Here and at the next occurrence of "third" the original says *première* (first).]

The ratio ρ for those of species c of the third kind have an upper limit A *which is essentially negative.*

The ratio ρ for those which are not of species c of the third kind have a lower limit A′ *which is essentially negative.*

We have

$$\mathrm{A} \leq \mathrm{A}'.$$

This is the first form of Carnot's theorem. The employment of reversible changes will allow us to give this theorem a more precise form.

7.5 Carnot's Theorem (Continued): The Use of Reversible Changes

To begin with, we will demonstrate that

$$\mathrm{A} = \mathrm{A}'.$$

Given [321] the two temperatures ϑ and ϑ', the latter higher than the former, suppose that it is always possible to find a system admitting four reversible changes with the following properties:

The first is a reversible isothermal change $\sum_{12}$, corresponding to the temperature ϑ' and taking the system from the state 1 to the state 2.

The second is a reversible adiabatic change $\sum_{23}$, taking the system from state 2, where it has the temperature ϑ', to state 3 where it has the temperature ϑ.

The third is a reversible isothermal change $\sum_{34}$, corresponding to the temperature ϑ and taking the system from state 3 to state 4.

The fourth is a reversible adiabatic change $\sum_{41}$, returning the system from state 4 to state 1.

We have thus formed a reversible Carnot cycle, described between the temperatures ϑ and ϑ'.

For this cycle, we will introduce the further hypothesis as follows: *It is possible to choose it in such a way that the change $\sum_{34}$ is athermic.*

In accordance with one of the hypotheses introduced at the end of Section 6.8, there is a continuously variable real isothermal change S_{12} taking the system from the state 1 with velocities equal to zero to the state 2 with its velocities equal to zero, and having as a limit the change $\sum_{12}$. Similarly, there is a continuously variable real isothermal change S_{21} taking the system from the state 2 with velocities equal to zero to the state 1 with its velocities equal to zero, and having as a limit the change $\sum_{21}$.

The isothermal change $\sum_{34}$ and the adiabatic changes $\sum_{23}$ and $\sum_{41}$ give rise to analogous observations.

The collection of changes

$$\mathrm{S}_{12}, \mathrm{S}_{23}, \mathrm{S}_{34}, \mathrm{S}_{41}$$

form a real Carnot cycle described between the temperatures ϑ and ϑ', [322] which is continuously variable and has as its limit the cycle

$$\sum_{12}, \sum_{23}, \sum_{34}, \sum_{41.}$$

Similarly, the collection of changes

$$\mathrm{S}_{43}, \mathrm{S}_{32}, \mathrm{S}_{21}, \mathrm{S}_{14}$$

form a real Carnot cycle described between the temperatures ϑ and ϑ', which is continuously variable and has as its limit the cycle

$$\sum_{43}, \sum_{32}, \sum_{21}, \sum_{14}.$$

Let χ_{12}, χ_{34} be the quantities of heat released by the reversible changes $\sum_{12}$, $\sum_{34}$. The changes $\sum_{21}$, $\sum_{43}$ release the quantities of heat $\chi_{21} = -\chi_{12}, \chi_{43} = -\chi_{34}$, so that for each of the two cycles

$$\left(\sum_{12}, \sum_{23}, \sum_{34}, \sum_{41}\right) \text{ and } \left(\sum 43, \sum_{32}, \sum_{21}, \sum_{14}\right),$$

the quantity analogous to ρ has the same value

$$r = \frac{\chi_{12} + \chi_{34}}{\chi_{34}}.$$

Let $\mathcal{Q}_{12}, \mathcal{Q}_{34}$ be the thermic effects of the changes S_{12}, S_{34}. For the cycle (S_{12}, S_{23}, S_{34}, S_{41}) the quantity analogous to ρ has the value

$$\rho_1 = \frac{\mathcal{Q}_{12} + \mathcal{Q}_{34}}{\mathcal{Q}_{34}}.$$

Let $\mathcal{Q}_{21}, \mathcal{Q}_{43}$ be the thermic effects of the changes S_{21}, S_{43}. For the cycle (S_{43}, S_{32}, S_{21}, S_{14}) the quantity analogous to ρ has the value

$$\rho_2 = \frac{\mathcal{Q}_{21} + \mathcal{Q}_{43}}{\mathcal{Q}_{43}}.$$

By hypothesis, the change $\sum_{34}$ is not athermic. To fix our ideas, suppose χ_{34} is negative. The changes S_{34} and S_{43} [323] can be taken to be sufficiently close to the changes $\sum_{34}$ and $\sum_{43}$ that $\mathcal{Q}_{34}$ has the same sign as χ_{34} and $\mathcal{Q}_{43}$ has the same sign as χ_{43}. We will then have

$$\mathcal{Q}_{34} < 0, \ \mathcal{Q}_{43} > 0,$$

so that ρ_1 certainly corresponds to a cycle of species c of the third kind and ρ_2 does not correspond to a cycle of species c of the third kind.

The theorem demonstrated in the preceding section will give us

$$\rho_1 \leq \mathrm{A}, \rho_2 \geq \mathrm{A}'.$$

But on the other hand, when the two cycles

$$(\mathrm{S}_{12}, \mathrm{S}_{23}, \mathrm{S}_{34}, \mathrm{S}_{41}) \text{ and } (\mathrm{S}_{43}, \mathrm{S}_{32}, \mathrm{S}_{21}, \mathrm{S}_{14})$$

tend towards the cycles

$$\left(\sum\nolimits_{12}, \sum\nolimits_{23}, \sum\nolimits_{34}, \sum\nolimits_{41}\right) \text{ and } \left(\sum\nolimits_{43}, \sum\nolimits_{32}, \sum\nolimits_{21}, \sum\nolimits_{14}\right),$$

respectively, the two ratios ρ_1, ρ_2 tend to the same limit r. Since the quantities A, A' do not vary when the temperatures ϑ and ϑ' are held constant, this can only be the case if we have

$$\mathrm{A} = \mathrm{A}', \tag{10}$$

as stated.

We see, moreover, that *if a reversible Carnot cycle is described between the temperatures ϑ and ϑ' (ϑ' being higher than ϑ) and, further, if the isotherm described at the temperature ϑ is not athermic, the ratio*

$$\rho = \frac{\mathcal{Q} + \mathcal{Q}'}{\mathcal{Q}}$$

has, for this cycle, the value A.

What happens to the ratio ρ for a reversible Carnot cycle described between the temperatures ϑ and ϑ' if the isotherm at the temperature ϑ is athermic?

Designating [324] this cycle by C_1, we have, by hypothesis,

$$\mathcal{Q}_1 = 0.$$

Let C_2 be another reversible Carnot cycle, described between the temperatures ϑ and ϑ', for which the isotherm at the temperature ϑ is not athermic. For this cycle, we have by the preceding proposition,

$$\frac{\mathcal{Q}_2 + \mathcal{Q}'_2}{\mathcal{Q}_2} = \mathrm{A}.$$

The two cycles C_1 and C_2 can be considered virtual. It is always possible to suppose that they run simultaneously and independently. Together they will thus form a new reversible Carnot cycle described between the temperatures ϑ and ϑ'. The isotherm described at the temperature ϑ corresponds to a thermic effect $\mathcal{Q}_2$, so that it will not be athermic. The isotherm described at the temperature ϑ' corresponds to a thermic effect $(\mathcal{Q}'_1 + \mathcal{Q}'_2)$. In accordance with the preceding theorem, we have for this cycle

$$\frac{\mathcal{Q}_2 + \mathcal{Q}'_1 + \mathcal{Q}'_2}{\mathcal{Q}_2} = \mathrm{A}.$$

This equation will only be compatible with the preceding one if

$$\mathcal{Q}'_1 = 0.$$

Whence this proposition:

If a reversible Carnot cycle is described between the temperatures ϑ and ϑ' (ϑ' being higher than ϑ) and if the isothermal change described at the temperature ϑ is athermic, then the isothermal change produced at the temperature ϑ'[6] *is also athermic.*

In that case, the ratio

$$\frac{\mathcal{Q} + \mathcal{Q}'}{\mathcal{Q}}$$

is meaningless.

We will now demonstrate that, *for any* [325] *realisable and irreversible cycle described between the temperatures ϑ and ϑ', the ratio*

$$\rho = \frac{\mathcal{Q} + \mathcal{Q}'}{\mathcal{Q}}$$

never reaches the value A.

Since the value A is essentially negative, the ratio ρ cannot achieve the value A unless the cycle belongs either to the second kind or to the species c of the third kind. Suppose that for a cycle C_1 (to fix our ideas, we take it to be of the second kind) we have

$$\rho_1 = \frac{\mathcal{Q}_1 + \mathcal{Q}'_1}{\mathcal{Q}_1} = A$$

or, since Equation (1) sanctions the replacement of $\left(\mathcal{Q}_1 + \mathcal{Q}'_1\right)$ by EW_1,

$$EW_1 = A\mathcal{Q}_1. \tag{11}$$

We have seen that the existence of real, reversible cycles is by no means absurd. We therefore admit that a real, reversible Carnot cycle C_2, described between the same temperatures ϑ, ϑ' as cycle C_1, has been constituted for which the quantity W_2 is not equal to zero.

---

[6] [ϑ in the original.]

The quantity W_2 will, therefore, be positive or negative. We can always suppose it to be positive since, if it were negative, it suffices to realise the reversible cycle[7] C_2 in the opposite sense to that in which it is positive.

By continually varying the Carnot cycle C_2, without changing either its reversibility or the temperatures between which it is described, we can always see to it that the following conditions are satisfied:

1. The duration T_1 of the Carnot cycle C_1 and the duration T_2 of the Carnot cycle C_2 are commensurable.
2. The quantities $|W_1|$ and W_2 are commensurable.
   Put

$$\frac{T_1}{T_2} = \frac{\mu_1}{\mu_2}, \quad \frac{W_2}{|W_1|} = \frac{m_2}{m_1} \tag{12}$$

where μ_1, μ_2, m_1, m_2 are four integers.

From [326] the cycles C_1 and C_2 we form a Carnot cycle Γ in the same way as in §4. For the cycle Γ we have

$$\begin{cases} W = \mu_1\mu_2\left(m_2 W_1 + m_1 W_2\right), \\ \mathcal{Q} = \mu_1\mu_2\left(m_2\mathcal{Q}_1 + m_1\mathcal{Q}_2\right), \\ \mathcal{Q}' = \mu_1\mu_2\left(m_2\mathcal{Q}'_1 + m_1\mathcal{Q}'_2\right). \end{cases} \tag{13}$$

The second Equation (12) together with the first Equation (13) shows us that

$$W = 0.$$

The cycle Γ is therefore a cycle of the first kind.

The quantity $\mathcal{Q}_2$ cannot be equal to zero. The cycle C_2 is, in fact, reversible. According to one of the propositions just demonstrated, the quantity $\mathcal{Q}_2$ cannot be equal to zero unless the quantity $\mathcal{Q}'_2$ is too. The equation

$$W_2 = E\left(\mathcal{Q}_2 + \mathcal{Q}'_2\right)$$

would therefore yield

$$W_2 = 0,$$

contrary to our hypothesis.

Since the quantity $\mathcal{Q}_2$ in the reversible cycle C_2 is not equal to zero, we know that

$$\frac{\mathcal{Q}_2 + \mathcal{Q}'_2}{\mathcal{Q}_2} = A$$

---

[7] [*cercle*, rather than *cycle*, in the original.]

or

$$EW_2 = A\mathfrak{Q}_2. \tag{14}$$

Equations (11) and (14), together with the second equality (13), show that, for the cycle Γ, we have

$$\mathfrak{Q} = \mu_1 \mu_2 \frac{E}{A} \left(m_2 W_1 + m_1 W_2\right) = 0.$$

The cycle Γ will therefore be a Carnot cycle of the first kind, described between the temperatures ϑ and ϑ', in which the isotherm described at the [327] temperature ϑ is athermic. But on the other hand, the cycle Γ would be a realisable Carnot cycle and it would not be exclusively composed of equilibrium states, since the cycle C_2 is not exclusively composed of equilibrium states. The existence of the cycle Γ is, therefore, in contradiction with the hypothesis stated in §2. Since we accept that the latter hypothesis is correct, we can formulate the following proposition:

For any realisable and irreversible cycle, the ratio

$$\rho = \frac{\mathfrak{Q} + \mathfrak{Q}'}{\mathfrak{Q}}$$

cannot reach the value A.

We will now combine the various propositions demonstrated in the preceding and present sections in a single theorem:

Let ϑ and ϑ' be two temperatures, with ϑ' higher than ϑ. There is a negative magnitude A, *depending solely on the two temperatures ϑ and ϑ', with the following properties:*

1. *For all reversible Carnot cycles, whether realisable or not, described between the temperatures ϑ and ϑ',*

$$\rho = \frac{\mathfrak{Q} + \mathfrak{Q}'}{\mathfrak{Q}} = A. \tag{15}$$

2. *For all Carnot cycles described between the temperatures ϑ and ϑ' which are realisable and irreversible, and of species c of the third kind,*

$$\rho = \frac{\mathfrak{Q} + \mathfrak{Q}'}{\mathfrak{Q}} < A. \tag{16}$$

3. *For all Carnot cycles described between the temperatures ϑ and ϑ' which are realisable and irreversible, and not of species c of the third kind,*

$$\rho = \frac{\mathfrak{Q} + \mathfrak{Q}'}{\mathfrak{Q}} > A \tag{17}$$

From [328] this statement are excluded:

1. Realisable and irreversible cycles for which

$$W > 0,\ \mathfrak{Q} = 0.$$

2. The reversible cycles for which

$$\mathcal{Q} = 0.$$

For the latter, it also holds that

$$\mathcal{Q}' = 0.$$

7.6 Absolute Temperature

The quantity A is a function of the temperatures ϑ and ϑ'; we will now study more deeply the nature of this function, or rather, the function

$$\psi(\vartheta', \vartheta) = \mathrm{A} - 1. \tag{18}$$

This function, which is only defined for values of ϑ' higher than ϑ, is negative and greater than 1 in absolute value.

Given Equation (18), the equality and the inequalities (15), (16) and (17) can be replaced by this equality and the inequalities

$$\frac{\mathcal{Q}'}{\mathcal{Q}} = \psi(\vartheta', \vartheta), \tag{15a}$$

$$\frac{\mathcal{Q}'}{\mathcal{Q}} > \psi(\vartheta', \vartheta), \tag{16a}$$

$$\frac{\mathcal{Q}'}{\mathcal{Q}} < \psi(\vartheta', \vartheta). \tag{17a}$$

Let $\vartheta, \vartheta', \vartheta''$ be three temperatures in increasing order of magnitude. We now propose to find a relation between the three quantities

$$\psi(\vartheta, \vartheta'), \psi(\vartheta', \vartheta''), \psi(\vartheta, \vartheta'').$$

Consider a *reversible* Carnot cycle described between the temperatures ϑ and ϑ''. The cycle takes the body to the temperature ϑ'', in the [329] state A$''$. It is brought to the state B$''$ by an isothermal transformation, and then to the state B by an adiabatic transformation, when the temperature is ϑ. A new isothermal transformation at the temperature ϑ brings it to the state A, and a new adiabatic transformation brings it back to the state A$''$.

Suppose that the calorific effect of the transformation BA, which we will designate by $\mathcal{Q}$(BA), is different from zero.

Then we will have

$$\frac{\mathcal{Q}\left(A''B''\right)}{\mathcal{Q}\left(BA\right)} = \psi(\vartheta, \vartheta''). \tag{a}$$

When undergoing the transformation B″B the body passes, at least once, through the temperature ϑ'. Let B′ be a state which has this temperature. Similarly, when undergoing the transformation AA″ the body passes, at least once, through the temperature ϑ'. Let A′ be a state in which it has this temperature. We connect the two states A′, B′, by a series of equilibrium states of the system all corresponding to the temperature ϑ', and we will obtain a reversible isothermal change A′B′.

The cycle A′B′BAA′ will be a reversible Carnot cycle described between the temperatures ϑ and ϑ'. Since $\mathfrak{Q}$(BA) is not zero, we will have

$$\frac{\mathfrak{Q}\left(A'B'\right)}{\mathfrak{Q}\left(BA\right)} = \psi(\vartheta, \vartheta'). \tag{b}$$

$\mathfrak{Q}$(A′B′) is certainly not zero since $\psi(\vartheta, \vartheta')$ is not zero. But clearly,

$$\mathfrak{Q}\left(A'B'\right) + \mathfrak{Q}\left(B'A'\right) = 0. \tag{c}$$

$\mathfrak{Q}$(B′A′) is therefore not zero. Consequently, in the reversible Carnot cycle A″B″B′A′A″, described between the temperatures ϑ and ϑ'', we have

$$\frac{\mathfrak{Q}\left(A''B''\right)}{\mathfrak{Q}\left(B'A'\right)} = \psi(\vartheta', \vartheta''). \tag{d}$$

Equations (*a*), (*b*), (*c*), (*d*) yield

$$\psi(\vartheta,\ \vartheta'') = -\psi(\vartheta,\ \vartheta')\psi(\vartheta',\ \vartheta''). \tag{19}$$

This [330] is the relation we wished to obtain.

The function $\psi(\vartheta, \vartheta')$ so far is meaningful only if ϑ' is higher than ϑ.

When ϑ' tends towards ϑ by values higher than ϑ, $\mathfrak{Q}'$ clearly tends, in a reversible Carnot cycle described between the temperatures ϑ and ϑ', towards the limit $(-\mathfrak{Q})$. Therefore, $\psi(\vartheta, \vartheta')$ tends towards –1. We will agree to put

$$\psi(\vartheta, \vartheta) = -1.$$

When ϑ' is less than ϑ, we define $\psi(\vartheta,\ \vartheta')$ by the equality

$$\psi(\vartheta, \vartheta') = -1/\psi(\vartheta', \vartheta).$$

In accordance with these definitions, the functional Equation (19), established under the supposition that

$$\vartheta < \vartheta' < \vartheta'',$$

remains true whatever $\vartheta, \vartheta', \vartheta''$ may be. Moreover, we are assured that the function $\psi(\vartheta, \vartheta')$ is continuous for all values of ϑ and ϑ'.

Take an arbitrary fixed temperature, ϑ_0. The functional Equation (19) gives us

$$\psi(\vartheta, \vartheta') = -\psi(\vartheta_0, \vartheta')/\psi(\vartheta_0, \vartheta).$$

Since the temperature ϑ_0 is fixed, $\psi(\vartheta_0, \vartheta)$ becomes a function of the single variable ϑ, and we put

$$F(\vartheta) = -\lambda\psi(\vartheta_0, \vartheta), \tag{20}$$

λ being a constant.

The preceding equation becomes

$$\psi(\vartheta, \vartheta') = -F(\vartheta')/F(\vartheta). \tag{21}$$

The function $\psi(\vartheta, \vartheta')$ is a continuous function of ϑ, ϑ'; when ϑ' is higher than ϑ, it is negative and greater than 1 in absolute value. The function $F(\vartheta)$ therefore has the following properties:

It [331] is essentially positive;

It varies continuously with the temperature ϑ;

It always increases at the same time as the temperature ϑ.

Instead of the quantity ϑ it is possible, in accordance with what we have said above (Section 3.6), to take the quantity $T = F(\vartheta)$, whose value for each temperature no longer depends on the choice of thermometer, as determining the temperature. T is called the *absolute temperature*.

If the absolute temperature T is adopted to represent temperature, and in all the preceding formulas the substitution

$$\vartheta = T$$

is made, then the substitution

$$F(\vartheta) = F(T) = T$$

should also be made. Recalling that

$$\psi(\vartheta_0, \vartheta_0) = -1,$$

it can be seen that Equation (20) yields

$$F(\vartheta_0) = -\lambda.$$

The absolute temperature is therefore not entirely determined; at an arbitrary temperature ϑ_0, it takes an arbitrary value λ. It is usual to take as the temperature ϑ_0 the temperature which serves as 0 on the centigrade scale and, for λ, the inverse of a certain constant encountered in the study of gases, *the coefficient of expansion of perfect gases.*

It is said that this definition of absolute temperature was introduced by Sir W. Thomson and set forth on several occasions by G. Lippmann.

7.7 A Definitive Statement of Carnot's Theorem

The determination of the function $\psi(\vartheta, \vartheta')$ provided by Equation (21) will allow us to give Carnot's theorem a new and definitive form.

We [332] first exclude:

1. Reversible Carnot cycles described between the temperatures ϑ and ϑ' in which the change produced at the temperature ϑ is athermic.
2. Realisable, irreversible Carnot cycles of the third kind described between the temperatures ϑ and ϑ', in which the change produced at the temperature ϑ is athermic.

For reversible cycles, whether realisable or not, Equations (15a) and (21) yield

$$\frac{\mathcal{Q}'}{\mathcal{Q}} = -\frac{F\left(\vartheta'\right)}{F\left(\vartheta\right)}$$

and, since $\mathcal{Q}$ is not zero,

$$\frac{\mathcal{Q}}{F\left(\vartheta\right)} + \frac{\mathcal{Q}'}{F\left(\vartheta'\right)} = 0.$$

For realisable, irreversible cycles of species c of the third kind, Equation (16b) and Equation (21) yield

$$\frac{\mathcal{Q}'}{\mathcal{Q}} < -\frac{F\left(\vartheta'\right)}{F\left(\vartheta\right)}$$

But in this case, the quantity $\mathcal{Q}$ is negative, so that

$$\frac{\mathcal{Q}}{F\left(\vartheta\right)} + \frac{\mathcal{Q}'}{F\left(\vartheta'\right)} > 0.$$

For the other irreversible cycles, the inequality (17b) together with Equation (21) yields

$$\frac{\mathcal{Q}'}{\mathcal{Q}} > -\frac{F\left(\vartheta'\right)}{F\left(\vartheta\right)}$$

For all these cycles, the quantity $\mathcal{Q}$ is positive, so that, again,

$$\frac{\mathcal{Q}}{F\left(\vartheta\right)} + \frac{\mathcal{Q}'}{F\left(\vartheta'\right)} > 0.$$

We now return to the two classes that we have excluded.

For all cycles of the first class, we know that not only [333] is $\mathcal{Q} = 0$, but also $\mathcal{Q}' = 0$. We can therefore write

$$\frac{\mathcal{Q}}{F(\vartheta)} + \frac{\mathcal{Q}'}{F\left(\vartheta'\right)} = 0.$$

For all cycles of the second class, we have

$$\mathcal{Q} = 0, \ W > 0.$$

Equation (1), which is reduced here to

$$W = E\mathcal{Q}',$$

then gives us

$$\mathcal{Q}' > 0.$$

We can therefore write, for all cycles of this class,

$$\frac{\mathcal{Q}}{F(\vartheta)} + \frac{\mathcal{Q}'}{F(\vartheta')} > 0.$$

Bringing together all the results that we have just obtained, we can state CARNOT'S THEOREM in the following general form:

1. *For all reversible Carnot cycles, whether realisable or not, described between the temperatures ϑ and ϑ', we have*
$$\frac{\mathcal{Q}}{F(\vartheta)} + \frac{\mathcal{Q}'}{F\left(\vartheta'\right)} = 0. \tag{22}$$
2. *For all real and irreversible Carnot cycles, whether realisable or not, described between the temperatures ϑ* and *ϑ', we have*
$$\frac{\mathcal{Q}}{F(\vartheta)} + \frac{\mathcal{Q}'}{F\left(\vartheta'\right)} > 0. \tag{23}$$

These statements can be put in somewhat more explicit form by reverting to the definition of the total calorific effect of a change or of several changes.

Let [334] Q be the sum of the quantities of heat released by the system during this collection of changes. If these changes are reversible, we have

$$\mathcal{Q} = Q,$$

allowing replacement of Equation (22) by

$$\frac{Q}{F(\vartheta)} + \frac{Q'}{F\left(\vartheta'\right)} = 0. \tag{22a}$$

If the changes under consideration are real and irreversible, let $[\mathfrak{T}]$ designate the sum of the increases that the kinetic energy of the system undergoes during these changes. We have

$$E\mathfrak{Q} = EQ + [\mathfrak{T}],$$

allowing us to replace the inequality (23) by the inequality

$$\frac{EQ + \left[\mathfrak{T}\right]}{F\left(\vartheta\right)} + \frac{EQ' + \left[\mathfrak{T}\right]'}{F\left(\vartheta'\right)} > 0 \tag{23a}$$

These various statements are not subject to further exceptions.

Chapter 8
Entropy and Clausius' Theorem

8.1 Conditions and Hypotheses

Carnot's theorem has, it is said, been generalised by R. Clausius. At all events, this generalisation is only justified provided a certain number of conditions and hypotheses are satisfied, some of which concern the system studied, others the changes undergone by the system.

It will not be useful to us in this chapter to distinguish, among the parameters defining the state of the system, those which we have designated by the letters *a, b, . . . , l* from those that we have designated by the letters $\alpha, \beta, \ldots, \lambda$. On the other hand, it will be necessary for us to [335] highlight the temperature ϑ amongst the parameters that define the state of the system. We will suppose, moreover, that *the latter has the same value at all points of the system*. Thus, the state of the system will be defined by the *n* parameters

$$\alpha, \beta, \ldots, \lambda, \vartheta.$$

The system that we will study will not only be subject to this restriction of having the same temperature at all of its points in each of its states, it being possible, moreover, for this temperature to vary from one state to another. We will also suppose that it is subject to two more fundamental restrictions:

> FIRST RESTRICTION.—*For any state of the system defined by the values*
>
> $$\alpha, \beta, \ldots, \lambda, \vartheta,$$
>
> *of the variable parameters, we admit that it is always possible to find, in at least one way, a system of external bodies, all at the temperature ϑ, such that the system under consideration remains indefinitely at equilibrium in the state $\alpha, \beta, \ldots, \lambda, \vartheta$ if subjected to the action of these external bodies, which don't change, and if it is taken with a collection of initial velocities equal to zero,*

The statement of this restriction is not a vain precaution. Systems are often encountered in physics which are not subject to it and consequently to which the considerations to follow are not applicable. We cite some examples:

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
DOI 10.1007/978-94-007-0311-7_8,

1. A conducting body is traversed by electric currents. There figure among the variable parameters determining the state of the conductor:

The components *u, v, w* of electric flux at each point (*x, y, z*) of the conductor;

The solid density ρ of the electricity at each point of the mass of the conductor;

The [336] surface density σ of the electricity at each point of the surfaces of discontinuity which divide the conductor or which limit it.

Is it possible, by making suitably chosen external bodies act, to maintain the conductor in question at equilibrium so that the variables just enumerated always have values independent of time? This is not possible unless the relation*

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}=0 \tag{i}$$

holds at each point of the mass of the conductor, and, at each point of a surface of discontinuity whose normal has the two orientations N_1, N_2,

$$\begin{cases} u_1\ \cos(N_1,\ x)+v_1\ \cos(N_1,y)+w_1\ \cos(N_1,z) \\ +u_2\ \cos(N_2,x)+v_2\ \cos(N_2,y)+w_2\ \cos(N_2,z)=0\,. \end{cases} \tag{ii}$$

In fact, if these two relations are not verified, the parameters ρ and σ necessarily vary with the time, *t*, in virtue the general equations

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}=-\frac{\partial \rho}{\partial t},$$

$$\begin{aligned} &u_1\ \cos(N_1,x)+v_1\ \cos(N_1,y)+w_1\ \cos(N_1,z)\\ &\quad +u_2\ \cos(N_2,x)+v_2\ \cos(N_2,y)+w_2\ \cos(N_2,z)=-\frac{\partial \sigma}{\partial t}\ . \end{aligned}$$

Relations (i) and (ii) characterise currents that are called *uniform*, and it is clear that it is possible to state the following proposition, which has profound consequences in electrodynamics[1]:

A system of non-uniform currents does not satisfy the forgoing restriction.

2. A closed circuit through which a uniform current flows encloses an electrolytic conductor. Among the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ defining the state of the system figure the intensity of the current and [337] variables which determine the chemical state of the system. Now, in virtue of the definition of electrolytes, known as *Faraday's law*, an electrolyte traversed by a current during each interval of time undergoes a chemical change proportional in magnitude to the interval of time and the intensity of the

---

*The following two equations, numbered (1) and (2) in the original, are renumbered here to avoid confusion with Equations (1) and (2) in the next section, which are referred to later.

[1] P. Duhem, *Leçons sur l'Électricité et le Magnétisme*, vol. III, p. 221.

current. It would therefore be contradictory to imagine external bodies whose action maintained the system at equilibrium, and, consequently, rendered invariable the current intensity and the chemical state of the circuit at the same time. Thus, a circuit through which even uniform currents run does not satisfy the preceding restriction if it encloses electrolytes. This conclusion is important in electrodynamics.[2]

The preceding restrictive hypothesis entails a remarkable corollary:

> COROLLARY.—*It is always possible to pass from any state* $(\alpha, \beta, \ldots, \lambda, \vartheta)$ *to any other* $(\alpha', \beta', \ldots, \lambda', \vartheta')$ *by an infinity of reversible changes.*

In fact, it is always possible to set up a continuous series of states of the system between the two states $(\alpha, \beta, \ldots, \lambda, \vartheta)$ and $(\alpha', \beta', \ldots, \lambda', \vartheta')$ in infinitely many ways. With suitably chosen external bodies, these states can be transformed into equilibrium states. Each of these series, constituted as we have just indicated, then forms a continuous series of equilibrium states, or, in virtue of a hypothesis mentioned in Section 6.8, a reversible change.

> SECOND RESTRICTION.—*Suppose that, beginning in a certain state* $(\alpha, \beta, \ldots, \lambda, \vartheta)$ *of the system, it is subject to a virtual change*

$$\delta\alpha, \delta\beta, \ldots, \delta\lambda, \delta\vartheta.$$

The actions of the external bodies maintaining it in equilibrium in the state $(\alpha, \beta, \ldots, \lambda, \vartheta)$ perform the virtual work

$$A\delta\alpha + B\delta\beta + \ldots + L\delta\lambda + \Theta\delta\vartheta.$$

We [338] suppose that *the quantities* $A, B, \ldots, L, \Theta$ *are finite, uniform and continuous functions of the parameters* $\alpha, \beta, \ldots, \lambda, \vartheta$.

As with the foregoing restriction, the statement of this one is not redundant because it is by no means evident that all systems studied in physics are subject to it. In particular, Marcel Brillouin[3] has provided a theory for permanent deformations which assumes that these quantities $A, B, \ldots, L, \Theta$ are continuous but non-uniform functions of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$.

We add the following hypothesis to that just stated:

> *The virtual work of the actions which must be applied to a given system to maintain it at equilibrium does not depend on the absolute position that the system occupies in space nor on the variation in this position.*

First of all, it follows from this hypothesis that the quantities $A, B, \ldots, L, \Theta$ do not depend on those of the variables among $\alpha, \beta, \ldots, \lambda, \vartheta$ which fix the absolute position in space of the system.

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[2] P. Duhem, *Leçons sur l'Électricité et le Magnétisme*, vol. III, p. 220. *Journ. de Math.* (4th. series), vol. IX.—No. III; 1893.

[3] Marcel Brillouin, *Déformations permanentes et Thermodynamique* (*Comptes rendus*, 6, 13, 20 and 27 February 1888).

Second, it follows that the virtual variations $\delta\alpha, \delta\beta, \ldots, \delta\lambda, \delta\vartheta$ corresponding to the variables fixing the absolute position of the system in space do not figure in the sum

$$A\delta\alpha + B\delta\beta + \ldots + L\delta\lambda + \Theta\delta\vartheta.$$

The coefficient of each of these is equal to zero.

8.2 Calorific Coefficients of the System at Equilibrium

In order to conveniently explain what is to follow, we will employ the language of the geometry of n dimensions, n being the number of the parameters $\alpha, \beta, \ldots, \lambda, \vartheta$ which define the state of the system. The statements at which we will arrive can always be represented by plane figures if there is just one of the parameters $\alpha, \beta, \ldots, \lambda$, and by figures in space if there are two of them.

A [339] state of the system, corresponding to a system of values of the coordinates $\alpha, \beta, \ldots, \lambda, \vartheta$, will be represented by a *point* in the space of n dimensions. A change, corresponding to a linear series of values of $\alpha, \beta, \ldots, \lambda, \vartheta$, will be represented by a *line*.

If the system is taken in a determinate state $(\alpha, \beta, \ldots, \lambda, \vartheta)$, the actions $A, B, \ldots, L, \Theta$ which allow it to remain at equilibrium in this state are, by hypothesis, uniform and continuous functions of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$.

$$\begin{cases} A = f_\alpha(\alpha,\ \beta,\ \ldots, \lambda,\ \vartheta), \\ B = f_\beta(\alpha,\ \beta,\ \ldots, \lambda,\ \vartheta), \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L = f_\lambda(\alpha,\ \beta,\ \ldots, \lambda,\ \vartheta), \\ \Theta = f_\vartheta(\alpha,\ \beta,\ \ldots, \lambda,\ \vartheta). \end{cases} \tag{1}$$

Equations (1) are the *equilibrium equations of the system*. These equations will be said to be *known* when the form of the n functions $\alpha, \beta, \ldots, \lambda, \vartheta$ is known.

Let U be a uniform and continuous function of $\alpha, \beta, \ldots, \lambda, \vartheta$ which represents the internal energy of the system. Put

$$\begin{cases} R_\alpha = \dfrac{\partial U}{\partial \alpha} - \dfrac{f_\alpha}{E}, \\ R_\beta = \dfrac{\partial U}{\partial \beta} - \dfrac{f_\beta}{E}, \\ \ldots\ldots\ldots\ldots\ldots, \\ R_\lambda = \dfrac{\partial U}{\partial \lambda} - \dfrac{f_\lambda}{E}, \\ C = \dfrac{\partial U}{\partial \vartheta} - \dfrac{f_\vartheta}{E}. \end{cases} \tag{2}$$

The n quantities $R_\alpha, R_\beta, \ldots, R_\lambda$ defined by these equations will be uniform functions of $\alpha, \beta, \ldots, \lambda, \vartheta$. They will be (Chapter 5, Equations (12) and (12a)) the *calorific coefficients of the system at equilibrium*. Among these parameters, there is one which will be distinguished from the others by specific properties, the coefficient [340] C. We will call it the *caloric capacity of the system, relative to the variables* $\alpha, \beta, \ldots, \lambda, \vartheta$.

Like, on the one hand the quantity U (Section 4.2, tenth convention) and on the other hand the quantities $A, B, \ldots, L$, Θ (this Chapter, §1), the quantities $R_\alpha, R_\beta, \ldots, R_\lambda, C$ do not depend on those among the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ which fix the absolute position of the system in space. Moreover, those of the calorific coefficients multiplying the variations of these latter variables in the expression of dQ are all zero.

The equation

$$dQ = -(R_\alpha\, \delta\alpha + R_\beta\, \delta\beta + \ldots + R_\lambda\, \delta\lambda + C\, \delta\vartheta) \tag{3}$$

determines (Chapter 5, Equations (13)) the quantity of heat released by the system while subject to the real or virtual change $(\delta\alpha, \delta\beta, \ldots, \delta\lambda, \delta\vartheta)$.

The differential equation

$$R_\alpha\, d\alpha + R_\beta\, d\beta + \ldots + R_\lambda\, d\lambda + C\, d\vartheta = 0 \tag{4}$$

represents, in the n-dimensional space considered, a family of spaces of $(n - 1)$ dimensions (of lines, in the space of two dimensions, of surfaces in the space of three dimensions). We accept that *through every point* $(\alpha, \beta, \ldots, \lambda, \vartheta)$ *of the n-dimensional space there passes one and only one of these spaces of* $(n - 1)$ *dimensions, and in addition that the space thus determined passing through the point* $(\alpha, \beta, \ldots, \lambda, \vartheta)$ *is displaced and deformed continuously when the point* $(\alpha, \beta, \ldots, \lambda, \vartheta)$ *is displaced continuously*.

We further accept that a space of reversible adiabats is never closed on itself like a closed line or a closed surface, but always forms a simply connected space extending to the limits of the field of values of $\alpha, \beta, \ldots, \lambda, \vartheta$.

Consider any line traced entirely within one of these spaces of $(n - 1)$ dimensions. This line represents a continuous series of states of the system. In each of these states $(\alpha, \beta, \ldots, \lambda, \vartheta)$, we suppose the system to be surrounded by bodies having the same temperature [341] as it and exerting on it actions given by Equations (1). This series of states will be a series of equilibrium states. In accordance with the hypothesis stated in Section 6.8, this series of equilibrium states constitutes a reversible change. Equations (3) and (4) show that, for all elements of this reversible change, we have

$$dQ = 0,$$

so that this reversible change will be adiabatic. Thus, *each line traced entirely in one of the spaces of* $(n - 1)$ *dimensions defined by Equation* (4) *represents a reversible adiabatic change of the system*. We call each of these $(n - 1)$-dimensional spaces defined by Equation (4) *a space of reversible adiabats*.

Take two points, m and n, in the space of n dimensions considered. Between these two points, m and n, we draw two lines, l and l', such that each of these has no more than one point in common with such a space of reversible adiabats. The following propositions, which are geometrically obvious when the space of reversible adiabats are lines ($n = 2$) or surfaces ($n = 3$), can be stated in entirely general fashion:

The space of reversible adiabats drawn through a point a on the line l intersects the line l' in one and only one point a'; these two points a and a' are called *corresponding points*.

If the three points a', b', c' of the line l' correspond, respectively, to three points a, b, c of the line l, and the point b is situated, on the line l, between the points a and c, then the point b' is situated on the line l', between the points a' and c'.

If two points a, b are infinitesimally close on the line l, their correspondents a', b' are infinitesimally close on the line l'.

To the point m on the line l there corresponds the same point m on the line l', and to the point n on the line l there corresponds the same point n on the line l'.

This mode of correspondence between the points of two lines will be useful to us in the demonstration of Clausius' theorem, to which we now proceed.

8.3 Demonstration of Clausius' Theorem

Any [342] line traced in the n-dimensional space under consideration represents a series of states of the system. If, in each of these states, we suppose the system surrounded by bodies at the same temperature as it and exerting actions on it given by Equations (1), then each of these states becomes an equilibrium state, and the series of these states will be a reversible change. Thus, *any line traced in the space of* $\alpha, \beta, \ldots, \lambda, \vartheta$ *always represents, in one and only one way, a reversible change of the system.*

We will study the properties of similar transformations, but we will provisionally suppose that each of these reversible changes under study is subject to certain restrictions that we will now enumerate:

1. The line representing one of these reversible changes under study has no part of finite extension traced in its entirety in a space of reversible adiabats.
2. The line representing one of these reversible changes under study never meets the same space of reversible adiabats more than once. This last restriction evidently presupposes another: the line considered never passes through the same point more than once.

Consider two reversible changes, l and l', subject to the preceding restrictions. Both take the system in the same initial state, represented by the point m, and lead it to the same final state, represented by the point n.

Let a, b be two infinitesimally close states of the change l, the state b coming after the state a when the change l is followed from m towards n. Let a', b' be two states of the change l' corresponding, respectively, to the two states a, b. In accordance with what we have seen, the two states a', b' are infinitesimally close on the change

l' and, when this change is followed from m to n, the state a' is encountered before the state b'.

Let ϑ be the temperature of the system in the state a and ϑ' the temperature of the system in the state a'. Let dQ be the quantity of heat released by the system while it undergoes the infinitesimal reversible change ab and dQ' the quantity of heat released by the [343] system while it undergoes the infinitesimal reversible change $a'b'$. We now propose to demonstrate that

$$\frac{dQ}{F(\vartheta)} = \frac{dQ'}{F(\vartheta')}. \tag{5}$$

Through the point a, we draw an isothermal line to the point c where it meets the space of reversible adiabats drawn through the point b. In general, the point c will be infinitesimally close to the two points a and b. Similarly, we draw an isothermal line through the point a' to the point c' where it meets the space of reversible adiabats drawn through the point b'. In general, the point c' will be infinitesimally close to the two points a' and b'. For the moment, we suppose that the hypotheses just mentioned are satisfied, leaving for treatment later the case where they are not satisfied.

We join the two points c, b by an infinitesimal line drawn in the space of reversible adiabats to which these two points belong, and similarly we join the two points c', b' by an infinitesimal line drawn in the space of reversible adiabats to which these two points belong.

The lines ac, cb, $a'c'$, $c'b'$ each represent an infinitesimal reversible change of the system.

The two reversible changes cb, $c'b'$ are adiabatic; when the system is subjected to any one of them, it releases a quantity of heat equal to zero.

Let dQ_1 be the quantity of heat released by the system while it describes the reversible isothermal ac and dQ'_1 the quantity of heat released by the system while it describes the reversible isothermal $c'a'$.

Consider the closed and reversible cycle *abca*. When the system describes this cycle, it releases a quantity of heat $(dQ - dQ_1)$. Applying Equation (16) (Chapter 5) to each of the elements of this cycle, we easily obtain the equation

$$E\ (dQ - dQ_1) = \int (A\, d\alpha + B\, d\beta + \ldots + L\, d\lambda + \Theta\, d\vartheta).$$

the integral extending over the entire cycle *abca*.

Let [344] $(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1)$ be one of the points of this cycle, and $A_1, B_1, \ldots, L_1, \Theta_1$, the values taken by the functions $A, B, \ldots, L, \Theta$ at this point; then we can write the preceding equation as

$$\begin{aligned} E\ (dQ - dQ_1) &= A_1 \int d\alpha + B_1 \int d\beta + \ldots + L_1 \int d\lambda + \Theta_1 \int d\vartheta \\ &\quad + \int \left[(A - A_1)\ d\alpha + (B - B_1)\ d\beta + \ldots + (L - L_1)\ d\lambda + (\Theta - \Theta_1)\ d\vartheta \right] \end{aligned}$$

But since the cycle is closed, we have

$$\int d\alpha = 0, \int d\beta = 0, \ldots, \int d\lambda = 0, \int d\vartheta = 0.$$

On the other hand, since, by hypothesis, the quantities $A, B, \ldots, L, \Theta$ vary continuously with the position of the point $(\alpha, \beta, \ldots, \lambda, \vartheta)$, the quantities

$$(A - A_1), \quad (B - B_1), \ldots, (L - L_1), \quad (\Theta - \Theta_1)$$

are infinitesimal, at least of the same order as the dimensions of the cycle. The quantity

$$\int [(A - A_1)\ d\alpha + (B - B_1)\ d\beta + \ldots + (L - L_1)\ d\lambda + (\Theta - \Theta_1)\ d\vartheta]$$

is therefore infinitesimal to a higher order than that of the dimensions of the cycle, so that the preceding equation can be written

$$dQ - dQ_1 = 0. \tag{6}$$

An analogous demonstration, applied to the cycle $a'b'c'a'$, yields the equation

$$dQ' + dQ'_1 = 0. \tag{7}$$

We can now describe the system by:

1. The reversible isothermal ac, relative to the temperature ϑ.
2. The [345] reversible adiabat cb.
3. The reversible adiabat bb'.
4. The reversible adiabat $b'c'$.
5. The reversible isothermal $c'a'$, relative to the temperature ϑ'.
6. The reversible adiabat $a'a$.

The system will have traced a reversible Carnot cycle between the temperatures ϑ and ϑ'. At the temperature ϑ, it will have released a quantity of heat dQ_1, and at the temperature ϑ', a quantity of heat dQ'_1. We therefore have (Chapter 7, Equation (22a))

$$\frac{dQ_1}{F(\vartheta)} + \frac{dQ'_1}{F(\vartheta')} = 0$$

In virtue of Equations (6) and (7), this equation yields Equation (5), which is what we wished to demonstrate.

Considering successively all the elements of the transformation l in moving from m to n, the elements corresponding to them in the transformation l' trace once and once only the transformation l' in going from m' to n'. For each group of corresponding elements, we write an equation analogous to Equation (5) and add one after another all the results obtained. We obtain the equation

$$\int_l \frac{dQ}{F(\vartheta)} = \int_{l'} \frac{dQ'}{F\left(\vartheta'\right)} \tag{8}$$

which leads us to state the following proposition:

> *Considering all the reversible changes (subject to the restrictions mentioned) leading the system from the state m to the state n, for any two such states whatever, the integral*
>
> $$\int \frac{dQ}{F(\vartheta)}$$
>
> *has the same value for all these changes.*

It remains now to successively lift the various restrictions introduced to obtain the foregoing demonstration.

We have supposed that from all points a of the line l it is possible to draw an isothermal meeting the space of reversible adiabats drawn [346] through the point b, infinitesimally close to the point a, in a point c, itself infinitesimally close to the point a. This comes down to accepting, as is easily shown, that the isothermal line issuing from point a is not tangent to the point a in the space of reversible adiabats which passes through this point. Such a hypothesis is made for all points a' of the line l'.

In the first place, it is easily shown that, if there is, either on the line l or on the line l' or on both, a limited number of points isolated from one another for which the preceding hypothesis ceases to hold, the preceding theorem will certainly not be incorrect. It could therefore only be incorrect if there exists on at least one of these lines, the line l for example, a finite extended portion, *fgh*, at every point of which the reversible isothermal would be tangent to the space of reversible adiabats.

If such conditions are fulfilled for the line *fgh*, two cases can be distinguished.

It is possible that, from the point f to the point h, lines $fg'h$ can be drawn infinitesimally close to the line *fgh* which escape the preceding conditions.

It is possible, on the contrary, that all the points of the line *fgh* belong to a domain D, drawn through the space $\alpha, \beta, \ldots, \lambda, \vartheta$, and that at every point of this domain the reversible isothermal is tangent to the space of reversible adiabats.

In the first case, the integral $\int \frac{dQ}{F(\vartheta)}$ over the line $mfg'hn$ will have, in accordance with the preceding demonstration, the same value as the integral of the same form over the line l'. Its value will therefore not vary when the line $mfg'hn$ varies continuously so as to tend towards the line *mfghn* or l. Now under these conditions, this integral will certainly tend towards

$$\int_l \frac{dQ}{F(\vartheta)}$$

We therefore have once more in this case

$$\int_{l} \frac{dQ}{F(\vartheta)} = \int_{l'} \frac{dQ'}{F\left(\vartheta'\right)}.$$

Only [347] the second of the two cases that we have just distinguished is still excluded from our investigations.

We will try to characterise this case more precisely.

A reversible isothermal satisfies the differential equation

$$d\vartheta = 0.$$

A space of reversible adiabats is defined by the differential equation

$$R_\alpha \, d\alpha + R_\beta \, d\beta + \ldots + R_\lambda \, d\lambda + C \, d\vartheta = 0 \tag{4}$$

In order that at every point $(\alpha, \beta, \ldots, \lambda, \vartheta)$ of the domain D any reversible isothermal be tangent to the space of reversible adiabats, it is necessary and sufficient that at each point of the domain,

$$R_\alpha = 0, \; R_\beta = 0, \; \ldots, \; R_\lambda = 0. \tag{9}$$

We therefore provisionally exclude from our investigations those systems which satisfy Equations (9) at all points of a domain of finite extent belonging to the space of $\alpha, \beta, \ldots, \lambda, \vartheta$.

We have so far supposed that each of the two changes l and l' do not meet the same space of reversible adiabats in more than one point. We will now relinquish this restriction and suppose that each of these two changes l and l' can meet the same space of reversible adiabats at a finite number of points, isolated from one another.

Take the space of reversible adiabats E(m) passing through the point m and the space of reversible adiabats E(n) passing through the point n. These two spaces of (n – 1) dimensions divide the space of n dimensions into three regions. One of these regions is included between the spaces E(m) and E(n); the other two are exterior. Following the straight line connecting the point m with the point n in such a way that the point m is met before arriving at point n, I will refer to the region traversed before reaching m as *the first*. Immediately after passing the point m [348] leads to what I will call the *second* region. Leaving this second region at the moment of passing point n leads to what I call the *third* region.[4]

It might happen that the line l has a point p in common with a space of reversible adiabats E, other than the space E(m) or E(n), without passing through this space in the meeting point. If two spaces of reversible adiabats are drawn infinitesimally close to the space E, and situated on either side of this space, one of them will not have any point in common with the line l infinitesimally close to the point p, while the other will have two points in common with the line l infinitesimally close to the point p.

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[4] In the case when the two points m and n lie in the same space of reversible adiabats, the first and third regions coincide.

Let us take all the points on the line l analogous to p where the line l comes into contact with a space of reversible adiabats without passing through it. Similarly, we take all the points on the line l' where the line l' comes into contact with a space of reversible adiabats without passing through it. We draw spaces of reversible adiabats through all these points. Joined to the spaces E(m) and E(n), they divide the space into a certain number of *subregions*.

All the spaces of reversible adiabats situated in the same subregion meet the line l in the same number N of points, and the line l' in the same number N$'$ of points. If the subregion in question is a part of the second region, the two numbers N and N$'$ are uneven; if the subregion at issue is situated in the first or the third region, N and N$'$ are even or zero.

Let us consider a subregion contained in the second region. A space of reversible adiabats E is drawn in this subregion, meeting the line l in $(2k + 1)$ points. These points are numbered in the order they occur on the line l moving from point m to point n; let them be $a_1, a_2, \ldots, a_{2k}, a_{2k+1}$. The same space of reversible adiabats meets the line l' in $(2k' + 1)$ points which are numbered in the order they occur on the line l' moving from point m to point n as $a'_1, a'_2, \ldots, a'_{2k'}, a'_{2k'+1}$.

Take a point b_1 on the line l drawn from m towards n [349] infinitesimally later than the point a_1, which is also in the same subregion as the point a_1. Through point b_1 we draw a space of reversible adiabats F. Given what we have assumed about spaces of reversible adiabats, the space F will be infinitesimally close to the space E without any points in common. The space F meets the line l in $(2k + 1)$ points $b_1, b_2, \ldots, b_{2k}$ close, respectively, to the points $a_1, a_2, \ldots, a_{2k}, a_{2k+1}$. And it meets the line l' in $(2k' + 1)$ points $b'_1, b'_2, \ldots, b'_{2k'}, b'_{2k'+1}$ close, respectively, to the points $a'_1, a'_2, \ldots, a'_{2k'}, a'_{2k'+1}$.

The points a_i and b_i occur on the line l taken in the direction from m towards n, in the following order:

$$a_1,\ b_1,\ b_2,\ a_2,\ a_3,\ b_3, \ldots, b_{2k},\ a_{2k},\ a_{2k+1},\ b_{2k+1},$$

which gives us $(2k + 1)$ infinitesimal reversible changes with their representative line between the spaces E and F. These changes are:

$$a_1b_1,\ b_2a_2,\ a_3b_3, \ldots, b_{2k}a_{2k},\ a_{2k+1}b_{2k+1}.$$

We adopt the following notations for these changes:

Change undergone by the system	Initial temperature of the system	Heat released by the system
a_1b_1	ϑ_1	dQ_1
b_2a_2	ϑ_2	dQ_2
a_3b_3	ϑ_3	dQ_3
...	...	...
$b_{2k}a_{2k}$	ϑ_{2k}	dQ_{2k}
$a_{2k+1}b_{2k+1}$	ϑ_{2k+1}	dQ_{2k+1}

The points a'_{i} and b'_{i} occur on the line l' taken in the direction from m towards n in the following order:

$$a'_1,\ b'_1,\ b'_2,\ a'_2,\ a'_3,\ b'_3,\ldots,\ b'_{2k'},\ a'_{2k'},\ a'_{2k'+1},\ b'_{2k'+1},$$

which gives us $(2k' + 1)$ infinitesimal reversible changes [350] with their representative line between the spaces E and F. These changes are:

$$a'_1 b'_1,\ b'_2 a'_2,\ a'_3 b'_3,\ldots,\ b'_{2k'} a'_{2k'},\ a'_{2k'+1} b'_{2k'+1}$$

We adopt the following notations for these changes:

Change undergone by the system	Initial temperature of the system	Heat released by the system
$a'_1 b'_1$	ϑ'_1	dQ'_1
$b'_2 a'_2$	ϑ'_2	dQ'_2
$a'_3 b'_3$	ϑ'_3	dQ'_3
…	…	…
$b'_{2k'} a'_{2k'}$	$\vartheta'_{2k'}$	$dQ'_{2k'}$
$a'_{2k'+1} b'_{2k'+1}$	$\vartheta'_{2k'+1}$	$dQ'_{2k'+1}$

Consider the two changes $a_1\ b_1$ and $b_2\ a_2$. An argument analogous to that which furnished Equation (5) yields without difficulty

$$\frac{dQ_1}{F(\vartheta_1)} + \frac{dQ_2}{F(\vartheta_2)} = 0.$$

Continuing in the same way up to the two changes $a_{2k-1}\ b_{2k-1}$ and $b_{2k}\ a_{2k}$ yields

$$\frac{dQ_{2k-1}}{F(\vartheta_{2k-1})} + \frac{dQ_{2k}}{F(\vartheta_{2k})} = 0.$$

Similarly, it can be shown that

$$\frac{dQ'_1}{F(\vartheta'_1)} + \frac{dQ'_2}{F(\vartheta'_2)} = 0,$$

$$\frac{dQ'_3}{F(\vartheta'_3)} + \frac{dQ'_4}{F(\vartheta'_4)} = 0,$$

$$\dots\dots\dots\dots\dots\dots\dots\dots,$$

$$\frac{dQ'_{2k'-1}}{F\left(\vartheta_{2k'-1}\right)} + \frac{dQ'_{2k'}}{F(\vartheta_{2k'})} = 0.$$

Finally, [351] the comparison between $a_{2k+1}b_{2k+1}$ and $a'_{2k'+1}b'_{2k'+1}$ yields the equation

$$\frac{dQ_{2k+1}}{F(\vartheta_{2k+1})}=\frac{dQ'_{2k'+1}}{F\left(\vartheta_{2k'+1}\right)}$$

These several equations allow us to write

$$\frac{dQ_1}{F(\vartheta_1)}+\frac{dQ_2}{F(\vartheta_2)}+\ldots+\frac{dQ_{2k}}{F(\vartheta_{2k})}+\frac{dQ_{2k+1}}{F(\vartheta_{2k+1})}=$$

$$\frac{dQ'_1}{F\left(\vartheta'_1\right)}+\frac{dQ'_2}{F\left(\vartheta'_2\right)}+\ldots+\frac{dQ'_{2k'}}{F\left(\vartheta'_{2k'}\right)}+\frac{dQ'_{2k'+1}}{F\left(\vartheta'_{2k'+1}\right)}.$$

An analogous equation can be written for all systems formed from two infinitesimally close spaces of reversible adiabats drawn in the subregions considered. Therefore, for the whole subregion considered,

$$\sum\frac{dQ}{F(\vartheta)}=\sum\frac{dQ'}{F\left(\vartheta'\right)}, \tag{10}$$

where the first $\sum$ sign ranges over all the elements of the change l situated in the subregion considered, and the second ranges over all the elements of the change l' situated in the same subregion.

The same argument can be applied to each subregion within the second region, furnishing an analogous equation, so that it may be supposed that Equation (10) extends to the whole of the second region.

Consider now a subregion falling either in the first or in the third region. In this subregion a space of reversible adiabats E is drawn meeting the line l in $2k$ points. These points are numbered in the order they occur on the line l in moving from point m to point n as $a_1, a_2, \ldots, a_{2k}$.

Take a point b_1 on the line l, drawn from m towards n, occurring infinitesimally later than the point a_1, and which therefore occurs in the same subregion as the point a_1. From point b_1 a space of reversible adiabats F is drawn. In accordance with what we have assumed [352] regarding spaces of reversible adiabats, the space F will be everywhere infinitesimally close to the space E without intersecting it. The space F intersects line l in $2k$ points $b_1, b_2, \ldots, b_{2k-1}, b_{2k}$, close, respectively, to the points $a_1, a_2, \ldots, a_{2k-1}, a_{2k}$.

The points a_i and b_i occur on the line l in the following order:

$$a_1, b_1, b_2, a_2, a_3, b_3, \ldots, a_{2k-1}, b_{2k-1}, b_{2k}, a_{2k},$$

which gives us $2k$ infinitesimal reversible changes with their representative line between the spaces E and F. These changes are:

$$a_1b_1, b_2a_2, a_3b_3, \ldots, a_{2k-1}b_{2k-1}, b_{2k}a_{2k}.$$

Consideration of these changes easily yields the equations

$$\frac{dQ_1}{F(\vartheta_1)} + \frac{dQ_2}{F(\vartheta_2)} = 0,$$

$$\frac{dQ_3}{F(\vartheta_3)} + \frac{dQ_4}{F(\vartheta_4)} = 0,$$

$$\dots\dots\dots\dots\dots\dots\dots,$$

$$\frac{dQ_{2k-1}}{F(\vartheta_{2k-1})} + \frac{dQ_{2k}}{F(\vartheta_{2k})} = 0,$$

which themselves give the equation

$$\frac{dQ_1}{F(\vartheta_1)} + \frac{dQ_2}{F(\vartheta_2)} + \ldots + \frac{dQ_{2k}}{F(\vartheta_{2k})} = 0.$$

An analogous equation can be written for every system formed by two infinitesimally close spaces of reversible adiabats occurring in the same subregion under consideration. Accordingly, for this whole subregion, we have

$$\sum \frac{dQ}{F(\vartheta)} = 0, \tag{11}$$

where the $\sum$ sign ranges over all the elements of the change l situated in the subregion at issue.

For [353] each subregion falling within the first region or the third region, a similar argument can be applied furnishing an analogous equation, so that Equation (11) can be extended to the sum of the first and the third regions.

The equation

$$\sum \frac{dQ'}{F(\vartheta')} = 0, \tag{11a}$$

in which the $\sum$ sign ranges over all the elements of the change l' situated in the first or the third regions, is demonstrated similarly.

From Equations (10), (11) and (11a) it is easy to deduce the equation

$$\int_l \frac{dQ}{F(\vartheta)} = \int_{l'} \frac{dQ'}{F(\vartheta')}. \tag{8}$$

It remains to lift the last restriction.

We have accepted that neither the change l nor the change l' contains a portion of finite extent falling entirely within a space of reversible adiabats.

Suppose now that the change l does have certain finitely extended portions $\lambda_1, \lambda_2, \ldots,$ falling entirely within the spaces of reversible adiabats E_1, E_2, ..., and similarly, that the change l' does have certain finitely extended portions $\lambda'_1, \lambda'_2, \ldots,$ falling entirely within the spaces of reversible adiabats E$'_1$, E$'_2$, ….

For all adiabatically reversible changes, it always holds that

$$dQ = 0.$$

Accordingly,

$$\int_{\lambda_1} \frac{dQ}{F(\vartheta)} = 0, \quad \int_{\lambda_2} \frac{dQ}{F(\vartheta)} = 0, \ldots, \tag{12}$$

and also

$$\int_{\lambda_1} \frac{dQ'}{F\left(\vartheta'\right)} = 0, \quad \int_{\lambda_2} \frac{dQ'}{F\left(\vartheta'\right)} = 0, \ldots. \tag{12a}$$

Therefore, [354] without changing the values of $\int_l \frac{dQ}{F(\vartheta)}$ or of $\int_{l'} \frac{dQ'}{F(\vartheta')}$, the portions $\lambda_1, \lambda_2, \ldots,$ can be subtracted from l and the portions $\lambda'_1, \lambda'_2, \ldots,$ from l'. It then suffices to represent the spaces E$_1$, E$_2$, … , and the spaces E$'_1$, E$'_2$, … among those which limit the subregions and then to reproduce the preceding argument to show that

$$\sum \frac{dQ}{F(\vartheta)} = \sum \frac{dQ'}{F\left(\vartheta'\right)}, \tag{13}$$

where the first $\sum$ sign ranges over all the elements of the change l not in the portions $\lambda_1, \lambda_2, \ldots,$ and the second ranges over all the elements of the change l' not in the portions $\lambda'_1, \lambda'_2, \ldots.$

The Equations (12), (12a) and (13) together easily furnish the equality

$$\int_l \frac{dQ}{F(\vartheta)} = \int_{l'} \frac{dQ'}{F\left(\vartheta'\right)}. \tag{8}$$

This equation is, then, not only subject to the restrictions mentioned in §1 but also *to the condition that it doesn't hold, for all the points of a domain of finite extension forming part of the space of* $\alpha, \beta, \ldots, \lambda, \vartheta$, *that*

$$R_\alpha = 0, \quad R_\beta = 0, \ldots, R_\lambda = 0. \tag{9}$$

8.4 A Property of Reversible Cycles

Suppose that the reversible change l returns the system to its initial state. The state n is therefore identical with the state m. Among the other reversible changes l' capable of leading the system from the same initial state to the same final state may also be reckoned those cases where there is no change at all. Evidently, in this case,

$$\int_{l'} \frac{dQ'}{F\left(\vartheta'\right)} = 0.$$

Equation [355] (8) then yields Clausius' celebrated theorem:

For a reversible cycle,

$$\int \frac{dQ}{F\left(\vartheta\right)} = 0. \tag{14}$$

Suppose in particular that the cycle is isothermal; the temperature ϑ remains constant throughout the course of the cycle, the same holds for the function $F(\vartheta)$, and Equation (14) can be written

$$\int dQ = 0,$$

or

$$\int \left(R_\alpha \, d\alpha + R_\beta \, d\beta + \ldots + R_\lambda \, d\lambda\right) = 0.$$

In virtue of Equations (2), this equality becomes

$$\int \left(\frac{\partial U}{\partial \alpha} \, d\alpha + \frac{\partial U}{\partial \beta} \, d\beta + \ldots + \frac{\partial U}{\partial \lambda} \, d\lambda\right) - \frac{1}{E} \int \left(A \, d\alpha + B \, d\beta + \ldots + L \, d\lambda\right) = 0.$$

But for an isothermal cycle, we have

$$\int \left(\frac{\partial U}{\partial \alpha} \, d\alpha + \frac{\partial U}{\partial \beta} \, d\beta + \ldots + \frac{\partial U}{\partial \lambda} \, d\lambda\right) = 0.$$

The preceding equation therefore becomes

$$\int \left(A \, d\alpha + B \, d\beta + \ldots + L \, d\lambda\right) = 0. \tag{15}$$

When a system traverses a reversible isothermal cycle, the external actions applied to the system effect a total work equal to zero.

This theorem is due to J. Moutier. Clausius and J. Moutier made frequent use of it. It may be remarked that it is exactly the same for systems for which Equations (9) are satisfied.

8.5 Entropy

[356] Equation (8) can be stated in the following way, designating the calorific coefficients of the system at equilibrium by $R_\alpha, \ldots, R_\lambda, C$,

The curvilinear integral

$$\int_l \frac{1}{F(\vartheta)} \left(R_\alpha \, d\alpha + R_\beta \, d\beta + \ldots + R_\lambda \, d\lambda + C \, d\vartheta \right)$$

has a value which depends uniquely on the initial point

$$(\alpha_0, \beta_0, \ldots, \lambda_0, \vartheta_0)$$

and the final point

$$(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1).$$

This theorem is known to be equivalent to the following:

There exists an infinity of uniform functions of the variables α, β, …, λ, ϑ, differing from one another by a constant, which are such that

$$\begin{cases} \dfrac{R_\alpha}{F(\vartheta)} = -\dfrac{\partial S}{\partial \alpha}, \\ \dfrac{R_\beta}{F(\vartheta)} = -\dfrac{\partial S}{\partial \beta}, \\ \ldots\ldots\ldots\ldots\ldots, \\ \dfrac{R_\lambda}{F(\vartheta)} = -\dfrac{\partial S}{\partial \lambda}, \\ \dfrac{C}{F(\vartheta)} = -\dfrac{\partial S}{\partial \vartheta}, \end{cases} \tag{16}$$

with $S(\alpha, \beta, \ldots, \lambda, \vartheta)$ designating any one of these functions.

This function has been called the *entropy of the system* by Clausius.

This theorem can be restated in abridged form in the following way:

For all infinitesimal reversible changes, we have

$$\frac{dQ}{F(\vartheta)} = dS. \tag{17}$$

If [357] we now recall, first that the quantities

$$R_\alpha, \ldots, R_\lambda, C$$

do not depend on those among the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ which determine the absolute position of the system in space, and second, that those of the variations $\delta\alpha, \delta\beta, \ldots, \delta\lambda, \delta\vartheta$ which only determine the absolute position of the system in space do not figure in the expression

$$R_\alpha\, \delta\alpha + R_\beta\, \delta\beta + \ldots + R_\lambda\, \delta\lambda + C\, \delta\vartheta,$$

then it is easily seen that the entropy does not depend on the absolute position in space.

8.6 On the Case Excepted from the preceding

On the case set aside where, in all the points of a domain D constituting part of the space of $\alpha, \beta, \ldots, \lambda, \vartheta$ it always holds that

$$R_\alpha = 0,\ R_\beta = 0, \ldots, R_\lambda = 0 \tag{9}$$

we consider whether the preceding theorems can be applied in this case.

In the first place, it is evident that they can be if only isothermal changes of the system are considered. For then, for all reversible changes,

$$dQ = 0,$$

and consequently

$$\frac{dQ}{F(\vartheta)} = dS,$$

where S designates any function of the temperature.

This particular case is important because it is really this that is envisaged in classical rational mechanics. In fact, in the classical exposition of rational mechanics, the notion of temperature is omitted (this is only admissible if the temperature is supposed invariable) and the notion of the quantity of heat [358] released by the system is also omitted. This is admissible only if the equalities (9) are satisfied.

In this case, Equations (2) and (9) yield[5]

$$A = E\,\frac{\partial U}{\partial \alpha},\ B = E\,\frac{\partial U}{\partial \beta}, \ldots, L = E\,\frac{\partial U}{\partial \lambda}. \tag{18}$$

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[5] [The second "E" is "A" in the original.]

This is the accepted form that is attributed in this case to the conditions of equilibrium (1). The product *EU* represents what is called in mechanics the *potential of the internal forces*.

But we no longer suppose that the temperature is invariable. We will show that, *if there exists a domain* D *where Equations* (9) *are satisfied, then in order for there to exist a uniform and continuous function S of the variables* $\alpha, \beta, \ldots, \lambda, \vartheta$ *such that, in every field of these variables,*

$$\left\{\begin{aligned} \frac{R_\alpha}{F(\vartheta)} &= -\frac{\partial S}{\partial \alpha}, \\ \frac{R_\beta}{F(\vartheta)} &= -\frac{\partial S}{\partial \beta}, \\ &\ldots\ldots\ldots\ldots\ldots, \\ \frac{R_\lambda}{F(\vartheta)} &= -\frac{\partial S}{\partial \lambda}, \\ \frac{C}{F(\vartheta)} &= -\frac{\partial S}{\partial \vartheta}, \end{aligned}\right. \tag{16}$$

it is necessary and sufficient that, in all of the domain D, *the caloric capacity C is a function of the temperature* ϑ *alone.*

If the domain D does not occupy the entire field of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ (which is the only case where the theorem is not evident), it is always possible to cut the part of the field exterior to the domain D into simply connected spaces. In the interior of each of these spaces, the preceding demonstrations are applicable. They allow one to write equations analogous to Equations (16) which entail in their turn equations of the type

$$\frac{\partial}{\partial \beta}\left[\frac{R_\alpha}{F(\vartheta)}\right] = \frac{\partial}{\partial \alpha}\left[\frac{R_\beta}{F(\vartheta)}\right] \tag{18}$$

and [359] equations of the type

$$\frac{\partial}{\partial \vartheta}\left[\frac{R_\alpha}{F(\vartheta)}\right] = \frac{\partial}{\partial \alpha}\left[\frac{C}{F(\vartheta)}\right]. \tag{18a}$$

On the other hand, in order that Equations (18) and (18a) can be written in the domain D, where Equations (9) are satisfied, it is necessary and sufficient that the quantity

$$\frac{dQ}{F(\vartheta)} = \frac{C}{F(\vartheta)} d\vartheta$$

be a total differential and, therefore, that the quantity C be a function of the temperature ϑ alone.

Moreover, the field of variables $\alpha, \beta, \ldots, \lambda, \vartheta$ being supposed simply connected, it is necessary and sufficient for the existence of a *uniform* and continuous function S of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ that Equations (18) and (18a) are satisfied in the whole field.

Thus, *if we accept that, in the entire domain* D *where Equations* (9) *are satisfied, the caloric capacity of the system is a function of the temperature alone,* the theorems demonstrated in the present chapter are subject only to the restrictions stated in Section 8.1.

Part IV

Commentary on the Principles of Thermodynamics: The General Equations of Thermodynamics (1894)*

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*“Commentaire aux principes de la Thermodynamique. Troisième Partie: Les équations générales de la Thermodynamique”, *Journal de Mathématiques Pure et Appliquées*, 10 (1894), 207–285. See vol. VIII, p. 269, and vol. IX, p. 293 [i.e. Parts One and Two.]

Chapter 9
Properties of a System at Equilibrium*

9.1 The Internal Thermodynamic Potential

Let

$$U(\alpha, \beta, \ldots, \lambda, \vartheta) \text{ and } S(\alpha, \beta, \ldots, \lambda, \vartheta)$$

be the internal energy and the entropy of a system. The system is, of course, [208] subject to the restrictions necessary for the definition of entropy. In particular, the temperature ϑ has the same value at all of its points.

Put

$$\mathcal{F}(\alpha, \beta, \ldots, \lambda, \vartheta) = E\,[U(\alpha, \beta, \ldots, \lambda, \vartheta) - F(\vartheta)\; S(\alpha, \beta, \ldots, \lambda, \vartheta)]. \quad (1)$$

The function $\mathcal{F}$ will, like the functions U and S, be a uniform and continuous function of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$, and like the functions U and S, it will be independent of any of these variables which serve solely to fix the position of the system in absolute space.

Since the two quantities U and S are each determined up to a constant, the function $\mathcal{F}$ is determined up to a function of the temperature, this function of the temperature being of the form

$$\mathrm{C} + \mathrm{C}' F(\vartheta),$$

where C and C$'$ are two arbitrary constants.

This function $\mathcal{F}$ is a generalisation of one of the *characteristic functions* of Massieu. It is the *available energy* of Gibbs and of Maxwell, and the *freie Energie* of H. von Helmholtz. We call it the *internal thermodynamic potential of the system.*

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[*] We have developed in detail the thermodynamic properties of systems at equilibrium in a recent memoir: *On the general equations of Thermodynamics* (*Annales de l'École Normale*, 3rd series, vol. VII, p. 231). In order to avoid as far as possible reproducing this memoir here, we have limited the present chapter to the exposition of properties necessary for understanding the following chapters.

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
DOI 10.1007/978-94-007-0311-7_9,

We have the following relations between the actions $A, B, \ldots, L, \Theta$, which maintain the system in equilibrium, and the calorific coefficients of the system at equilibrium, $R_\alpha, R_\beta, \ldots, R_\lambda, C$ (Section 8.2, Equation (2)):

$$\begin{cases} R_\alpha = \dfrac{\partial U}{\partial \alpha} - \dfrac{A}{E}, \qquad R_\beta = \dfrac{\partial U}{\partial \beta} - \dfrac{B}{E}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ R_\lambda = \dfrac{\partial U}{\partial \lambda} - \dfrac{L}{E}, \qquad C = \dfrac{\partial U}{\partial \vartheta} - \dfrac{\Theta}{E}. \end{cases} \tag{2}$$

On [209] the other hand, we have (Chapter 8, Equations (16)),

$$\begin{cases} R_\alpha = F(\vartheta) \dfrac{\partial S}{\partial \alpha}, \qquad R_\beta = F(\vartheta) \dfrac{\partial S}{\partial \beta}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ R_\lambda = F(\vartheta) \dfrac{\partial S}{\partial \lambda}, \qquad C = F(\vartheta) \dfrac{\partial S}{\partial \vartheta}. \end{cases} \tag{3}$$

Equations (1), (2) and (3) easily yield

$$\begin{cases} A = \dfrac{\partial \mathfrak{F}}{\partial \alpha}, \\ B = \dfrac{\partial \mathfrak{F}}{\partial \beta}, \\ \ldots\ldots\ldots\ldots\ldots, \\ L = \dfrac{\partial \mathfrak{F}}{\partial \lambda}, \\ \Theta = \dfrac{\partial \mathfrak{F}}{\partial \vartheta} + E S \dfrac{d \mathfrak{F}(\vartheta)}{d\vartheta}. \end{cases} \tag{4}$$

Necessary and sufficient conditions for the equilibrium of the system are obtained by adding to these equations the condition that the bodies external to the system have the same temperature as it has.

The last of Equations (4) yields

$$E S = \frac{1}{d F(\vartheta) \big/ d\vartheta} \left(\Theta - \frac{\partial \mathfrak{F}}{\partial \vartheta} \right) \tag{5}$$

Equations (1) and (5) yield

$$E U = F + \frac{F(\vartheta)}{d F(\vartheta) \big/ d\vartheta} \left(\Theta - \frac{\partial \mathfrak{F}}{\partial \vartheta} \right) \tag{6}$$

Equations [210] (3) and (5) yield

$$\left\{\begin{array}{l} R_\alpha = \dfrac{F(\vartheta)}{dF(\vartheta)\big/d\vartheta}\left(\dfrac{\partial\Theta}{\partial\alpha} - \dfrac{\partial^2\boldsymbol{\mathfrak{F}}}{\partial\vartheta\,\partial\alpha}\right), \\ R_\beta = \dfrac{F(\vartheta)}{dF(\vartheta)\big/d\vartheta}\left(\dfrac{\partial\Theta}{\partial\beta} - \dfrac{\partial^2\boldsymbol{\mathfrak{F}}}{\partial\vartheta\,\partial\beta}\right), \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ R_\lambda = \dfrac{F(\vartheta)}{dF(\vartheta)\big/d\vartheta}\left(\dfrac{\partial\Theta}{\partial\lambda} - \dfrac{\partial^2\boldsymbol{\mathfrak{F}}}{\partial\vartheta\,\partial\lambda}\right), \\ C = \dfrac{F(\vartheta)}{dF(\vartheta)\big/d\vartheta}\left(\dfrac{\partial\Theta}{\partial\vartheta} - \dfrac{\partial^2\boldsymbol{\mathfrak{F}}}{\partial\vartheta^2}\right) - \dfrac{F(\vartheta)\;F''(\vartheta)}{\left[F'(\vartheta)\right]^2}\left(\Theta - \dfrac{\partial\boldsymbol{\mathfrak{F}}}{\partial\vartheta}\right). \end{array}\right. \tag{7}$$

Thus, *if the following is known:*

1. *the expression for the internal thermodynamic potential of the system;*
2. *the expression*

$$\Theta = f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta)$$

for the quantity Θ *for the system at equilibrium,*

then the following can be determined:

1. *the internal energy and the entropy of the system in any state;*
2. *the necessary and sufficient conditions for equilibrium of the system;*
3. *the calorific coefficients of the system at equilibrium.*

This is the generalisation of a proposition well known from Massieu.

9.2 Properties of a System Formed from Several Independent Parts with the Same Temperature

In order not to unnecessarily complicate the arguments from the point of view of generality, we will suppose that the system is formed from just two distinct parts, independent of one another, which we designate by the indices 1 and 2. Each of these two parts will be supposed to have the same [211] temperature at all of its points. ϑ_1 is the temperature of part 1 and ϑ_2 the temperature of part 2. For the moment, we will suppose these to be any temperatures whatsoever; presently, we impose on them the condition of being equal to one another.

Let $\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1$ be the independent variables which determine the state of system 1, including its absolute position in space. The internal energy, the entropy and the internal thermodynamic potential of system 1 are uniform functions of these variables, or, at least, of those not serving solely to determine the absolute position of the system in space. These three functions are designated, respectively, by

$$\Upsilon_1(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1),$$

$$\sum\nolimits_1 (\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1),$$

$$\mathscr{F}_1(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1).$$

Similarly, let $\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2$ be the independent variables which define the state of system 2. Let

$$\Upsilon_2(\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2),$$

$$\sum\nolimits_2 ({}_2\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2),$$

$$\mathscr{F}_2(\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2).$$

be the internal energy, the entropy and the internal thermodynamic potential of system 2.

The state of the complex system (1, 2), formed from the aggregate of the two systems 1 and 2, and its absolute position in space, are determined when the collection of variables

$$\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1, \alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2$$

is known. The internal energy of the system (1, 2) will therefore have the value

$$\begin{aligned} U = \Upsilon_1(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1) + \Upsilon_2(\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2) \\ + \mathrm{X}_{12}(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta, \alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2), \end{aligned} \tag{8}$$

where X_{12} is a uniform function of the variables as shown, or, [212] at least, of those variables not serving solely to determine the absolute position of the system (1, 2) in space. Further, it can be agreed that this function has the value 0 when the two systems 1 and 2 are infinitely separated from one another.

If we designate the internal energy of the bodies external to the system (1, 2) by U', the internal energy of the system formed from the system (1, 2) and the external bodies will have the value

$$\mathfrak{U} = U + U' + \Psi. \tag{9}$$

The function Ψ will depend on the variables $\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1,$ $\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2$, and also on the variables determining the state of the bodies external to the system (1, 2).

The external actions exerted on the system (1, 2) will have the values (Chapter 5, Equations (4))

$$\begin{cases} \mathcal{A}_1 = -E\dfrac{\partial \Psi}{\partial \alpha_1}, & \mathcal{A}_2 = -E\dfrac{\partial \Psi}{\partial \alpha_2}, \\ \mathcal{B}_1 = -E\dfrac{\partial \Psi}{\partial \beta_1}, & \mathcal{B}_2 = -E\dfrac{\partial \Psi}{\partial \beta_2}, \\ \dots\dots\dots\dots\dots, & \dots\dots\dots\dots\dots, \\ \mathcal{L}_1 = -E\dfrac{\partial \Psi}{\partial \lambda_1}, & \mathcal{L}_2 = -E\dfrac{\partial \Psi}{\partial \lambda_2}, \\ W_1 = -E\dfrac{\partial \Psi}{\partial \vartheta_1}, & W_2 = -E\dfrac{\partial \Psi}{\partial \vartheta_2}. \end{cases} \tag{10}$$

On the other hand, the bodies external to the system 1 comprise:

1. The bodies external to the system (1, 2):
2. The bodies of [system] 2.

Accordingly, it is easily seen that the external actions applied to system 1 have the values

$$\begin{cases} A_1 = -E\dfrac{\partial}{\partial \alpha_1}\left(\mathrm{X}_{12} + \Psi\right), \\ B_1 = -E\dfrac{\partial}{\partial \beta_1}\left(\mathrm{X}_{12} + \Psi\right), \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ L_1 = -E\dfrac{\partial}{\partial \lambda_1}\left(\mathrm{X}_{12} + \Psi\right), \\ \Theta_1 = -E\dfrac{\partial}{\partial \vartheta_1}\left(\mathrm{X}_{12} + \Psi\right). \end{cases} \tag{11}$$

Similarly, [213] the external actions applied to system 2 have the values

$$\begin{cases} A_2 = -E\dfrac{\partial}{\partial \alpha_2}\left(\mathrm{X}_{12} + \Psi\right), \\ B_2 = -E\dfrac{\partial}{\partial \beta_2}\left(\mathrm{X}_{12} + \Psi\right), \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ L_2 = -E\dfrac{\partial}{\partial \lambda_2}\left(\mathrm{X}_{12} + \Psi\right), \\ \Theta_2 = -E\dfrac{\partial}{\partial \vartheta_2}\left(\mathrm{X}_{12} + \Psi\right). \end{cases} \tag{11a}$$

All this is general. Suppose now that system (1, 2) is at equilibrium, and we apply this principle, which evidently accords with the definition of equilibrium: *in order that the system* (1, 2) *be at equilibrium, it is necessary and sufficient that each of the two systems* 1 *and* 2 *are at equilibrium.*

In order that system 1 be at equilibrium, it is necessary and sufficient that, in the first place,

$$\vartheta_1 = \vartheta_2 = \vartheta, \tag{12}$$

where ϑ is the temperature common to the bodies external to system (1, 2).

In the second place, in virtue of Equations (4) and (11),

$$\begin{cases} E\dfrac{\partial}{\partial\alpha_1}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\alpha_1}, \\ E\dfrac{\partial}{\partial\beta_1}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\beta_1}, \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ E\dfrac{\partial}{\partial\lambda_1}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\lambda_1}, \\ E\dfrac{\partial}{\partial\vartheta_1}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\vartheta_1} - E\,F'(\vartheta_1)\ \Sigma_1. \end{cases} \tag{13}$$

In order that system 2 is at equilibrium, it is necessary and sufficient that:

In the first place, Equations (12) hold;

In [214] the second place, in virtue of Equations (4) and (11a),

$$\begin{cases} E\dfrac{\partial}{\partial\alpha_2}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_2}{\partial\alpha_2}, \\ E\dfrac{\partial}{\partial\beta_2}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_2}{\partial\beta_2}, \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ E\dfrac{\partial}{\partial\lambda_2}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_2}{\partial\lambda_2}, \\ E\dfrac{\partial}{\partial\vartheta_2}(\mathrm{X}_{12}+\Psi) = -\dfrac{\partial\boldsymbol{\mathcal{F}}_2}{\partial\vartheta_2} - E\,F'(\vartheta_2)\ \Sigma_2. \end{cases} \tag{13a}$$

When Equations (12) are satisfied, the system (1, 2) has an internal thermodynamic potential that we designate by $\mathfrak{F}$ and an entropy that we designate by S.

In general, the virtual work of the external forces applied to this system is expressed by[1]

$$\begin{gathered} \boldsymbol{\mathcal{A}}_1\delta\alpha_1 + \boldsymbol{\mathcal{B}}_1\delta\beta_1 + \ldots + \boldsymbol{\mathcal{L}}_1\delta\lambda_1 + W_1\delta\vartheta_1 \\ + \boldsymbol{\mathcal{A}}_2\delta\alpha_2 + \boldsymbol{\mathcal{B}}_2\delta\beta_2 + \ldots + \boldsymbol{\mathcal{L}}_2\delta\lambda_2 + W_2\delta\vartheta_2, \end{gathered}$$

---

[1] [$\boldsymbol{\mathcal{A}}_2$ and $\boldsymbol{\mathcal{L}}_2$ are, respectively, $\boldsymbol{\mathcal{A}}_1$ and $\boldsymbol{\mathcal{L}}_1$ in the original.]

where $\boldsymbol{\mathcal{A}}_1, \boldsymbol{\mathcal{B}}_1, \ldots, \boldsymbol{\mathcal{L}}_1, W_1, \boldsymbol{\mathcal{A}}_2, \boldsymbol{\mathcal{B}}_2, \ldots, \boldsymbol{\mathcal{L}}_2, W_2$, are given by the Equations (10). In the particular case where the Equations (12) are constantly satisfied, the virtual work becomes

$$\begin{aligned} &\boldsymbol{\mathcal{A}}_1 \delta\alpha_1 + \boldsymbol{\mathcal{B}}_1 \delta\beta_1 + \ldots + \boldsymbol{\mathcal{L}}_1 \delta\lambda_1 \\ &+ \boldsymbol{\mathcal{A}}_2 \delta\alpha_2 + \boldsymbol{\mathcal{B}}_2 \delta\beta_2 + \ldots + \boldsymbol{\mathcal{L}}_2 \delta\lambda_2 + W \delta\vartheta, \end{aligned}$$

where W is defined by the equality

$$W = W_1 + W_2 = -E \left(\frac{\partial \Psi}{\partial \vartheta_1} + \frac{\partial \Psi}{\partial \vartheta_2} \right)_{\vartheta_1 = \vartheta_2 = \vartheta} . \tag{14}$$

Then, for equilibrium of the system (1, 2), it is necessary and sufficient that:

In the first place, Equations (12) hold;

In [215] the second place, in virtue of Equations (4), (10) and (14),

$$\left\{ \begin{array}{ll} E \dfrac{\partial \Psi}{\partial \alpha_1} = -\dfrac{\partial \mathfrak{F}}{\partial \alpha_1}, & E \dfrac{\partial \Psi}{\partial \alpha_2} = -\dfrac{\partial \mathfrak{F}}{\partial \alpha_2}, \\ E \dfrac{\partial \Psi}{\partial \beta_1} = -\dfrac{\partial \mathfrak{F}}{\partial \beta_1}, & E \dfrac{\partial \Psi}{\partial \beta_2} = -\dfrac{\partial \mathfrak{F}}{\partial \beta_2}, \\ \ldots\ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots, \\ E \dfrac{\partial \Psi}{\partial \lambda_1} = -\dfrac{\partial \mathfrak{F}}{\partial \lambda_1}, & E \dfrac{\partial \Psi}{\partial \lambda_2} = -\dfrac{\partial \mathfrak{F}}{\partial \lambda_2}, \\ \multicolumn{2}{l}{E \left(\dfrac{\partial \Psi}{\partial \vartheta_1} + \dfrac{\partial \Psi}{\partial \vartheta_2} \right) = -\dfrac{\partial \mathfrak{F}}{\partial \vartheta} - E\,F'(\vartheta)\,S.} \end{array} \right. \tag{15}$$

The principle just stated requires that, given Equations (12), the collection of Equations (15) is equivalent to the collection of equalities (13) and (13a). This condition is expressed by the equations

$$\left\{ \begin{array}{ll} \dfrac{\partial}{\partial \alpha_1} \left(\mathfrak{F} - \mathcal{F}_1 - E\,\mathrm{X}_{12} \right) = 0, & \dfrac{\partial}{\partial \alpha_2} \left(\mathfrak{F} - \mathcal{F}_2 - E\,\mathrm{X}_{12} \right) = 0, \\ \dfrac{\partial}{\partial \beta_1} \left(\mathfrak{F} - \mathcal{F}_1 - E\,\mathrm{X}_{12} \right) = 0, & \dfrac{\partial}{\partial \beta_2} \left(\mathfrak{F} - \mathcal{F}_2 - E\,\mathrm{X}_{12} \right) = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial}{\partial \lambda_1} \left(\mathfrak{F} - \mathcal{F}_1 - E\,\mathrm{X}_{12} \right) = 0, & \dfrac{\partial}{\partial \lambda_2} \left(\mathfrak{F} - \mathcal{F}_2 - E\,\mathrm{X}_{12} \right) = 0, \end{array} \right. \tag{16}$$

$$\left\{ \begin{aligned} &\frac{\partial \mathfrak{F}}{\partial \vartheta} - \frac{\partial}{\partial \vartheta_1} \left(\mathcal{F}_1 + E\,\mathrm{X}_{12} \right) - \frac{\partial}{\partial \vartheta_2} \left(\mathcal{F}_2 + E\,\mathrm{X}_{12} \right) \\ &\qquad\qquad + E\,F'(\vartheta)\ \left(S - \Sigma_1 - \Sigma_2 \right) = 0. \end{aligned} \right. \tag{17}$$

The function $\mathscr{F}_1$ does not depend on the variables $\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2$, and the function $\mathscr{F}_2$ does not depend on the variables $\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1$. The equalities (16) can therefore be written[2].

$$\begin{cases} \dfrac{\partial}{\partial \alpha_1} (\mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} - \mathscr{F}) = 0, \\ \dfrac{\partial}{\partial \beta_1} (\mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} - \mathscr{F}) = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ \dfrac{\partial}{\partial \lambda_1} (\mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} - \mathscr{F}) = 0, \\ \dfrac{\partial}{\partial \alpha_2} (\mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} - \mathscr{F}) = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ \dfrac{\partial}{\partial \lambda_2} (\mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} - \mathscr{F}) = 0. \end{cases} \tag{18}$$

In [216] virtue of the Equations (12), it holds that

$$\frac{\partial \mathscr{F}_1}{\partial \vartheta_1} = \frac{\partial \mathscr{F}_1}{\partial \vartheta}, \qquad \frac{\partial \mathscr{F}_2}{\partial \vartheta_2} = \frac{\partial \mathscr{F}_2}{\partial \vartheta}$$

In virtue of the same equations, X_{12} can be regarded as a function of the variables

$$\alpha_1, \beta_1, \ldots, \lambda_1, \alpha_2, \beta_2, \ldots, \lambda_2, \vartheta,$$

and so

$$\frac{\partial \mathrm{X}_{12}}{\partial \vartheta} = \frac{\partial \mathrm{X}_{12}}{\partial \vartheta_1} + \frac{\partial \mathrm{X}_{12}}{\partial \vartheta_2}.$$

Equation (17) can therefore be written

$$\frac{\partial}{\partial \vartheta} (\mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} - \mathrm{F}) + E\,F'(\vartheta)\ (\Sigma_1 + \Sigma_2 - S) = 0. \tag{19}$$

Equations (18) yield

$$\mathrm{F} = \mathscr{F}_1 + \mathscr{F}_2 + E\,\mathrm{X}_{12} + f(\vartheta), \tag{20}$$

where $f(\vartheta)$ is an arbitrary function of the temperature ϑ. Equation (19) then yields

$$S = \Sigma_1 + \Sigma_2 - \frac{f'(\vartheta)}{E\,F'(\vartheta)}. \tag{21}$$

---

[2] [“λ_1” is written “λ_2” in the original.]

If it is agreed to take as the internal thermodynamic potential of a system formed from two parts at the same temperature, infinitely separated from one another, the sum of the internal thermodynamic potentials of the two parts, then it always holds, in accordance with Equation (20), that

$$f(\vartheta) = 0.$$

Equations (20) and (21) will therefore become

$$\mathcal{F} = \mathcal{F}_1 + \mathcal{F}_2 + E\,\mathrm{X}_{12}, \tag{20a}$$

$$S = \Sigma_1 + \Sigma_2. \tag{21a}$$

When [217] *a system is formed from several independent parts all at the same temperature, the internal thermodynamic potential of the system is obtained by taking the sum of the internal thermodynamic potential of the parts, and adding the determination of the potential of the mutual actions of these parts which cancels when the parts are separated infinitely far from one another.*

The entropy of the system is equal to the sum of the entropies of the various parts.

These theorems are applied frequently in thermodynamics. They can be compared with an analogous theorem concerning the internal energy demonstrated in the 1st Part (Section 5.2). But the latter was general, whereas the theorems that we have just demonstrated presuppose that the various parts of the system are at the same temperature, and that each of them satisfies the conditions mentioned in Chapter 8.

Equation (21a) entails an important new consequence:

The calorific coefficients of system 1 at equilibrium are

$$R_{\alpha_1}, R_{\beta_1}, \ldots, R_{\lambda_1}, C_1.$$

The calorific coefficients of system 2 at equilibrium are

$$R_{\alpha_2}, R_{\beta_2}, \ldots, R_{\lambda_2}, C_2.$$

The calorific coefficients of system (1, 2) at equilibrium are

$$\rho_{\alpha_1}, \rho_{\beta_1}, \ldots, \rho_{\lambda_1}, \rho_{\alpha_2}, \rho_{\beta_2}, \ldots, \rho_{\lambda_2}, \gamma.$$

We have, in virtue of Equations (3),

$$\begin{aligned}
\rho_{\alpha_1} &= F(\vartheta)\,\frac{\partial S}{\partial \alpha_1}, & \rho_{\alpha_2} &= F(\vartheta)\,\frac{\partial S}{\partial \alpha_2},\\
&\ldots\ldots\ldots\ldots\ldots, & &\ldots\ldots\ldots\ldots\ldots,\\
\rho_{\lambda_1} &= F(\vartheta)\,\frac{\partial S}{\partial \lambda_1}, & \rho_{\lambda_2} &= F(\vartheta)\,\frac{\partial S}{\partial \lambda_2},
\end{aligned}$$

$$\gamma = F(\vartheta)\,\frac{\partial S}{\partial \vartheta}.$$

Taking [218] into account Equation (21a) and noting that

$$\begin{array}{ll} \dfrac{\partial \sum_1}{\partial \alpha_2} = 0, & \dfrac{\partial \sum_2}{\partial \alpha_1} = 0, \\ \ldots\ldots\ldots, & \ldots\ldots\ldots, \\ \dfrac{\partial \sum_1}{\partial \lambda_2} = 0, & \dfrac{\partial \sum_2}{\partial \lambda_1} = 0, \end{array}$$

we can write

$$\begin{array}{ll} \rho_{\alpha_1} = F(\vartheta)\,\dfrac{\partial \sum_1}{\partial \alpha_1}, & \rho_{\alpha_2} = F(\vartheta)\,\dfrac{\partial \sum_2}{\partial \alpha_2}, \\ \ldots\ldots\ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots\ldots, \\ \rho_{\lambda_1} = F(\vartheta)\,\dfrac{\partial \sum_1}{\partial \lambda_1}, & \rho_{\lambda_2} = F(\vartheta)\,\dfrac{\partial \sum_2}{\partial \lambda_2}, \end{array}$$

$$\gamma = F(\vartheta)\left(\frac{\partial \sum_1}{\partial \vartheta} + \frac{\partial \sum_2}{\partial \vartheta}\right),$$

or, in virtue of Equations (3),

$$\begin{cases} \rho_{\alpha_1} = R_{\alpha_1}, \qquad \rho_{\alpha_2} = R_{\alpha_2}, \\ \ldots\ldots\ldots, \qquad \ldots\ldots\ldots\ldots\ldots, \\ \rho_{\lambda_1} = R_{\lambda_1}, \qquad \rho_{\lambda_2} = R_{\lambda_2}, \\ \qquad \gamma = C_1 + C_2. \end{cases} \tag{22}$$

The remarkable Equations (22) are subject to the same restrictions as Equation (21a).

9.3 The Fundamental Hypothesis; Normal Variables

We will now invoke a fundamental hypothesis which is generally accepted implicitly in treatises on thermodynamics.

Let an independent system 1, with the same temperature at all its points, be defined by the variables $\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1$. Then let any other independent system 2, without necessarily having the same temperature at all its points and being defined by the variables $\alpha_2, \beta_2, \ldots, \lambda_2, \vartheta_2$, constitute the bodies external to system 1.

The [219] internal energy U of the system (1, 2) can be written

$$U = \Upsilon_1(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1) + \Upsilon_2(\alpha_2, \beta_2, \ldots, \lambda_2)$$
$$+ \Psi(\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1, \alpha_2, \beta_2, \ldots, \lambda_2),$$

where Υ_1 is the internal energy of system 1 and Υ_2 is the internal energy of system 2.

The hypothesis that we wish to state is the following:

The variables $\alpha_1, \beta_1, \ldots, \lambda_1, \vartheta_1$ can be chosen so that:

1. When ϑ_1 varies, and $\alpha_1, \beta_1, \ldots, \lambda_1$ retain constant values, no material point of system 1 is displaced in space. The kinetic energy, $\mathfrak{T}_1$, of system 1 is then independent of ϑ_1 and of $d\vartheta_1/dt$;
2. the function Ψ does not depend on the variable ϑ_1, and whatever bodies compose system 2.

When the variables $\alpha_1, \beta_1, \ldots, \lambda_1$ have been chosen in that way, we will say that *the system* $\alpha_1, \beta_1, \ldots, \lambda_1$ *constitutes a system of normal variables* defining system 1.

The virtual work of the external actions to which system 1 is subject is an expression of the form

$$A_1\delta\alpha_1 + B_1\delta\beta_1 + \ldots + L_1\delta\lambda_1 + \Theta_1\delta\vartheta_1,$$

In accordance with Equations (4) of Chapter 5,

$$\Theta_1 = -E\,\frac{\partial\Psi}{\partial\vartheta_1}.$$

If, therefore, the system of variables $\alpha_1, \beta_1, \ldots, \lambda_1$ is a system of normal variables, then

$$\Theta_1 = 0.$$

If a system with the same temperature at all of its points is defined by normal variables, then whatever the bodies external to the system, the actions they exert on the system do not perform any work when the temperature alone varies.

This [220] proposition does not presuppose that the system is at equilibrium.

What are the properties of a system at equilibrium when it is defined by normal variables?

For such a system, the quantity

$$\Theta = f_\vartheta(\alpha, \beta, \ldots, \lambda, \vartheta)$$

is always zero.

Consequently, Equations (4), (5), (6) and (7) become

$$A = \frac{\partial\mathfrak{F}}{\partial\alpha}, \quad B = \frac{\partial\mathfrak{F}}{\partial\beta}, \quad \ldots, \quad L = \frac{\partial\mathfrak{F}}{\partial\lambda} \tag{4a}$$

$$E\,F'(\vartheta)\,S = -\frac{\partial\mathfrak{F}}{\partial\vartheta} \tag{5a}$$

$$E\,U = \mathfrak{F} + \frac{F\,(\vartheta)}{F'\,(\vartheta)}\,\frac{\partial\mathfrak{F}}{\partial\vartheta} \tag{6a}$$

$$\begin{cases} R_\alpha = -\dfrac{F(\vartheta)}{E F'(\vartheta)} \dfrac{\partial^2 \mathfrak{F}}{\partial \alpha \partial \beta}, \\ R_\beta = -\dfrac{F(\vartheta)}{E F'(\vartheta)} \dfrac{\partial^2 \mathfrak{F}}{\partial \beta \partial \vartheta}, \\ \dots\dots\dots\dots\dots\dots\dots\dots, \\ R_\lambda = -\dfrac{F(\vartheta)}{E F'(\vartheta)} \dfrac{\partial^2 \mathfrak{F}}{\partial \lambda \partial \vartheta}, \\ C = -\dfrac{F(\vartheta)}{E F'(\vartheta)} \dfrac{\partial^2 \mathfrak{F}}{\partial \vartheta^2} + \dfrac{F(\vartheta)\, F''(\vartheta)}{E\left[F'(\vartheta)\right]^2} \dfrac{\partial \mathfrak{F}}{\partial \vartheta}. \end{cases} \tag{7a}$$

Thus, when a system is defined by normal variables, it suffices to know the internal thermodynamic potential of the system in order to be able to determine the equations of equilibrium, the energy, the entropy and the calorific coefficients. This is a well-known proposition of F. Massieu.

Henceforth, when we consider a system all the points of which are at the same temperature, we will suppose it to be defined by normal variables.

9.4 The Problem of Equilibrium

How, in general, is the problem [221] of equilibrium of a system posed when the expression for the internal thermodynamic potential of the system is known?

The state of the bodies external to this system is supposed given. These bodies have a uniform temperature θ, and it is proposed to determine the state taken by the system under the action of these bodies.

The function Ψ, considered in the preceding section, becomes a function of the variables $\alpha, \beta, \dots, \lambda$ alone when the state of the bodies external to the system is determined, where $\alpha, \beta, \dots, \lambda, \vartheta$ designate the normal variables defining the system.

In virtue of Equations (4) (Chapter 5) and Equations (4a) of the present chapter,

$$\begin{cases} E \dfrac{\partial \Psi}{\partial \alpha} + \dfrac{\partial \mathfrak{F}}{\partial \alpha} = 0, \\ E \dfrac{\partial \Psi}{\partial \beta} + \dfrac{\partial \mathfrak{F}}{\partial \beta} = 0, \\ \dots\dots\dots\dots\dots, \\ E \dfrac{\partial \Psi}{\partial \lambda} + \dfrac{\partial \mathfrak{F}}{\partial \lambda} = 0. \end{cases} \tag{23}$$

If the equation

$$\vartheta = \theta, \tag{24}$$

is added, expressing the equality of the temperature of the system with that of the external bodies, a number of equations is obtained equal to the number of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ whose values we wish to determine. These equations therefore allow the determination of the state of equilibrium of the system, provided that the expression for the quantities

$$\frac{\partial \Psi}{\partial \alpha}, \frac{\partial \Psi}{\partial \beta}, \ldots, \frac{\partial \Psi}{\partial \lambda},$$

is known as a function of $\alpha, \beta, \ldots, \lambda$, that is, provided that it is known how the external actions applied to the system vary with the state of the system. Moreover, if the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ are normal variables, these actions do not depend on the temperature of the system.

Once [222] the state of the system is known, Equations (5a), (6a) and (7a) tell us the energy, the entropy and the calorific coefficients.

Chapter 10
Properties of a System in Motion

10.1 Meaning of the Word "Motion"

In this chapter, we take the word *motion* to designate not only a change of position in space, but also any change of state, even if not accompanied by any displacement. Thus, there would be motion if only the variables that we have designated by *a, b, . . . , l* (Section 5.4) vary, the variables $\alpha, \beta, \ldots, \lambda$ retaining fixed values. Consequently, the word *motion* does not stand in opposition to the word *rest*, but to the word *equilibrium*.

10.2 Motion of a System with the Same Temperature at All Points

Imagine a system with the same temperature at all of its points, this temperature not necessarily being the same as that of the external bodies. This system is not at equilibrium; it remains to determine the laws of its motion.

At each instant *t*, the state of the external bodies is supposed given. The external actions which affect the system are, in general, functions of the variables $\alpha, \beta, \ldots, \lambda$ defining the system and the variables defining the external bodies. The latter are given functions of *t*, and the external actions are, to be precise, given functions of $\alpha, \beta, \ldots, \lambda, t$ which we designate by

$$\begin{gathered} A'(\alpha, \beta, \ldots, \lambda, t), \\ B'(\alpha, \beta, \ldots, \lambda, t), \\ \ldots\ldots\ldots\ldots\ldots, \\ L'(\alpha, \beta, \ldots, \lambda, t). \end{gathered}$$

For [223] brevity, we put

$$\alpha' = \frac{\partial \alpha}{\partial t}, \quad \beta' = \frac{\partial \beta}{\partial t}, \ldots, \lambda' = \frac{\partial \lambda}{\partial t}.$$

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
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When the system is at equilibrium, we have (Chapter 9, Equation (23))

$$A' - \frac{\partial \mathfrak{F}}{\partial \alpha} = 0, \quad B' - \frac{\partial \mathfrak{F}}{\partial \beta} = 0, \ldots, L' - \frac{\partial \mathfrak{F}}{\partial \lambda} = 0.$$

On the other hand, it holds identically that

$$\frac{\partial \mathfrak{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \alpha'} = 0, \quad \frac{\partial \mathfrak{T}}{\partial \beta} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \beta'} = 0, \ldots, \quad \frac{\partial \mathfrak{T}}{\partial \lambda} - \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \lambda'} = 0.$$

Therefore, in the case when the system is at equilibrium,

$$\begin{cases} A' - \dfrac{\partial \mathfrak{F}}{\partial \alpha} + \dfrac{\partial \mathfrak{T}}{\partial \alpha} - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'} = 0, \\ B' - \dfrac{\partial \mathfrak{F}}{\partial \beta} + \dfrac{\partial \mathfrak{T}}{\partial \beta} - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \beta'} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L' - \dfrac{\partial \mathfrak{F}}{\partial \lambda} + \dfrac{\partial \mathfrak{T}}{\partial \lambda} - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'} = 0. \end{cases} \tag{1}$$

When the system is not at equilibrium, it is not certain that these equations are satisfied. The left-hand sides could have values differing from 0; we designate these values by $-f_\alpha, -f_\beta, \ldots, -f_\lambda$, and can write, *without any hypothesis*,

$$\begin{cases} \dfrac{\partial(\mathfrak{T} - \mathfrak{F})}{\partial \alpha} - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'} + A' + f_\alpha = 0, \\ \dfrac{\partial(\mathfrak{T} - \mathfrak{F})}{\partial \beta} - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \beta'} + B' + f_\beta = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial(\mathfrak{T} - \mathfrak{F})}{\partial \lambda} - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'} + L' + f_\lambda = 0. \end{cases} \tag{2}$$

The quantities f_α, $f_\beta, \ldots, f_\lambda$, will be called the *passive resistances* [224] that the system has to overcome. The quantity

$$f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda$$

is called the *elementary work of the passive resistances.*

So far, we have said, the Equations (2) are in no way hypothetical. They only take on a hypothetical character when we assign a particular form to the passive resistances. With this in mind, we now make some assumptions:

FIRST CONVENTION.—*The passive resistances $f_\alpha, f_\beta, \ldots, f_\lambda$ depend uniquely on the variables*

$$\alpha, \beta, \ldots, \lambda, \vartheta,$$

$$\alpha' = \frac{\partial \alpha}{\partial t}, \quad \beta' = \frac{\partial \beta}{\partial t}, \ldots, \quad \lambda' = \frac{\partial \lambda}{\partial t}$$

relative to the system, and the analogous variables relative to the external bodies.

SECOND CONVENTION.—*The passive resistances do not change their values if the absolute position or the absolute motion of the complex system formed by the system under study and the bodies external to it change. They depend only on the* relative position *of the parts of the system and the external bodies, and on the* relative motion *of the parts of the system and the external bodies.*

Like all the hypotheses we have made, these assumptions, although very natural, are not logically necessary. They can only be verified by noting the agreement of the consequences of Equations (2) with the facts of experience.

When the state of the external bodies is given at each instant t, the passive resistances become functions of the variables

$$\alpha, \quad \beta, \ldots, \quad \lambda, \quad \vartheta, \quad \alpha', \quad \beta', \ldots, \quad \lambda', \quad t.$$

Equations (2) then become second order differential equations which would determine the values of the variables $\alpha, \beta, \ldots, \lambda, \vartheta$ [225] as a function of t and, therefore, the motion of the system, if they were sufficiently many. But *the number of variables whose value must be determined at each instant exceeds by one the number of equations of motion provided by thermodynamics*. It is therefore necessary, in order to complete the formulation of the equations of the problem, to borrow a last equation from physical theory foreign to thermodynamics, such as, for example, the equation

$$\vartheta = \varphi(t),$$

which tells us the temperature of the system at each instant.

10.3 Calorific Coefficients of a System in Motion

The calorific coefficients of a system whatever its state of motion are defined by the equations (Chapter 5, Equations (12))

$$\left\{\begin{aligned}
&E\frac{\partial U}{\partial \alpha} - \frac{\partial \mathfrak{T}}{\partial \alpha} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \alpha'} - A' = ER'_\alpha,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,\\
&E\frac{\partial U}{\partial \lambda} - \frac{\partial \mathfrak{T}}{\partial \lambda} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \lambda'} - L' = ER'_\lambda,\\
&E\frac{\partial U}{\partial \vartheta} = EC'.
\end{aligned}\right. \tag{3}$$

But we have (Chapter 9, Equations (1))

$$E\,U = \mathfrak{F} + E\,F\,(\vartheta)\,S.$$

Equations (3) can therefore be written

$$\begin{cases} \dfrac{\partial \mathfrak{F}}{\partial \alpha} - \dfrac{\partial \mathfrak{T}}{\partial \alpha} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'} + E\,F\,(\vartheta)\,\dfrac{\partial S}{\partial \vartheta} - A' = ER'_\alpha, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ \dfrac{\partial \mathfrak{F}}{\partial \lambda} - \dfrac{\partial \mathfrak{T}}{\partial \lambda} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'} + E\,F\,(\vartheta)\,\dfrac{\partial S}{\partial \vartheta} - L' = ER'_\lambda, \\ \dfrac{\partial \mathfrak{F}}{\partial \vartheta} + E\,F\,(\vartheta)\,\dfrac{\partial S}{\partial \vartheta} + E\,F'\,(\vartheta)\,S = EC', \end{cases}$$

or, [226] taking into account Equations (2) of the present chapter and the Equation (5a) of Chapter 9,

$$\begin{cases} ER'_\alpha = E\,F\,(\vartheta)\,\dfrac{\partial S}{\partial \vartheta} + f_\alpha, \\ \dots\dots\dots\dots\dots\dots, \\ ER'_\lambda = E\,F\,(\vartheta)\,\dfrac{\partial S}{\partial \vartheta} + f_\lambda, \\ EC' = E\,F\,(\vartheta)\,\dfrac{\partial S}{\partial \vartheta}. \end{cases} \tag{4}$$

Let $R_\alpha, \dots, R_\lambda$, C be the calorific coefficients of the system at equilibrium in the state $(\alpha, \beta, \dots, \lambda, \vartheta)$. Comparing the Equations (4) that we have just written with Equations (3) of Chapter 9, we have[1]

$$\begin{cases} R'{}_\alpha = R_\alpha + \dfrac{f_\alpha}{E}, \\ \dots\dots\dots, \\ R'{}_\lambda = R_\lambda + \dfrac{f_\lambda}{E}, \\ C' = C. \end{cases} \tag*{$(5)^1$}$$

The specific heat of a system taken in a determinate state is the same whether the system is at equilibrium or in motion. If a variable other than the temperature is considered, the calorific coefficient corresponding to this variable does not have the same value, depending on whether the system is at equilibrium or in motion; the second value exceeds the first by a quantity equivalent to the passive resistance corresponding to that variable.

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[1] ["f_λ" is "f_β" in the original.]

10.4 Fundamental Property of the Passive Resistances

Let A, B, ..., L be external actions maintaining the system at equilibrium in the state $(\alpha, \beta, \ldots, \lambda, \vartheta)$. These forces are given by Equations (4a) of Chapter 9.

Equations [227] (2) can be written

$$\begin{cases} A' - A = -\dfrac{\partial \mathfrak{T}}{\partial \alpha} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'} - f_\alpha, \\ B' - B = -\dfrac{\partial \mathfrak{T}}{\partial \beta} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \beta'} - f_\beta, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L' - L = -\dfrac{\partial \mathfrak{T}}{\partial \lambda} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'} - f_\lambda. \end{cases} \tag{6}$$

We call the quantities $(A' - A), (B' - B), \ldots, (L' - L)$ the *effective actions* exerted on the system, and the quantity

$$(A' - A)d\alpha + (B' - B)d\beta + \ldots + (L' - L)d\lambda$$

is called the *effective work*.

Multiplying Equations (6) by, respectively, $d\alpha, d\beta, \ldots, d\lambda$, and adding the left-hand sides and right-hand sides yields

$$\begin{aligned} &(A' - A)d\alpha + (B' - B)d\beta + \ldots + (L' - L)d\lambda \\ &\quad = d\mathfrak{T} - (f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda). \end{aligned} \tag{7}$$

With this equality established, we now make the following fundamental hypothesis:

HYPOTHESIS.—*The effective work of the external actions on a system is, in any real change, at least equal to the increase in the kinetic energy.*

In accordance with this hypothesis, in any real transformation,

$$(A' - A)d\alpha + (B' - B)d\beta + \ldots + (L' - L)d\lambda \geq d\mathfrak{T},$$

and consequently, in accordance with Equation (7),

$$f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda \leq 0. \tag{8}$$

The preceding hypothesis is therefore equivalent to the following proposition:

In any real change of a system, the work of the passive resistances is either zero or negative.

Multiplying [228] in the same way the two sides of Equations (4) by $d\alpha, d\beta, \ldots, d\lambda, d\vartheta$, and adding the two sides of the equations obtained yields

$$E\left(R'_\alpha\,d\alpha + R'_\beta\,d\beta + \ldots R'_\lambda\,d\lambda + C\,d\vartheta\right)$$
$$= E\,F(\vartheta)dS + f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda,$$

or, designating by dQ the quantity of heat released by the system in an elementary transformation,

$$E\,dQ = -\,E\,F(\vartheta)\,dS - \left(f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda\right). \tag{9}$$

We write a similar equation for all the elements of a closed cycle and add the left-hand and right-hand sides of these equations after dividing the two sides of each by $F(\vartheta)$. Since the integral

$$\int dS,$$

taken over a closed cycle, is equal to 0, we have

$$\int \frac{dQ}{F\,(\vartheta)} = -\frac{1}{E}\int \frac{f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda}{F\,(\vartheta)}$$

Since the quantity $(f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda)$ can never be positive, it is clear that, for any real closed cycle,

$$\int \frac{dQ}{F\,(\vartheta)} \quad \geq \quad 0. \tag{10}$$

This famous inequality is due to Clausius.

Clausius has called the quantity

$$-\,(f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda),$$

which is equal to the work of the passive resistances but with changed sign, and which, therefore, is not negative in any real change of the system, the *uncompensated work done* during this [229] change. By contrast, the quantity $E\,F(\vartheta)dS$ is for him *the compensated work done* during this same change.

In accordance with Equations (2), we have

$$-\left(f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda\right) = A'd\alpha + B'd\beta + \ldots + L'd\lambda$$
$$-\left(\frac{\partial \mathfrak{F}}{\partial \alpha}d\alpha + \frac{\partial \mathfrak{F}}{\partial \beta}d\beta + \ldots + \frac{\partial \mathfrak{F}}{\partial \lambda}d\lambda\right) - d\mathfrak{T}$$

or, if dW designates the work of the actions external to the system,

$$-\left(f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda\right) = dW - d\mathfrak{T} - dF + \frac{\partial \mathfrak{F}}{\partial \vartheta}d\vartheta. \tag{11}$$

In the case where the change is isothermal, $d\vartheta$ is equal to 0 and Equation (11) becomes

$$-\left(f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda\right) = dW - d\mathfrak{T} - d\mathfrak{F}. \tag{11a}$$

> *In order to calculate the uncompensated work done in an isothermal change, take the external work and deduct from it the sum of the increases in the kinetic energy and the internal thermodynamic potential*. This theorem has many applications.

We apply Equation (9) to the transformations in a system isolated in space. For such a system we have, by definition,

$$dQ = 0.$$

Equation (9) therefore becomes

$$dS = -\frac{f_\alpha d\alpha + f_\beta d\beta + \ldots + f_\lambda d\lambda}{E\,F\,(\vartheta)}.$$

The right-hand side cannot be negative for any real change of the system. Therefore, *no real transformation of an isolated system can decrease the entropy of the system*. This proposition is said to be due to Clausius. He has demonstrated it only in the case where the kinetic energy of the system is equal to 0.

10.5 Systems Without Viscosity

In [230] each particular case the hypotheses already introduced in connection with passive resistances must be supplemented with additional hypotheses appropriate to the determination of the form of the functions f_α, $f_\beta, \ldots, f_\lambda$.

Among these hypotheses, the simplest that can be made, and the one that is always tried, at least as a first approximation, consists in putting

$$f_\alpha = 0, \quad f_\beta = 0, \ldots, \quad f_\lambda = 0. \tag{12}$$

When Equations (12) are assumed to be satisfied, the system is said to be *without viscosity*.

In order to study the properties of systems without viscosity, we distinguish the variables $\alpha, \beta, \ldots, \lambda$, on which the kinetic energy depends, from the variables *a, b, . . . , l,* on which it doesn't. The temperature, ϑ, should be added to the latter.

Given the Equations (12), Equations (2) become

$$\begin{cases} \dfrac{\partial(\mathfrak{T} - \mathfrak{F})}{\partial\alpha} - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\alpha'} + A'\,(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, t) = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial\,(\mathfrak{T} - \mathfrak{F})}{\partial\lambda} - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\lambda'} + L'\,(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, t) = 0, \end{cases} \tag{13}$$

$$\begin{cases} -\dfrac{\partial\mathfrak{F}}{\partial\alpha} + \mathfrak{A}'\,(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, t) = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ -\dfrac{\partial\mathfrak{F}}{\partial\lambda} + \mathfrak{L}'\,(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, t) = 0. \end{cases} \tag{13a}$$

These equations are fewer in number than the variables to be determined, and determining the motion of the system requires the addition of a further equation furnished by special hypotheses.

These equations are of two quite distinct kinds. Equations (13a), which correspond to the variables *a, b, ..., l,* are equations in the ordinary sense of the word. Equations (13), on the other hand, which correspond to the variables $\alpha, \beta, \ldots, \lambda$, are second-order partial differential equations of the kind given by Lagrange. [231] The supplementary equation, which corresponds to the variable θ, can clearly be of a third kind.

In the case where this supplementary equation makes the temperature a known function of the time, which occurs, in particular, in the case when the temperature is constant, the problem of the motion of the system can be treated as follows.

Equations (13a) are solved for *a, b, ..., l,* as functions of $\alpha, \beta, \ldots, \lambda, \vartheta, t$, and since ϑ is known as a function of t, they are known as functions of $\alpha, \beta, \ldots, \lambda, t$. If the values of the variables *a, b, ..., l* are related in the function $\mathfrak{F}(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l)$, these will be transformed to a function of the variables $\alpha, \beta, \ldots, \lambda, t$, which we designate by

$$\mathfrak{G}(\alpha, \beta, \ldots, \lambda, t).$$

Similarly, the functions

$$A'(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, t),$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,$$
$$L'(\alpha, \beta, \ldots, \lambda, a, b, \ldots, l, t)$$

become functions of the variables $\alpha, \beta, \ldots, \lambda, t$, which we designate by

$$\mathfrak{A}'(\alpha, \beta, \ldots, \lambda, t),$$
$$\ldots\ldots\ldots,$$
$$\mathfrak{L}'(\alpha, \beta, \ldots, \lambda, t).$$

The variables $\alpha, \beta, \ldots, \lambda$ will then be determined as a function of t by the equations

$$\left\{\begin{array}{l} \dfrac{\partial}{\partial\alpha}\mathfrak{G}(\alpha, \beta, \ldots, \lambda, t) + \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\alpha'} - \dfrac{\partial\mathfrak{T}}{\partial\alpha} = \mathfrak{A}'(\alpha, \beta, \ldots, \lambda, t), \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial}{\partial\lambda}\mathfrak{G}(\alpha, \beta, \ldots, \lambda, t) + \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\lambda'} - \dfrac{\partial\mathfrak{T}}{\partial\lambda} = \mathfrak{L}'(\alpha, \beta, \ldots, \lambda, t), \end{array}\right. \tag{14}$$

which have the most general form of the classical equations of dynamics.

The [232] method that we have just outlined is used to study the motion of bodies which are good electric conductors, bodies which are perfectly softly magnetic, etc.

In the case of the *classic problem of dynamics*, the question is raised in a yet more simple form. In dynamics, the variable ϑ is not introduced. It is implicitly assumed that the temperature remains invariable. The other variables introduced all figure in the expression for the kinetic energy. The problem is therefore reduced to the integration of the equations

$$\begin{cases} \dfrac{\partial}{\partial \alpha} \mathcal{F}(\alpha, \beta, \ldots, \lambda) + \dfrac{d}{dt}\dfrac{\partial W}{\partial \alpha'} - \dfrac{\partial W}{\partial \alpha} = A'(\alpha, \beta, \ldots, \lambda, t), \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial}{\partial \lambda} \mathcal{F}(\alpha, \beta, \ldots, \lambda) + \dfrac{d}{dt}\dfrac{\partial W}{\partial \lambda'} - \dfrac{\partial W}{\partial \lambda} = L'(\alpha, \beta, \ldots, \lambda, t), \end{cases} \tag{15}$$

which differ from the Equations (14) in so far as the function $\mathcal{F}$ does not depend explicitly on the temperature, whereas the function $\mathcal{G}$ does.

The classical problem of dynamics is thus logically connected by way of being a special case of thermodynamics. We have indicated (Section 5.4) a method which was presented for bringing about this reconciliation and we have shown the limitations of this method. We now see that this method leads, in general, to incorrect results. In fact, it would lead to the replacement in Equations (15) of the internal thermodynamic potential, $\mathcal{F}$, by the product EU of the internal energy and the mechanical equivalent of heat, and these two functions are not ordinarily equal to one another.

There is, however, one case, particularly in theory, but virtually the only one treated in classical dynamics, and mainly in celestial mechanics, where the two methods lead to identical results.

Consider a system formed from a certain number of independent parts 1, 2, … n, each one of which can be displaced in space, but remains in the same invariable state. Let $\Upsilon_1, \Upsilon_2, \ldots, \Upsilon_n$ be the internal energies of these various parts, which are constant. Let $\mathcal{F}_1, \mathcal{F}_2, \ldots, \mathcal{F}_n$ be the internal thermodynamic potentials of these parts, [233] which are also constant. We know, on the one hand (Section 5.2), that

$$U = \Upsilon_1 + \Upsilon_2 + \ldots + \Upsilon_n + \Psi$$

and, on the other hand (Section 9.2), that

$$\mathcal{F} = \mathcal{F}_1 + \mathcal{F}_2 + \ldots + \mathcal{F}_n + E\,\Psi,$$

where $E\,\Psi$ is one of the determinations of the *potential of mutual actions* of the parts 1, 2, … n, which is annulled when the parts are infinitely separated from one another. The three quantities $\mathcal{F}$, $E\,U$ and $E\,\Psi$ differ from one another only by constants.

Thus, *to write the equations of motion of a system formed from independent parts which are displaced without change of state, the following three functions can be substituted for one another in Lagrange's equations:*

The internal thermodynamic potential,
The product of the internal energy and the mechanical equivalent of heat,
The potential of the mutual actions of the various parts of the system.

Apart from this particular case, such a substitution would in general entail an error—an error which is frequently committed.

Returning to the general properties of systems without viscosity, Equations (4) become for such a system

$$\begin{cases} R'_\alpha = F(\vartheta)\,\dfrac{\partial S}{\partial \alpha}, \dots, R'_\lambda = E\,F(\vartheta)\,\dfrac{\partial S}{\partial \lambda}, \\ C' = F(\vartheta)\,\dfrac{\partial S}{\partial \vartheta}. \end{cases} \tag{16}$$

In a system without viscosity, the calorific coefficients have the same value, whether the system is at equilibrium or in motion.

From [234] Equations (16) it can be deduced that

$$\frac{1}{F(\vartheta)}\left(R'_\alpha\,d\alpha + \ldots + R'_\lambda\,d\lambda + C'\,d\vartheta\right) = dS,$$

or, designating by dQ the quantity of heat released in an elementary change,

$$\frac{dQ}{F(\vartheta)} = -dS$$

Integrating this equation over a closed cycle leads to the following proposition:

When a system without viscosity traverses a real closed cycle, then for the entire cycle,

$$\int \frac{dQ}{F(\vartheta)} = 0$$

We apply Equations (16) to a system formed of n independent parts which are displaced in relation to one another while the state of the system remains unchanged. Designating the entropies of various parts, which are constant, by $\sum 1, \sum 2, \ldots, \sum \mathrm{n}$, we have (Chapter 9, Equations (21a))

$$S = \Sigma_1 + \Sigma_2 + \ldots + \Sigma_n;$$

the entropy of the system will also be constant. Equations (16) then yield for us the following proposition:

When a system is formed from independent parts which are displaced without change of state, all the calorific coefficients of the system are equal to 0.

We can see from this theorem why the method presented in the 1st Part (Section 5.4) for connecting the classical problem of dynamics and thermodynamics is legitimate in this special case.

In order to bring to an end the consideration of systems without viscosity, [235] we state a CONJECTURE. It seems *probable* to us that the following supposition might hold for all physical phenomena:

> *The passive resistances corresponding to the variables a, b, ... , l not figuring in the expression of the kinetic energy are always equal to* 0.

In that case, it would be possible to replace Equations (2) in all circumstances with the equalities

$$\begin{cases} \dfrac{\partial(\mathfrak{F}-W)}{\partial\alpha} - \dfrac{d}{dt}\dfrac{\partial W}{\partial\alpha'} = A' + f_\alpha, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ \dfrac{\partial(\mathfrak{F}-W)}{\partial\lambda} - \dfrac{d}{dt}\dfrac{\partial W}{\partial\lambda'} = L' + f_\lambda, \end{cases} \tag{17}$$

$$\begin{cases} \dfrac{\partial\mathfrak{F}}{\partial\alpha} = \boldsymbol{\mathfrak{A}}', \\ \dots\dots\dots, \\ \dfrac{\partial\mathfrak{F}}{\partial\lambda} = \boldsymbol{\mathfrak{L}}'. \end{cases} \tag{18}$$

This will be the general form of Thermodynamic equations for a system of uniform temperature. We repeat that we have given this hypothesis the status of a conjecture; the developments to follow are independent of it.

10.6 Systems Formed of Independent Parts with Different Temperatures

We will now examine a case much more general than all the preceding ones. We will study a system formed from any number of parts independent of one another. We will assume that the temperature of each of these parts is uniform at each instant, while being capable of varying from one instant to another. *We will not suppose that this temperature has the same value for all these parts at each instant.*

In order not to complicate the discussion unnecessarily, we will consider just two independent parts, which we designate with the indices 1 and 2.

Let [236] $\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1$ be the normal variables defining the state of part 1 and its absolute position in space. Let $\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2$ be the normal variables defining the state of part 2 and its absolute position in space.

The internal energy of the system will have a value

$$\left\{\begin{aligned} U = {} & \Upsilon_1\left(\alpha_1,\beta_1,\ldots,\lambda_1,\vartheta_1\right)+\Upsilon_2\left(\alpha_2,\beta_2,\ldots,\lambda_2,\vartheta_2\right) \\ & +X_{12}\left(\alpha_1,\beta_1,\ldots,\lambda_1,\vartheta_1,\alpha_2,\beta_2,\ldots,\lambda_2,\vartheta_2\right). \end{aligned}\right. \tag{19}$$

Let

$$A_1''\,d\alpha_1+B_1''\,d\beta_1+\ldots+L_1''\,d\lambda_1+A_2''\,d\alpha_2+B_2''\,d\beta_2+\ldots+L_2''\,d\lambda_2$$

be the virtual work of the external actions acting on the system.

Each of the two parts 1 and 2 are regarded as independent systems. The virtual work of the external actions on each of the two systems is represented by the expressions

$$\begin{aligned} & A_1'd\alpha_1+B_1'd\beta_1+\ldots+L_1'd\lambda_1, \\ & A_2'd\alpha_2+B_2'd\beta_2+\ldots+L_2'd\lambda_2, \end{aligned}$$

with

$$\left\{\begin{array}{ll} A_1'=A_1''-E\,\dfrac{\partial X_{12}}{\partial\alpha_1}, & A_2'=A_2''-E\,\dfrac{\partial X_{12}}{\partial\alpha_2}, \\ \ldots\ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L_1'=L_1''-E\,\dfrac{\partial X_{12}}{\partial\lambda_1}, & L_2'=L_2''-E\,\dfrac{\partial X_{12}}{\partial\lambda_2}. \end{array}\right. \tag{20}$$

Part 1 forms an independent system with uniform temperature, this temperature not necessarily being the same as that of the external bodies. The considerations developed in the preceding sections can be applied to this system, which has an internal thermodynamic potential $\mathscr{F}_1$ and, at each instant,

$$\left\{\begin{array}{l} \dfrac{\partial\left(\mathscr{F}_1-\mathfrak{T}_1\right)}{\partial\alpha_1}+\dfrac{d}{dt}\dfrac{\partial\mathfrak{T}_1}{\partial\alpha_1'}=A_1''+f_{\alpha_1}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial\left(\mathscr{F}_1-\mathfrak{T}_1\right)}{\partial\lambda_1}+\dfrac{d}{dt}\dfrac{\partial\mathfrak{T}_1}{\partial\lambda_1'}=L_1''+f_{\lambda_1}. \end{array}\right. \tag{21}$$

Similarly, [237] letting $\mathscr{F}_2$ designate the internal thermodynamic potential of system 2,

$$\left\{\begin{array}{l} \dfrac{\partial\left(\mathscr{F}_2-\mathfrak{T}_2\right)}{\partial\alpha_2}+\dfrac{d}{dt}\dfrac{\partial\mathfrak{T}_2}{\partial\alpha_2'}=A_2''+f_{\alpha_2}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial\left(\mathscr{F}_2-\mathfrak{T}_2\right)}{\partial\lambda_2}+\dfrac{d}{dt}\dfrac{\partial\mathfrak{T}_2}{\partial\lambda_2'}=L_2''+f_{\lambda_2}. \end{array}\right. \tag{21a}$$

Taking Equations (20) into account, we observe that $\mathscr{F}_1$ doesn't depend on $\alpha_2, \beta_2, \ldots, \lambda_2$, that $\mathscr{F}_2$ doesn't depend on $\alpha_1, \beta_1, \ldots, \lambda_1$, that $\mathfrak{T}_1$ doesn't depend on $\alpha_2, \beta_2, \ldots, \lambda_2, \alpha'_2, \beta'_2, \ldots, \lambda'_2$, nor does $\mathfrak{T}_2$ depend on $\alpha_1, \beta_1, \ldots, \lambda_1, \alpha'_1, \beta'_1, \ldots, \lambda'_1$. We put

$$\mathfrak{T} = \mathfrak{T}_1 + \mathfrak{T}_2, \tag{22}$$

$$\mathscr{F} = \mathscr{F}_1 + \mathscr{F}_2 + EX_{12}, \tag{23}$$

and Equations (21) and (21a) can be replaced by the equations

$$\left\{ \begin{array}{l} \dfrac{\partial(\mathscr{F} - \mathfrak{T})}{\partial \alpha_1} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'_1} = A''_1 + f_{\alpha_1}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial(\mathscr{F} - \mathfrak{T})}{\partial \lambda_1} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'_1} = L''_1 + f_{\lambda_1}, \\ \dfrac{\partial(\mathscr{F} - \mathfrak{T})}{\partial \alpha_2} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'_2} = A''_2 + f_{\alpha_2}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial(\mathscr{F} - \mathfrak{T})}{\partial \lambda_2} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'_2} = L''_2 + f_{\lambda_2}. \end{array} \right. \tag{24}$$

These Equations (24) are all entirely of the same form as Equations (2) which govern the motion of a system with uniform temperature. If the system is composed of n independent parts, then they are 2 less in number of the variables whose values must be determined as a function of time. Two equations must therefore be added drawn from considerations outside thermodynamics, such as, for example, [238] the two equations

$$\vartheta_1 = \varphi_1(t), \quad \vartheta_2 = \varphi_2(t), \tag{25}$$

which tell us, at each instant, the temperature of each of the two independent parts composing the system.

We now calculate the quantity of heat dQ released by the system during an elementary change.

We have (Section 5.5)

$$dQ = dQ_1 + dQ_2,$$

where dQ_1 and dQ_2 are quantities of heat released by parts 1 and 2 during the same change.

Let S_1 and S_2 be the entropies of parts 1 and 2. We have (Equation (9)),

$$\begin{cases} E\,dQ_1 = -E\,F(\vartheta_1)\;dS_1 - \left(f_{\alpha_1}\,d\alpha_1 + f_{\beta_1}\,d\beta_1 + \ldots + f_{\lambda_1}\,d\lambda_1\right), \\ E\,dQ_2 = -E\,F(\vartheta_2)\;dS_2 - \left(f_{\alpha_2}\,d\alpha_2 + f_{\beta_2}\,d\beta_2 + \ldots + f_{\lambda_2}\,d\lambda_2\right). \end{cases} \tag{26}$$

We deduce from Equations (26)

$$\begin{cases} \dfrac{dQ_1}{F(\vartheta_1)} + \dfrac{dQ_2}{F(\vartheta_2)} = -d\,(S_1 + S_2) - \dfrac{f_{\alpha_1}\,d\alpha_1 + f_{\beta_1}\,d\beta_1 + \ldots + f_{\lambda_1}\,d\lambda_1}{E\,F(\vartheta_1)} \\ \qquad\qquad\qquad\qquad - \dfrac{f_{\alpha_2}\,d\alpha_2 + f_{\beta_2}\,d\beta_2 + \ldots + f_{\lambda_2}\,d\lambda_2}{E\,F(\vartheta_2)}. \end{cases} \tag{27}$$

Integrating Equation (27) over a closed cycle gives us the generalisation of Clausius' theorem due to H. Poincaré:

> *When a system formed from n independent parts, each with a distinct uniform temperature, describes a closed cycle, then*
>
> $$\int \left[\frac{dQ_1}{F(\vartheta_1)} + \frac{dQ_2}{F(\vartheta_2)} + \ldots + \frac{dQ_n}{F(\vartheta_n)}\right] \geq 0. \tag{28}$$
>
> *In the particular case where the system is without viscosity, the inequality sign disappears.*

Thus, [239] we see how several properties of a system of uniform temperature can be extended to a system composed of independent parts with temperatures different from one another.

Chapter 11
Connections

11.1 Bilateral and Unilateral Connections

Consider a system formed from separate parts which are independent of one another. In order to simplify and make the arguments concise without detracting from their generality, we will reduce the number of parts to two and designate them by the indices 1 and 2.

We assume that each of these parts has uniform temperature and is defined by normal variables; $\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, \vartheta_1$ are the normal variables defining part 1, and $\alpha_2, \beta_2, \ldots, \lambda_2, a_2, b_2, \ldots, l_2, \vartheta_2$ are the normal variables defining part 2.

Suppose that the parts are brought into contact by a continuous displacement. While the parts approach contact, the variables

$$\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, \vartheta_1,$$
$$\alpha_2, \beta_2, \ldots, \lambda_2, a_2, b_2, \ldots, l_2, \vartheta_2$$

tend towards limiting values, and knowledge of these limiting values suffices to determine the state of the system at the moment when contact is established.

This amounts to making the FOLLOWING HYPOTHESIS: *The state of the system at the moment when the parts 1 and 2 are contiguous differs infinitesimally from the state of the system when the parts are infinitesimally close to touching*. What is about to follow is not applicable to a system which does not satisfy this hypothesis.

In general, once contact has been established, the parts 1 and 2 cease to be independent.

In [240] the first place, it is sometimes possible to impose on the system, once contact has been established, virtual changes in which the state of each of the parts 1 and 2 undergoes variations which would be impossible if the parts were not contiguous.

If, for example, the parts 1 and 2 are electrified bodies, the distribution of electricity may vary on each of them, but as long as they are separated, the total charge of each of them necessarily remains constant. On the other hand, when contact is established between them, the total charge of the one might diminish provided that the change on the other increases by an equal amount.

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
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Similarly, when the parts 1 and 2 are in contact, they might mix with one another, which would be inconceivable while they are separate.

Putting aside these cases where contact between the various parts introduces new modes of variation into the system, we assume that in all virtual variations of the system, both of the parts undergo a change which would still be a virtual variation of this part if it were isolated. The two parts will, nevertheless, not be two independent systems.

In fact, once contact is established, the virtual displacements of each of the two parts are not absolutely arbitrary. These virtual displacements may either maintain the contact of the parts or break the contact, whether at certain points or entirely, and they may even establish new contacts. But since we exclude the hypothesis of mixture, the two parts cannot begin to penetrate into one another, leading to a portion of the one and a portion of the other being in the same place.

We seek an analytic method appropriate for excluding displacements which would lead the two parts to penetrate one another.

Suppose that the surface S_1 delimiting part 1 and the surface S_2 delimiting part 2 are in contact at a certain point p. Let p_1 be the material point of part 1 and p_2 the material point of part 2 which occur at p. Let N_1, N_2 be the normals at p to the surfaces S_1 and S_2, directed towards the interiors of parts 1 and 2, respectively. In order that a displacement $(\delta x_1, \delta y_1, \delta z_1)$ of the point p_1 and a displacement $(\delta x_2, \delta y_2, \delta z_2)$ of the point p_2 should lead parts 1 and 2 to penetrate the [241] neighbourhood of these points, it is necessary and sufficient that

$$\begin{aligned} &\cos(N_1,x)\delta x_1 + \cos(N_1,y)\delta y_1 + \cos(N_1,z)\delta z_1 \\ &\quad + \cos(N_2,x)\delta x_2 + \cos(N_2,y)\delta y_2 + \cos(N_2,z)\delta z_2 < 0. \end{aligned}$$

Displacements tending to make the two bodies penetrate one another are therefore excluded by imposing on virtual displacements the condition

$$\begin{aligned} &\cos(N_1,x)\delta x_1 + \cos(N_1,y)\delta y_1 + \cos(N_1,z)\delta z_1 \\ &\quad + \cos(N_2,x)\delta x_2 + \cos(N_2,y)\delta y_2 + \cos(N_2,z)\delta z_2 \geq 0. \end{aligned}$$

Now $\delta x_1, \delta y_1, \delta z_1$ are expressed as linear and homogeneous functions of $\delta\alpha_1, \delta\beta_1, \ldots, \delta\lambda_1$, and $\delta x_2, \delta y_2, \delta z_2$ are expressed as linear and homogeneous functions of $\delta\alpha_2, \delta\beta_2, \ldots, \delta\lambda_2$ (Chapter 3, Equation (2)). The preceding condition can therefore be written

$$\begin{aligned} &M_1\delta\alpha_1 + N_1\delta\beta_1 + \ldots + P_1\delta\lambda_1 \\ &\quad + M_2\delta\alpha_2 + N_2\delta\beta_2 + \ldots + P_2\delta\lambda_2 \geq 0, \end{aligned}$$

where $M_1, N_1, \ldots, P_1$ are functions of the variables $\alpha_1, \beta_1, \ldots, \lambda_1$, and $M_2, N_2, \ldots, P_2$ are functions of the variables $\alpha_2, \beta_2, \ldots, \lambda_2$.

Thus, the virtual displacements of a system formed from various parts in contact are subject to a certain number of conditions of the form

$$\begin{cases} M_1\delta\alpha_1 + N_1\delta\beta_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 \geq 0, \\ M_1'\delta\alpha_1 + N_1'\delta\beta_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2 \geq 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \end{cases} \tag{1}$$

which are called *connecting conditions for the system.*

If just the virtual displacements which do not change the contact of parts 1 and 2 are to be retained, then the *conditions* (1) must be replaced by the *equations*

$$\begin{cases} M_1\delta\alpha_1 + N_1\delta\beta_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 = 0, \\ M_1'\delta\alpha_1 + N_1'\delta\beta_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2 = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{cases} \tag{2}$$

When [242] the virtual displacements which break a contact are excluded and, consequently, all the virtual displacements are taken to be subject to the Equations (2), the system is said to be subject solely to *bilateral connections*. In that case, if

$$\delta\alpha_1, \ldots, \delta\lambda_1, \quad \delta\alpha_2, \ldots, \delta\lambda_2$$

is a virtual displacement of the system,

$$(-\delta\alpha_1), \ldots, (-\delta\lambda_1), \quad (-\delta\alpha_2), \ldots, (-\delta\lambda_2)$$

is also a virtual displacement of the system, so that all the virtual displacements of the system are *reversible*.

When, on the other hand, displacements which break contacts are allowed, the connections of the system, expressed by the conditions (1), are said to be *unilateral connections*. The virtual displacements *are no longer all reversible*.

11.2 The Internal Energy of a System with Connections

Consider a system formed from two parts 1 and 2 which might be separated or in contact. The internal energy of the system is designated by U when the two parts 1 and 2 are in contact.

When the two parts are separated infinitesimally, the internal energy of the system will have the value

$$\begin{cases} \Upsilon_1\left(\alpha_1, \ldots, \lambda_1, a_1, \ldots, l_1, \vartheta_1\right) + \Upsilon_2\left(\alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2, \vartheta_2\right) \\ + \Psi\left(\alpha_1, \ldots, \lambda_1, a_1, \ldots, l_1, \alpha_2, \ldots, \lambda_2, a_2, \ldots, l_2\right), \end{cases} \tag{3}$$

where the variables have values infinitesimally close to those which ensure contact of the parts 1 and 2.

But, by hypothesis, the change that we have just considered changes the state of the system infinitesimally. Consequently, the mechanical work[1] performed in this change is infinitesimal. And so the internal energy of the system also varies infinitesimally. The quantity U is equal to the limit towards which the quantity (3) tends when the parts 1 and 2 tend to touch one another. Thereof the following proposition:

> *The internal energy of a system formed from several parts in* [243] *contact is equal to the limit towards which the internal energy tends when the various parts, separated from one another, tend to come into contact with one another.*

Consider an isolated system formed from several parts in a state when the parts 1 and 2 are infinitesimally close to being in contact. We calculate the quantities

$$\left.\begin{array}{ll} E\dfrac{\partial\Psi}{\partial\alpha_1} = -A_1, & E\dfrac{\partial\Psi}{\partial\alpha_2} = -A_2, \\ \ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots, \\ E\dfrac{\partial\Psi}{\partial\lambda_1} = -L_1, & E\dfrac{\partial\Psi}{\partial\lambda_2} = -L_2, \\ E\dfrac{\partial\Psi}{\partial\alpha_1} = -\boldsymbol{\mathcal{A}}_1, & E\dfrac{\partial\Psi}{\partial\alpha_2} = -\boldsymbol{\mathcal{A}}_2, \\ \ldots\ldots\ldots\ldots, & \ldots\ldots\ldots\ldots\ldots, \\ E\dfrac{\partial\Psi}{\partial\lambda_1} = -\boldsymbol{\mathcal{L}}_1, & E\dfrac{\partial\Psi}{\partial\lambda_2} = -\boldsymbol{\mathcal{L}}_2 \end{array}\right. .$$

We calculate the *limiting values* towards which these quantities tend when the parts 1 and 2 tend to touch one another. *By definition*, the limits of the quantities $A_1, \ldots, L_1, \boldsymbol{\mathcal{A}}_1, \ldots, \boldsymbol{\mathcal{L}}_1$ are the actions that part 2, acting against part 1, exerts on part 1. Similarly, the limits of the quantities $A_2, \ldots, L_2, \boldsymbol{\mathcal{A}}_2, \ldots, \boldsymbol{\mathcal{L}}_2$ are the actions that part 1 exerts on part 2. The virtual work of these actions will have the values

$$\begin{aligned} &A_1\delta\alpha_1 + \ldots + L_1\delta\lambda_1 + \boldsymbol{\mathcal{A}}_1\delta a_1 + \ldots + \boldsymbol{\mathcal{L}}_1\delta l_1, \\ &A_2\delta\alpha_2 + \ldots + L_2\delta\lambda_2 + \boldsymbol{\mathcal{A}}_2\delta a_2 + \ldots + \boldsymbol{\mathcal{L}}_2\delta l_2, \end{aligned}$$

respectively, where $\delta\alpha_1, \ldots, \delta\lambda_1,\ \ \delta\alpha_2, \ldots, \delta\lambda_2$ are, moreover, subject to the connecting conditions.

What we have just said amounts to a definition: In fact, the mutual actions of the two systems 1 and 2 have so far only been defined where these systems are independent, and that is not the case here.

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[1] *oeuvre*.

11.3 Entropy [244] and the Thermodynamic Potential of a System with Connections

Consider once more a system formed from several parts, two for example, and suppose that these parts 1 and 2 are both at the same temperature. The system will then have an entropy and an internal thermodynamic potential whether or not the parts which compose it are in contact or not. Reasoning as in the preceding case, it will be shown that *the entropy and the internal thermodynamic potential of a system of uniform temperature composed of several parts in contact are equal, respectively, to the limits towards which the entropy and the internal thermodynamic potential of the system tend when the several isolated parts tend to meet one another.*

If we stick to our usual notation, this entropy S and internal thermodynamic potential $\mathcal{F}$ will be the limiting values of the quantities

$$\begin{gathered}
S = \sum{}_1(\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, \vartheta) + \\
\sum{}_2(\alpha_2, \beta_2, \ldots, \lambda_2, a_2, b_2, \ldots, l_2, \vartheta), \\
\mathcal{F} = \mathcal{F}_1(\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, \vartheta) + \\
\mathcal{F}_2(\alpha_2, \beta_2, \ldots, \lambda_2, a_2, b_2, \ldots, l_2, \vartheta) + \\
E\Psi(\alpha_1, \beta_1, \ldots, \lambda_1, a_1, b_1, \ldots, l_1, \alpha_2, \beta_2, \ldots, \lambda_2, a_2, b_2, \ldots, l_2, \vartheta).
\end{gathered}$$

11.4 Equilibrium of a System Subject to Bilateral Connections

Consider a system formed of two parts 1 and 2 between which there obtains the connecting conditions

$$\begin{cases}
M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 \geq 0, \\
M'_1\delta\alpha_1 + \ldots + P'_1\delta\lambda_1 + M'_2\delta\alpha_2 + \ldots + P'_2\delta\lambda_2 \geq 0, \\
\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots
\end{cases} \tag{1}$$

Suppose that we are assured in some way that the system cannot make any movement during which one of the inequalities

$$\begin{gathered}
M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 > 0, \\
M'_1\delta\alpha_1 + \ldots + P'_1\delta\lambda_1 + M'_2\delta\alpha_2 + \ldots + P'_2\delta\lambda_2 > 0, \\
\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots
\end{gathered}$$

is satisfied.

Consequently, [245] when the connecting conditions (1) are replaced by the connecting conditions (2), we can be certain that nothing changes the state of equilibrium or motion of the system. We can therefore consider the system to be subject solely to the bilateral connections

$$\begin{cases} M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 = 0, \\ M_1'\delta\alpha_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2 = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{cases} \tag{2}$$

Suppose that the two parts 1 and 2 are at the same temperature, ϑ. We seek the conditions necessary and sufficient for the equilibrium of the system comprising these two parts.

We give the system a virtual isothermal displacement compatible with Equations (2). The external actions perform the virtual work dW. The internal thermodynamic potential undergoes a variation $d\mathfrak{F}$. In accordance with what we have seen in Chapter 9, the necessary and sufficient conditions that we seek are obtained by writing that, for all virtual isothermal displacements, we have

$$d\mathfrak{F} = dW. \tag{4}$$

Now we can write

$$\begin{aligned} dW = {} & A_1\delta\alpha_1 + \ldots + L_1\delta\lambda_1 + \mathfrak{A}_1\delta a_1 + \ldots + \mathfrak{L}_1\delta l_1 \\ & + A_2\delta\alpha_2 + \ldots + L_2\delta\lambda_2 + \mathfrak{A}_2\delta a_2 + \ldots + \mathfrak{L}_2\delta l_2, \\ \delta\mathfrak{F} = {} & \frac{\partial\mathfrak{F}_1}{\partial\alpha_1}\delta\alpha_1 + \ldots + \frac{\partial\mathfrak{F}_1}{\partial\lambda_1}\delta\lambda_1 + \frac{\partial\mathfrak{F}_1}{\partial a_1}\delta a_1 + \ldots + \frac{\partial\mathfrak{F}_1}{\partial l_1}\delta l_1 \\ & + \frac{\partial\mathfrak{F}_2}{\partial\alpha_2}\delta\alpha_2 + \ldots + \frac{\partial\mathfrak{F}_2}{\partial\lambda_2}\delta\lambda_2 + \frac{\partial\mathfrak{F}_2}{\partial a_2}\delta a_2 + \ldots + \frac{\partial\mathfrak{F}_2}{\partial l_2}\delta l_2 \\ & + E\frac{\partial\Psi}{\partial\alpha_1}\delta\alpha_1 + \ldots + E\frac{\partial\Psi}{\partial\lambda_1}\delta\lambda_1 + E\frac{\partial\Psi}{\partial a_1}\delta a_1 + \ldots + E\frac{\partial\Psi}{\partial l_1}\delta l_1 \\ & + E\frac{\partial\Psi}{\partial\alpha_2}\delta\alpha_2 + \ldots + E\frac{\partial\Psi}{\partial\lambda_2}\delta\lambda_2 + E\frac{\partial\Psi}{\partial a_2}\delta a_2 + \ldots + E\frac{\partial\Psi}{\partial l_2}\delta l_2. \end{aligned}$$

Equation [246] (4) can therefore be written

$$\begin{cases} \left(A_1 - E\dfrac{\partial\Psi}{\partial\alpha_1} - \dfrac{\partial\mathfrak{F}_1}{\partial\alpha_1}\right)\delta\alpha_1 + \ldots + \left(L_1 - E\dfrac{\partial\Psi}{\partial\lambda_1} - \dfrac{\partial\mathfrak{F}_1}{\partial\lambda_1}\right)\delta\lambda_1 \\ + \left(A_1 - E\dfrac{\partial\Psi}{\partial a_1} - \dfrac{\partial\mathfrak{F}_1}{\partial a_1}\right)\delta a_1 + \ldots + \left(L_1 - E\dfrac{\partial\Psi}{\partial l_1} - \dfrac{\partial\mathfrak{F}_1}{\partial l_1}\right)\delta l_1 \\ + \left(A_2 - E\dfrac{\partial\Psi}{\partial\alpha_2} - \dfrac{\partial\mathfrak{F}_2}{\partial\alpha_2}\right)\delta\alpha_2 + \ldots + \left(L_2 - E\dfrac{\partial\Psi}{\partial\lambda_2} - \dfrac{\partial\mathfrak{F}_2}{\partial\lambda_2}\right)\delta\lambda_2 \\ + \left(A_2 - E\dfrac{\partial\Psi}{\partial a_2} - \dfrac{\partial\mathfrak{F}_2}{\partial a_2}\right)\delta a_2 + \ldots + \left(L_2 - E\dfrac{\partial\Psi}{\partial l_2} - \dfrac{\partial\mathfrak{F}_2}{\partial l_2}\right)\delta l_2 = 0. \end{cases} \tag{5}$$

But this equality should not be satisfied for all values of the variations

$$\delta\alpha_1, \ldots, \delta\lambda_1, \quad \delta a_1, \ldots, \delta l_1, \quad \delta\alpha_2, \ldots, \delta\lambda_2, \quad \delta a_2, \ldots, \delta l_2,$$

but only when Equations (2) are satisfied.

For this, it is necessary and sufficient that there exists as many factors $\Pi, \Pi', \ldots,$ as there are Equations (2) *depending solely on the variables* $\alpha_1, \beta_1, \ldots, \lambda_1, \alpha_2, \beta_2, \ldots, \lambda_2$, such that Equation (5) obtains whatever

$$\delta\alpha_1, \ldots, \delta\lambda_1, \quad \delta a_1, \ldots, \delta l_1, \quad \delta\alpha_2, \ldots, \delta\lambda_2, \quad \delta a_2, \ldots, \delta l_2,$$

might be when to its left-hand side is added the expression

$$\begin{aligned} &\Pi(M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2) \\ +\, &\Pi'(M_1'\delta\alpha_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2) \\ +\, &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}$$

In other words, in order that the system subject to the bilateral [246] connections (2) be at equilibrium, it is necessary and sufficient that

$$\begin{cases} A_1 - E\dfrac{\partial\Psi}{\partial\alpha_1} + \Pi M_1 + \Pi' M_1' + \ldots = \dfrac{\partial\mathcal{F}_1}{\partial\alpha_1}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L_1 - E\dfrac{\partial\Psi}{\partial\lambda_1} + \Pi P_1 + \Pi' P_1' + \ldots = \dfrac{\partial\mathcal{F}_1}{\partial\lambda_1}, \end{cases} \tag{6}$$

$$\begin{cases} \mathcal{A}_1 - E\dfrac{\partial\Psi}{\partial a_1} = \dfrac{\partial\mathcal{F}_1}{\partial a_1}, \\ \ldots\ldots\ldots\ldots\ldots\ldots, \\ \mathcal{L}_1 - E\dfrac{\partial\Psi}{\partial l_1} = \dfrac{\partial\mathcal{F}_1}{\partial l_1}, \end{cases} \tag{7}$$

$$\begin{cases} A_2 - E\dfrac{\partial\Psi}{\partial\alpha_2} + \Pi M_2 + \Pi' M_2' + \ldots = \dfrac{\partial\mathcal{F}_2}{\partial\alpha_2}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L_2 - E\dfrac{\partial\Psi}{\partial\lambda_2} + \Pi P_2 + \Pi' P_2' + \ldots = \dfrac{\partial\mathcal{F}_2}{\partial\lambda_2}, \end{cases} \tag{6a}$$

$$\begin{cases} \mathcal{A}_2 - E\dfrac{\partial\Psi}{\partial a_2} = \dfrac{\partial\mathcal{F}_2}{\partial a_2}, \\ \ldots\ldots\ldots\ldots\ldots\ldots, \\ \mathcal{L}_2 - E\dfrac{\partial\Psi}{\partial l_2} = \dfrac{\partial\mathcal{F}_2}{\partial l_2}, \end{cases} \tag{7a}$$

We will examine the consequences of Equations (6), (7), (6a) and (7a).

In accordance with the definition of actions exerted by part 2 on part 1, we can say that

$$A_1 - E\,\frac{\partial\Psi}{\partial\alpha_1}, \ldots,\ L_1 - E\,\frac{\partial\Psi}{\partial\lambda_1},\quad \boldsymbol{\mathcal{A}}_1 - E\,\frac{\partial\Psi}{\partial a_1}, \ldots,\ \boldsymbol{\mathcal{L}}_1 - E\,\frac{\partial\Psi}{\partial l_1}$$

are the actions exerted on part 1 by the bodies external to this part. Thus, we see that Equations (6) and (7) lead to the following important theorem:

> *The conditions of equilibrium of a system which, instead of being independent contain bilateral connections with the bodies encircling it, are written as the conditions of equilibrium of an independent system,* [248] *provided that to the external forces to which the system is subject are associated the fictive forces*
>
> $$\begin{cases} F_{\alpha_1} = \Pi\, M_1 + \Pi'\, M_1' + \ldots, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ F_{\lambda_1}' = \Pi\, P_1 + \Pi'\, P_1' + \ldots. \end{cases} \tag{8}$$
>
> *These fictive forces, called* connecting forces, *depend only on the variables which fix the position relative to the system and the external bodies, and not on the variables which change the state of the system or the external bodies without changing their relative position.*

The virtual work of the external connecting forces applied to system (1) has the value

$$\begin{aligned} F_{\alpha_1}\,\delta\alpha_1 + \ldots + F_{\lambda_1}\,\delta\lambda_1 = {} & \left(\Pi\, M_1 + \Pi'\, M_1' + \ldots\right)\,\delta\alpha_1 \\ & + \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ & + \left(\Pi\, P_1 + \Pi'\, P_1' + \ldots\right)\,\delta\lambda_1\,. \end{aligned}$$

Similarly, system 1 exerts on the external bodies connecting forces

$$\begin{cases} F_{\alpha_2} = \Pi\, M_2 + \Pi'\, M_2' + \ldots, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ F_{\lambda_2} = \Pi\, P_2 + \Pi'\, P_2' + \ldots\ldots. \end{cases} \tag{8a}$$

for which the virtual work has the value

$$\begin{aligned} F_{\alpha_2}\,\delta\alpha_2 + \ldots + F_{\lambda_2}\,\delta\lambda_2 = {} & \left(\Pi\, M_2 + \Pi'\, M_2' + \ldots\right)\,\delta\alpha_2 \\ & + \ldots\ldots\ldots\ldots\ldots\ldots \\ & + \left(\Pi\, P_2 + \Pi'\, P_2' + \ldots\right)\,\delta\lambda_2\,. \end{aligned}$$

The total virtual work of the connecting forces exerted between the two systems 1 and 2 has the value

$$\begin{aligned}F_{\alpha_1}\,\delta\alpha_1 + \ldots + F_{\lambda_1}\,\delta\lambda_1 + F_{\alpha_2}\,\delta\alpha_2 + \ldots + F_{\lambda_2}\,\delta\lambda_2 \\ = \Pi\ (M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2) \\ + \Pi'\left(M_1'\delta\alpha_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2\right) \\ + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\end{aligned}$$

If [249] Equations (2) are taken into account, the following theorem can be stated:

The virtual work of all the connecting forces exerted between the two systems (1) *and* (2) *is zero for all virtual displacements which respect the bilateral connections existing between the two systems.*

The conditions of equilibrium of a system which is subject to bilateral connections with external bodies differ from conditions of equilibrium of an independent system in one essential point.

Suppose that an independent system is subject to a virtual change $\delta\alpha, \ldots, \delta\lambda, \delta a, \ldots, \delta l$, while the state of the external bodies remains invariable. The virtual work of the external actions will, in this case, be the total differential of a function of the variables $\alpha, \ldots, \lambda, a, \ldots, l$ (*see* Section 9.4). If, on the other hand, we consider a system subject to bilateral connections with the external bodies, the virtual work of the external actions and the connecting forces, which should, in this case, replace the work of just the external actions, will not, in general, be a total differential. Since we have taken care never to assume in our demonstrations that the virtual work of the external actions is a total differential, the results of these demonstrations are applicable to systems subject to bilateral connections with the external bodies.

11.5 Equilibrium of a System Subject to Unilateral Connections

Why, when dealing with the equilibrium of a system subject to connections in the preceding section, did we add the restriction that these connections are bilateral? The reason is simple. We have made use of the laws of equilibrium of systems as these were established in Chapter 9. Now, throughout the establishing of these laws, it was supposed that the system is defined, in the neighbourhood of the state under study, by a single system of parameters continuously varying arbitrarily. This condition is not realised by a system subject to unilateral connections. Take a system comprising various parts which, in the state under study, are in contact. Two different systems of [250] variables must be employed to define the neighbouring states of the system depending on whether the contact in these states is preserved or discontinued. It is therefore clear that our arguments will fail if the system exhibits unilateral connections.

The preceding arguments presuppose the following proposition: The system cannot, starting from the state at issue where the velocities of the various parts are all equal to 0, take on a movement whose first element would represent an irreversible virtual displacement. We therefore have necessary and sufficient conditions for equilibrium for a system if we add to the conditions established in the preceding section necessary and sufficient conditions for excluding any movement of this type.

Unfortunately, we cannot establish with complete rigour the necessary and sufficient conditions. We can only put forward with confidence a condition which is *sufficient* for rendering impossible any movement of the system beginning, without initial velocity, with an irreversible displacement.

This condition is as follows:

If in any irreversible virtual change, the inequality

$$\begin{aligned}
&\left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial \alpha_1} - A_1\right) \delta\alpha_1 + \ldots + \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial \lambda_1} - L_1\right) \delta\lambda_1 \\
&+ \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial a_1} - \boldsymbol{\mathcal{A}}_1\right) \delta a_1 + \ldots + \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial l_1} - \boldsymbol{\mathcal{L}}_1\right) \delta l_1 \\
&+ \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial \alpha_2} - A_2\right) \delta\alpha_2 + \ldots + \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial \lambda_2} - L_2\right) \delta\lambda_2 \\
&+ \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial a_2} - \boldsymbol{\mathcal{A}}_2\right) \delta a_2 + \ldots + \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial l_2} - \boldsymbol{\mathcal{L}}_2\right) \delta l_2 > 0,
\end{aligned}$$

holds, then it is certain that the system cannot make any movement, without an initial velocity, beginning with an irreversible virtual displacement.

For suppose that the system could make such a movement. Let t_0 be the initial instant of this motion. Let $d\alpha_1, \ldots, d\lambda_1, da_1, \ldots, dl_1, d\alpha_2, \ldots, d\lambda_2, da_2, \ldots, dl_2$ be the first element of [251] this movement. Suppose that

$$\left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial \alpha_1} - A_1\right) d\alpha_1 + \ldots + \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial l_2} - \boldsymbol{\mathcal{L}}_2\right) dl_2 > 0$$

The first term of this inequality varies continuously during the motion of the system. We could therefore determine an instant t_1, later than but quite close to t_0, such that, between these two instants t_0 and t_1, this first term always remains positive. We would then certainly have[2]

$$\int_{t_0}^{t_1} \left[\left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial \alpha_1} - A_1\right) d\alpha_1 + \ldots + \left(\frac{\partial \boldsymbol{\mathcal{F}}}{\partial l_2} - \boldsymbol{\mathcal{L}}_2\right) dl_2\right] > 0.$$

But having disrupted certain unilateral connections at the instant t_0, the system may always be supposed to be exclusively subject to bilateral connections during the time between t_0 and the instant t_1 quite close to the instant t_0. During this time, its state will be defined by a single system of continuously but arbitrarily varying parameters. Since its temperature is uniform the laws of motion for a system of uniform temperature, such as those established in Chapter 10, can be applied. These

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[2] [The limits of integration are written “$\int_{t_1}^{t_1}$” in the original.]

laws give us immediately the equation

$$\begin{gathered}\int_{t_0}^{t_1}\left[\left(\frac{\partial\mathfrak{F}}{\partial\alpha_1}-A_1\right)d\alpha_1+\ldots+\left(\frac{\partial\mathfrak{F}}{\partial l_2}-\mathfrak{L}_2\right)dl_2\right]\\ \mathfrak{T}_0-\mathfrak{T}_1+\int_{t_0}^{t_1}\left(f_{\alpha_1}d\alpha_1+\ldots+f_{l_2}dl_2\right).\end{gathered}$$

Since the initial velocities are, by hypothesis, all equal to 0, the same holds for $\mathfrak{T}_0$, and the preceding equation gives us the inequality

$$\int_{t_0}^{t_1}\left[\left(\frac{\partial\mathfrak{F}}{\partial\alpha_1}-A_1\right)d\alpha_1+\ldots+\left(\frac{\partial\mathfrak{F}}{\partial l_2}-\mathfrak{L}_2\right)dl_2\right]<0,$$

which contradicts the preceding inequality.

This contradiction demonstrates the truth of the proposition stated.

Is the preceding condition, sufficient to impede any motion beginning with an irreversible displacement, at the same time necessary for this purpose? Fourier, Gauss, Cauchy and [252] many other geometers after them have thought so. But it seems difficult to rigorously prove this by relying solely on what precedes.

11.6 Motion of a System with Uniform Temperature Subject to Bilateral Connections

In order not to further lengthen the present work, we will only study the motion of a system in as much as the connections between its various parts remain bilateral.

Consider a system formed of two parts 1 and 2 between which there exist bilateral connections. Assume that the two parts 1 and 2 have the same temperature, ϑ. The aggregate of these two parts then forms a system to which the general laws of motion developed in Chapter II can be applied.

We can, without needing to know explicitly the independent variables which define the system, state the laws of motion in the following way:
Let

dW be the virtual work of the external forces,
$\delta\mathfrak{F}$ be the isothermal variation of the internal thermodynamic potential,
$d\tau$ be the virtual work of the forces of inertia,
$d\varphi$ be the virtual work of the passive resistances.

For any virtual displacement of the system, we must have

$$dW+d\varphi-\delta\mathfrak{F}=d\tau. \tag{9}$$

Now we can write

$$\begin{aligned} dW = {} & A_1\,\delta\alpha_1 + \ldots + L_1\,\delta\lambda_1 + \boldsymbol{\mathcal{A}}_1\,\delta a_1 + \ldots + \boldsymbol{\mathcal{L}}_1\,\delta l_1 \\ & + A_2\,\delta\alpha_2 + \ldots + L_2\,\delta\lambda_2 + \boldsymbol{\mathcal{A}}_2\,\delta a_2 + \ldots + \boldsymbol{\mathcal{L}}_2\,\delta l_2, \end{aligned}$$

$$\begin{aligned} \delta\boldsymbol{\mathcal{F}} = {} & \frac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\alpha_1}\,\delta\alpha_1 + \ldots + \frac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\lambda_1}\,\delta\lambda_1 + \frac{\partial\boldsymbol{\mathcal{F}}_1}{\partial a_1}\,\delta a_1 + \ldots + \frac{\partial\boldsymbol{\mathcal{F}}_1}{\partial l_1}\,\delta l_1 \\ & + \frac{\partial\boldsymbol{\mathcal{F}}_2}{\partial\alpha_2}\,\delta\alpha_2 + \ldots + \frac{\partial\boldsymbol{\mathcal{F}}_2}{\partial\lambda_2}\,\delta\lambda_2 + \frac{\partial\boldsymbol{\mathcal{F}}_2}{\partial a_2}\,\delta a_2 + \ldots + \frac{\partial\boldsymbol{\mathcal{F}}_2}{\partial l_2}\,\delta l_2 \\ & + E\,\frac{\partial\Psi}{\partial\alpha_1}\,\delta\alpha_1 + \ldots + E\,\frac{\partial\Psi}{\partial\lambda_1}\,\delta\lambda_1 + E\,\frac{\partial\Psi}{\partial a_1}\,\delta a_1 + \ldots + E\,\frac{\partial\Psi}{\partial l_1}\,\delta l_1 \\ & + E\,\frac{\partial\Psi}{\partial\alpha_2}\,\delta\alpha_2 + \ldots + E\,\frac{\partial\Psi}{\partial\lambda_2}\,\delta\lambda_2 + E\,\frac{\partial\Psi}{\partial a_2}\,\delta a_2 + \ldots + E\,\frac{\partial\Psi}{\partial l_2}\,\delta l_2, \end{aligned}$$

[253]

$$\begin{aligned} d\varphi = {} & f_{\alpha_1}\,\delta\alpha_1 + \ldots + f_{\lambda_1}\,\delta\lambda_1 + f_{a_1}\,\delta a_1 + \ldots + f_{l_1}\,\delta l_1 \\ & + f_{\alpha_2}\,\delta\alpha_2 + \ldots + f_{\lambda_2}\,\delta\lambda_2 + f_{a_2}\,\delta a_2 + \ldots + f_{l_2}\,\delta l_2, \end{aligned}$$

$$\begin{aligned} d\tau = {} & \left(\frac{\partial\mathfrak{T}_1}{\partial\alpha_1} - \frac{d}{dt}\frac{\partial\mathfrak{T}_1}{\partial\alpha_1'}\right)\delta\alpha_1 + \ldots + \left(\frac{\partial\mathfrak{T}_1}{\partial\lambda_1} - \frac{d}{dt}\frac{\partial\mathfrak{T}_1}{\partial\lambda_1'}\right)\delta\lambda_1 \\ & + \left(\frac{\partial\mathfrak{T}_2}{\partial\alpha_2} - \frac{d}{dt}\frac{\partial\mathfrak{T}_2}{\partial\alpha_2'}\right)\delta\alpha_2 + \ldots + \left(\frac{\partial\mathfrak{T}_2}{\partial\lambda_2} - \frac{d}{dt}\frac{\partial\mathfrak{T}_2}{\partial\lambda_2'}\right)\delta\lambda_2. \end{aligned}$$

Equation (9) can therefore be written

$$\left\{\begin{aligned} & A_1\,\delta\alpha_1 + \ldots + \boldsymbol{\mathcal{L}}_2\,\delta l_2 - \frac{\partial\boldsymbol{\mathcal{F}}_1}{\partial\alpha_1}\delta\alpha_1 + \ldots - \frac{\partial\boldsymbol{\mathcal{F}}_2}{\partial l_2}\delta l_2 \\ & -E\frac{\partial\Psi}{\partial\alpha_1}\delta\alpha_1 - \ldots - E\frac{\partial\Psi}{\partial l_2}\delta l_2 + f_{\alpha_1}\,\delta\alpha_1 + \ldots + f_{l_2}\,\delta l_2 \\ & = \left(\frac{\partial\mathfrak{T}_1}{\partial\alpha_1} - \frac{d}{dt}\frac{\partial\mathfrak{T}_1}{\partial\alpha_1'}\right)\delta\alpha_1 + \ldots + \left(\frac{\partial\mathfrak{T}_2}{\partial\lambda_2} - \frac{d}{dt}\frac{\partial\mathfrak{T}_2}{\partial\lambda_2'}\right)\delta\lambda_2. \end{aligned}\right. \tag{9a}$$

But in this Equation (9a) the quantities $\delta\alpha_1, \ldots, \delta\lambda_2$ do not have arbitrary values. They are subject to the equations of connection

$$\left\{\begin{aligned} & M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 = 0, \\ & M_1'\delta\alpha_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2 = 0, \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right. \tag{2}$$

Then there exists factors $\Pi, \Pi', \ldots$ such that on multiplying the left-hand side of the first Equation (2) by Π, multiplying the left-hand side of the second Equation (2) by Π', etc., and adding the results obtained to the left-hand side of Equation (9a), this would hold whatever the quantities $\delta\alpha_1, \ldots, \delta\lambda_2$ might be.

The factors $\Pi, \Pi', \ldots$ depend solely on the variables $\alpha_1, \ldots, \lambda_1, \alpha_2, \ldots, \lambda_2$ and their first and second derivatives with respect to time and not on the variables $a_1, \ldots, l_1, a_2, \ldots, l_2$ nor their derivatives with respect to time.

It therefore holds, at each instant of the motion, that

$$\begin{cases} A_1 - E\dfrac{\partial \Psi}{\partial \alpha_1} + \Pi M_1 + \Pi' M_1' + \ldots + f_{\alpha_1} - \dfrac{\partial \mathfrak{T}_1}{\partial \alpha_1} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}_1}{\partial \alpha_1'} - \dfrac{\partial \mathcal{F}_1}{\partial \alpha_1} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L_1 - E\dfrac{\partial \Psi}{\partial \lambda_1} + \Pi P_1 + \Pi' P_1' + \ldots + f_{\lambda_1} - \dfrac{\partial \mathfrak{T}_1}{\partial \lambda_1} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}_1}{\partial \lambda_1'} - \dfrac{\partial \mathcal{F}_1}{\partial \lambda_1} = 0; \end{cases} \tag{10}$$

[254]

$$\begin{cases} \mathcal{A}_1 - E\dfrac{\partial \Psi}{\partial \alpha_1} + f_{\alpha_1} - \dfrac{\partial \mathcal{F}_1}{\partial \alpha_1} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \mathcal{L}_1 - E\dfrac{\partial \Psi}{\partial \lambda_1} + f_{\lambda_1} - \dfrac{\partial \mathcal{F}_1}{\partial \lambda_1} = 0. \end{cases} \tag{11}$$

$$\begin{cases} A_2 - E\dfrac{\partial \Psi}{\partial \alpha_2} + \Pi M_2 + \Pi' M_2' + \ldots + f_{\alpha_2} - \dfrac{\partial \mathfrak{T}_2}{\partial \alpha_2} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}_2}{\partial \alpha_2'} - \dfrac{\partial \mathcal{F}_2}{\partial \alpha_2} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ L_2 - E\dfrac{\partial \Psi}{\partial \lambda_2} + \Pi P_2 + \Pi' P_2' + \ldots + f_{\lambda_2} - \dfrac{\partial \mathfrak{T}_2}{\partial \lambda_2} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}_2}{\partial \lambda_2'} - \dfrac{\partial \mathcal{F}_2}{\partial \lambda_2} = 0; \end{cases} \tag{10a}$$

$$\begin{cases} \mathcal{A}_2 - E\dfrac{\partial \Psi}{\partial \alpha_2} + f_{\alpha_2} - \dfrac{\partial \mathcal{F}_2}{\partial \alpha_2} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \mathcal{L}_2 - E\dfrac{\partial \Psi}{\partial \lambda_2} + f_{\lambda_2} - \dfrac{\partial \mathcal{F}_2}{\partial \lambda_2} = 0. \end{cases} \tag{11a}$$

All the equations of motion of the system are obtained by adding to these equations a final equation showing how the temperature ϑ of the system varies with time.

Equations (10) and (10a) lead to the following consequence:

> *It is possible to extend to a system exhibiting bilateral connections with the external bodies all the laws of motion of a system independent of external bodies, provided that fictive forces*

$$F_{\alpha_1} = \Pi M_1 + \Pi' M_1' + \ldots,$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,$$

$$F_{\lambda_1}' = \Pi P_1 + \Pi' P_1' + \ldots.$$

are added to the external forces.

These forces of connection depend solely on the variables $\alpha_1, \ldots, \lambda_1, \alpha_2, \ldots, \lambda_2$ which fix the position of the system and the external bodies, and the first and second derivatives of these variables with respect to time.

This [255] proposition is only demonstrated, however, in so far as the aggregate formed by the system and the external bodies has a uniform temperature at each instant.

Consider any infinitesimal change of the system whose two parts 1 and 2, at the same temperature, sustain bilateral connections. The total work of the forces of connection exerted between the two parts will have the value

$$\Big[\big(\Pi M_1 + \Pi' M_1' + \ldots\big)\,\frac{d\alpha_1}{dt} + \ldots + \big(\Pi P_1 + \Pi' P_1' + \ldots\big)\,\frac{d\lambda_1}{dt}$$
$$+ \big(\Pi M_2 + \Pi' M_2' + \ldots\big)\,\frac{d\alpha_2}{dt} + \ldots + \big(\Pi P_2 + \Pi' P_2' + \ldots\big)\,\frac{d\lambda_2}{dt}\Big]\,dt.$$

But the equations of connection (2) must be satisfied by putting

$$\frac{d\alpha_1}{dt}\,dt = \delta\alpha_1, \qquad \frac{d\alpha_2}{dt}\,dt = \delta\alpha_2,$$
$$\ldots\ldots\ldots\ldots, \qquad \ldots\ldots\ldots\ldots,$$
$$\frac{d\lambda_1}{dt}\,dt = \delta\lambda_1, \qquad \frac{d\lambda_2}{dt}\,dt = \delta\lambda_2.$$

The preceding work is thus equal to 0.

11.7 Motion of a System Whose Various Parts, Taken to Different Temperatures, Are Subject to Bilateral Connections

All that we have hitherto said on connections has been deduced from what has been established in the two preceding chapters, without needing to invoke any new hypothesis. This will not be the case in the present section.

In Section 10.6, we treated the motion of a system comprising several independent parts at different temperatures. The equations obtained can be condensed in the following proposition:

Assume that the system is formed from two parts 1 and 2. Let

$$\mathfrak{U} = \Upsilon_1 + \Upsilon_2 + \Psi$$

be the internal energy of this system, and put

$$\mathcal{F} = \mathcal{F}_1 + \mathcal{F}_2 + E\,\Psi,$$

where [256] $\mathcal{F}_1$ and $\mathcal{F}_2$ are the internal thermodynamic potentials of parts 1 and 2, assumed isolated. If we give the system any virtual displacement, we will have

$$dW + d\varphi - \delta\mathcal{F} = d\tau, \tag{12}$$

the various symbols having the same sense as in Equation (9).

This said, here is the hypothesis that we introduce:

> HYPOTHESIS.—*The preceding results remain true even in the case where the various parts constituting the system are taken to different temperatures and exhibit bilateral connections between one another.*

Once this hypothesis is accepted, it suffices to revive the considerations of the preceding section in order to be able to extend all the results obtained there to a system with non-uniform temperature.

11.8 Calorific Coefficients of a System Subject to Bilateral Connections

We only know the sense of the expression *quantity of heat released by a system* in so far as this system is independent of external bodies. Where a system exhibiting bilateral connections with external bodies is concerned, we cannot employ this expression before giving a definition.

Consider, then, a system subject to bilateral connections with external bodies. Let U be the internal energy of the system and $F_\alpha, \ldots, F_\lambda$ the forces of connection.

Put

$$\left\{\begin{aligned}
&E\frac{\partial U}{\partial \alpha} - \frac{\partial \mathfrak{T}}{\partial \alpha} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \alpha'} - (A + F_\alpha) = E R_\alpha,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,\\
&E\frac{\partial U}{\partial \lambda} - \frac{\partial \mathfrak{T}}{\partial \lambda} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \lambda'} - (A + F_\lambda) = E R_\lambda,\\
&E\frac{\partial U}{\partial a} - \mathcal{A} = E\,\mathfrak{R}_a,\\
&\ldots\ldots\ldots\ldots\ldots\ldots,\\
&E\frac{\partial U}{\partial l} - \mathcal{L} = E\,\mathfrak{R}_l.
\end{aligned}\right. \tag{13}$$

The [257] sum

$$-\left(R_{\alpha}\delta\alpha+\ldots+R_{\lambda}\delta\lambda+\boldsymbol{\mathcal{R}}_{a}\delta a+\ldots+\boldsymbol{\mathcal{R}}_{l}\delta l\right)$$

will, by definition, be the *quantity of heat released by a system* during the real or virtual change $\delta\alpha,\ldots,\delta\lambda,\delta a,\ldots,\delta l$.

It evidently follows from this definition, which includes as a particular case what we have called an independent system (Section 5.5), that *a real or virtual change of an isolated system entails a release of heat equal to* 0.

Consider a system formed from two parts 1 and 2. Let $\alpha_1,\ldots,\lambda_1,a_1,\ldots,l_1$ be the variables defining the first part, and $\alpha_2,\ldots,\lambda_2,a_2,\ldots,l_2$ the variables defining the second part.

The two parts exhibit between them contacts expressed by the equations of connection

$$\begin{cases} M_1\delta\alpha_1+\ldots+P_1\delta\lambda_1+M_2\delta\alpha_2+\ldots+P_2\delta\lambda_2=0, \\ M_1'\delta\alpha_1+\ldots+P_1'\delta\lambda_1+M_2'\delta\alpha_2+\ldots+P_2'\delta\lambda_2=0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{cases} \tag{14}$$

Moreover, they exhibit contacts with the external bodies expressed by the equations of connection

$$\begin{cases} m_1\,\delta\alpha_1+\ldots+p_1\,\delta\lambda_1+\mu_1\,\delta a+\ldots+\varpi_1\,\delta l, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ m_2\,\delta\alpha_2+\ldots+p_2\,\delta\lambda_2+\mu_2\,\delta a+\ldots+\varpi_2\,\delta l, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \end{cases} \tag{15}$$

where $a,\ldots,l$ are the variables defining the position of the external bodies.

The internal energy of the system formed by the ensemble of the two parts will be designated by

$$\mathfrak{U}=\Upsilon_1+\Upsilon_2+\Psi.$$

The external actions applied to the system formed from two parts [258] will be designated by $A_1,\ldots,L_1,A_2,\ldots,L_2,\boldsymbol{\mathcal{A}}_1,\ldots,\boldsymbol{\mathcal{L}}_1,\boldsymbol{\mathcal{A}}_2,\ldots,\boldsymbol{\mathcal{L}}_2$,.

During any change of the system, part 1 releases a quantity of heat dQ_1 given by the equation

$$
\begin{aligned}
-E\,dQ_1 = \Bigg[& E\,\frac{\partial \Upsilon_1}{\partial \alpha_1} - \frac{\partial \mathfrak{T}_1}{\partial \alpha_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}_1}{\partial \alpha_1'} \\
& - \left(A_1 - E\,\frac{\partial \Psi}{\partial \alpha_1} + \Pi\, M_1 + \Pi'\, M_1' + \ldots + \boldsymbol{\mathscr{P}}_1\, m_1 + \ldots \right) \Bigg]\, \delta\alpha_1 \\
& + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
& + \Bigg[E\,\frac{\partial \Upsilon_1}{\partial \lambda_1} - \frac{\partial \mathfrak{T}_1}{\partial \lambda_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}_1}{\partial \lambda_1'} \\
& - \left(L_1 - E\,\frac{\partial \Psi}{\partial \lambda_1} + \Pi\, P_1 + \Pi'\, P_1' + \ldots + \boldsymbol{\mathscr{P}}_1\, p_1 + \ldots \right) \Bigg]\, \delta\lambda_1 \\
& + \left(E\,\frac{\partial \Upsilon_1}{\partial \alpha_1} + E\,\frac{\partial \Psi}{\partial \alpha_1} - \boldsymbol{\mathscr{A}}_1 \right) \delta a_1 + \ldots + \left(E\,\frac{\partial \Upsilon_1}{\partial l_1} + E\,\frac{\partial \Psi}{\partial l_1} - \boldsymbol{\mathscr{L}}_1 \right) \delta l_1 .
\end{aligned}
$$

Similarly, part 2 releases a quantity of heat dQ_2 given by the equation

$$
\begin{aligned}
-E\,dQ_2 = \Bigg[& E\frac{\partial \Upsilon_2}{\partial \alpha_2} - \frac{\partial \mathfrak{T}_2}{\partial \alpha_2} + \frac{d}{dt}\frac{\partial \mathfrak{T}_2}{\partial \alpha_2'} \\
& - \left(A_2 - E\frac{\partial \Psi}{\partial \alpha_2} + \Pi\, M_2 + \Pi'\, M_2' + \ldots + \boldsymbol{\mathscr{P}}_2\, m_2 + \ldots \right) \Bigg]\, \delta\alpha_2 \\
& + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
& + \Bigg[E\frac{\partial \Upsilon_2}{\partial \lambda_2} - \frac{\partial \mathfrak{T}_2}{\partial \lambda_2} + \frac{d}{dt}\frac{\partial \mathfrak{T}_2}{\partial \lambda_2'} \\
& - \left(L_2 - E\frac{\partial \Psi}{\partial \lambda_2} + \Pi\, P_2 + \Pi'\, P_2' + \ldots + \boldsymbol{\mathscr{P}}_2\, p_2 + \ldots \right) \Bigg]\, \delta\lambda_2 \\
& + \left(E\frac{\partial \Upsilon_2}{\partial \alpha_2} + E\frac{\partial \Psi}{\partial \alpha_2} - \boldsymbol{\mathscr{A}}_2 \right) \delta a_2 + \ldots + \left(E\frac{\partial \Upsilon_2}{\partial l_2} + E\frac{\partial \Psi}{\partial l_2} - \boldsymbol{\mathscr{L}}_2 \right) \delta l_2 .
\end{aligned}
$$

In virtue of Equations (14), we have

$$
\begin{aligned}
& \Pi\ \left(M_1\delta\alpha_1 + \ldots + P_1\delta\lambda_1 + M_2\delta\alpha_2 + \ldots + P_2\delta\lambda_2 \right) = 0, \\
& \Pi'\ \left(M_1'\delta\alpha_1 + \ldots + P_1'\delta\lambda_1 + M_2'\delta\alpha_2 + \ldots + P_2'\delta\lambda_2 \right) = 0, \\
& \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots
\end{aligned}
$$

The [259] two preceding equations then straightforwardly yield

$$\begin{aligned}
-E\,(dQ_1 + dQ_2) = {} & \left[E\,\frac{\partial U}{\partial \alpha_1} - \frac{\partial \mathfrak{T}}{\partial \alpha_1} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \alpha_1'} - (A_1 + \mathscr{P}_1\, m_1 + \ldots)\right] \delta\alpha_1 \\
& + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
& + \left[E\,\frac{\partial U}{\partial \lambda_2} - \frac{\partial \mathfrak{T}}{\partial \lambda_2} + \frac{d}{dt}\frac{\partial \mathfrak{T}}{\partial \lambda_2'} - (L_2 + \mathscr{P}_2\, p_2 + \ldots)\right] \delta\lambda_2 \\
& + \left(E\,\frac{\partial U}{\partial a_1} - \mathscr{a}_2\right) \delta a_1 + \ldots + \left(E\,\frac{\partial U}{\partial l_2} - \mathscr{L}_2\right) \delta l_2.
\end{aligned}$$

If dQ designates the quantity of heat released in the change considered by the system comprising the two parts 1 and 2, the right-hand side of the preceding equation represents the quantity $E\,dQ$, and so

$$dQ = dQ_1 + dQ_2.$$

> *If, therefore, a system which can exhibit bilateral connections with neighbouring bodies is formed from parts which can exhibit bilateral connections between one another, then the quantity of heat released by the system in any change is the algebraic sum of the quantities of heat released in the same change by the various parts.*

Bringing this proposition together with the preceding one, we obtain the following:

> *When an isolated system is formed of two parts between which there are bilateral connections, the quantity of heat released by the one part, in a real or virtual change of the system, is equal to the quantity of heat absorbed by the other.*

We have studied (Section 5.3) calorimetric procedures. We have considered three systems S_1, S_2, S_3 that were assumed independent. The preceding propositions allow the theory of calorimetry to be extended to the case where the systems S_1, S_2, S_3 exhibit bilateral connections between one another. This is the case which is, in general, encountered in practice.

From Equations (13), the following consequence is easily deduced:

For a real or virtual change of a system [260] exhibiting bilateral connections with external bodies, let dW be the work of the external actions and the external forces of connection, and $d\tau$ the work of the forces of inertia. We have

$$E\,\delta U + d\tau = dW + dQ.$$

In the case of a real change, this equation becomes

$$E\,\delta U + \delta\mathfrak{T} = dW + dQ.$$

These equations express the principle of the equivalence of heat and work for a system subjected to bilateral connections with neighbouring bodies.

All that we have just said remains true even when the temperature of the system is not uniform. Suppose now that this temperature is uniform. The equations

$$\left\{\begin{array}{l} E\dfrac{\partial U}{\partial \alpha} - \dfrac{\partial \mathfrak{T}}{\partial \alpha} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'} - (A + F_\alpha) = E R_\alpha, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ E\dfrac{\partial U}{\partial \lambda} - \dfrac{\partial \mathfrak{T}}{\partial \lambda} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'} - (L + F_\lambda) = E R_\lambda, \\ E\dfrac{\partial U}{\partial a} - \boldsymbol{\mathcal{A}} = E\mathfrak{R}_a, \ \ldots, \ E\dfrac{\partial U}{\partial l} - \boldsymbol{\mathcal{L}} = E\mathfrak{R}_l \\ \qquad E\dfrac{\partial U}{\partial \vartheta} = E C, \end{array}\right. \tag{13a}$$

which define the calorific coefficients of the system, together with the equations of motion

$$\left\{\begin{array}{l} E\dfrac{\partial \mathcal{F}}{\partial \alpha} - \dfrac{\partial \mathfrak{T}}{\partial \alpha} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha'} - (A + F_\alpha + f_\alpha) = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ E\dfrac{\partial \mathcal{F}}{\partial \lambda} - \dfrac{\partial \mathfrak{T}}{\partial \lambda} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda'} - (L + F_\lambda + f_\lambda) = 0, \\ E\dfrac{\partial \mathcal{F}}{\partial a} - (\boldsymbol{\mathcal{A}} + f_\lambda) = 0, \ldots, E\dfrac{\partial \mathcal{F}}{\partial l} - (\boldsymbol{\mathcal{L}} + f_l) = 0, \end{array}\right. \tag{10b}$$

and the identities

$$\mathcal{F} = E\ [U - F(\vartheta)\ S]$$

$$\frac{\partial U}{\partial \vartheta} = F(\vartheta)\ \frac{\partial S}{\partial \vartheta}\,,$$

[261] yield

$$\left\{\begin{array}{l} E R_\alpha = E F(\vartheta)\ \dfrac{\partial S}{\partial \alpha} + f_\alpha\,, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ E R_\lambda = E F(\vartheta)\ \dfrac{\partial S}{\partial \lambda} + f_\lambda\,, \\ E \mathfrak{R}_a = E F(\vartheta)\ \dfrac{\partial S}{\partial a} + f_a\,, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ E \mathfrak{R}_l = E F(\vartheta)\ \dfrac{\partial S}{\partial l} + f_l\,, \\ E C = E F(\vartheta)\ \dfrac{\partial S}{\partial \vartheta}\,, \end{array}\right. \tag{16}$$

which are equations similar to those obtained for an independent system.

From this it can be deduced that, for any real change,

$$\frac{E\,dQ}{F\,(\vartheta)} = -E\,dS - \frac{f_\alpha\,d\alpha + \ldots + f_l\,dl}{F\,(\vartheta)}. \tag{17}$$

Consider a system formed from n independent parts $1, 2, \ldots, n$ exhibiting bilateral connections between one another. Each of these parts has a uniform temperature, but this temperature is not necessarily the same for all the parts. The system itself can exhibit bilateral connections with neighbouring bodies.

For each of these parts, we write an equation analogous to Equation (17) and add term by term these various equations. If we put

$$S = S_1 + S_2 + \ldots + S_{\mathrm{n}}, \tag{18}$$

we will find

$$E\left[\frac{dQ_1}{F\,(\vartheta_1)} + \frac{dQ_2}{F\,(\vartheta_2)} + \ldots + \frac{dQ_n}{F\,(\vartheta_n)}\right] = -E\,d\boldsymbol{S} - \frac{f_{\alpha_1}\,d\alpha_1 + \ldots + f_{l_1}\,dl_1}{F\,(\vartheta_1)}$$

$$-\frac{f_{\alpha_2}\,d\alpha_2 + \ldots + f_{l_2}\,dl_2}{F\,(\vartheta_2)} - \ldots - \frac{f_{\alpha_n}\,d\alpha_n + \ldots + f_{l_n}\,dl_n}{F\,(\vartheta_n)}.$$

Integrating [262] this equation over a closed cycle, and noting that

$$\begin{gathered}
\int d\boldsymbol{S} = 0 \\
f_{\alpha_1}\,d\alpha_1 + \ldots + f_{l_1}\,dl_1 \leq 0 \\
f_{\alpha_2}\,d\alpha_2 + \ldots + f_{l_2}\,dl_2 \leq 0 \\
\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\
f_{\alpha_n}\,d\alpha_n + \ldots + f_{l_n}\,dl_n \leq 0.
\end{gathered}$$

we will arrive at the inequality

$$\int\left[\frac{dQ_1}{F\,(\vartheta_1)} + \frac{dQ_2}{F\,(\vartheta_2)} + \ldots + \frac{dQ_n}{F\,(\vartheta_n)}\right] \geq 0. \tag{19}$$

This inequality is thus extended to systems formed from parts at different temperatures exhibiting bilateral connections between one another.

Chapter 12
Stability and Displacement of Equilibrium

12.1 On the Total Thermodynamic Potential

The virtual work of the external actions on a system (including, if necessary, the forces of the external connections),

$$A\delta\alpha + B\delta\beta + \ldots + L\delta\lambda + \boldsymbol{\mathcal{A}}\delta a + \boldsymbol{\mathcal{B}}\delta b + \ldots + \boldsymbol{\mathcal{L}}\delta l,$$

is not, in general, the total differential of a uniform function of the normal variables $\alpha, \beta, \ldots, \lambda, a, b, \ldots, l$. However, if it is not so in general, it is in a large number of important particular cases.

When there is a uniform function Ω such that

$$A d\alpha + B d\beta + \ldots + L d\lambda + \boldsymbol{\mathcal{A}} da + \boldsymbol{\mathcal{B}} db + \ldots + \boldsymbol{\mathcal{L}} dl = -d\Omega, \qquad (1)$$

it is said that *the external actions of the system sustain a potential* [263] and this potential is Ω. When it exists, this potential is evidently determined up to a constant.

When the external actions of the system sustain a potential we call the sum

$$\Phi = \mathcal{F} + d\Omega \qquad (2)$$

of the internal thermodynamic potential and the potential of the external actions, the *total thermodynamic potential* of the system.

Here is an important case where the system sustains a total thermodynamic potential:

Suppose the real or imaginary variations of the external bodies to be tied to the real or virtual variations of the system in such a way that the external actions $A, B, \ldots, L, \boldsymbol{\mathcal{A}}, \boldsymbol{\mathcal{B}}, \ldots, \boldsymbol{\mathcal{L}}$ maintain fixed values. It is then possible to write

$$\begin{aligned} & A d\alpha + B d\beta + \ldots + L d\lambda + \boldsymbol{\mathcal{A}} a + \boldsymbol{\mathcal{B}} b + \ldots + \boldsymbol{\mathcal{L}} l \\ & = -d(A\alpha + B\beta + \ldots + L\lambda + \boldsymbol{\mathcal{A}} a + \boldsymbol{\mathcal{B}} b + \ldots + \boldsymbol{\mathcal{L}} l) \end{aligned}$$

and the system sustains the total thermodynamic potential

P. Needham (ed.), *Commentary on the Principles of Thermodynamics by Pierre Duhem*, Boston Studies in the Philosophy of Science 277,
DOI 10.1007/978-94-007-0311-7_12,

$$\Phi = \mathfrak{F} - (A\alpha + B\beta + \ldots + L\lambda + \mathfrak{A}da + \mathfrak{B}db + \ldots + \mathfrak{L}dl). \tag{3}$$

This quantity, which is often considered in applications, is called the *thermodynamic potential under constant actions*.

12.2 Stability of the Equilibrium at Constant Temperature

From now on there will be no point in distinguishing the variables $a, b, \ldots, l$ from the variables $\alpha, \beta, \ldots, \lambda$. We therefore consider a system whose temperature is uniform and which is defined by the normal variables $\alpha, \beta, \ldots, \lambda, \vartheta$. For any real motion of the system, we have (Chapter 10, Equation (11))

$$\begin{aligned} d\mathfrak{F} - \frac{\partial \mathfrak{F}}{\partial \vartheta} d\vartheta &- (Ad\alpha + Bd\beta + \ldots + Ld\lambda) \\ &= -d\mathfrak{T} + \left(f_\alpha\, d\alpha + f_\beta\, d\beta + \ldots + f_\lambda\, d\lambda\right). \end{aligned}$$

If [264] the external actions sustain a potential Ω, this equation, together with Equations (1) and (2), becomes

$$d\Phi - \frac{\partial \mathfrak{F}}{\partial \vartheta} d\vartheta = -d\mathfrak{T} + f_\alpha\, d\alpha + f_\beta\, d\beta + \ldots + f_\lambda\, d\lambda.$$

If the change is isothermal, this equation becomes

$$\Phi = -d\mathfrak{T} + f_\alpha\, d\alpha + f_\beta\, d\beta + \ldots + f_\lambda\, d\lambda. \tag{4}$$

Integrating between the initial state 0 and a final state 1 of the system, it becomes

$$\Phi_0 - \Phi_1 = -\mathfrak{T}_1 - \mathfrak{T}_0 + \int_0^1 \left(f_\alpha\, d\alpha + f_\beta\, d\beta + \ldots + f_\lambda\, d\lambda\right). \tag{4a}$$

It then suffices to note that the quantity

$$\int_0^1 \left(f_\alpha\, d\alpha + f_\beta\, d\beta + \ldots + f_\lambda\, d\lambda\right)$$

can never be positive, and to repeat almost word-for-word the demonstration of Lejeune-Dirichlet[1] that has now become classic, to arrive at the following theorem:

> *A system whose temperature is maintained constant is definitely in stable equilibrium in a state in which the total thermodynamic potential takes on a minimum value amongst all those that it could take at the same temperature.*

---

[1] Lejeune-Dirichlet, *Ueber die Stabilität des Gleichgewichts* (*Journal de Crelle*, vol. 22, p. 85; 1846).

It is not at all certain that there are not states of stable equilibrium of a system other than those corresponding to a minimum of the total thermodynamic potential.

In what follows, when we speak of a system *at equilibrium*, we will understand it to designate, for the sake of brevity, a system [265] whose total thermodynamic potential has a minimum value amongst all those that it can take at the same temperature.

12.3 Displacement of Equilibrium by a Variation of Temperature

A system is at equilibrium at a given temperature ϑ when it is subject to actions $A, B, \ldots, L$. The normal variables $\alpha, \beta, \ldots, \lambda$ which, along with the temperature ϑ, completely determine the system, have, in this state, values given by the equations

$$\frac{\partial \mathcal{F}}{\partial \alpha} = A, \quad \frac{\partial \mathcal{F}}{\partial \beta} = B, \ldots, \frac{\partial \mathcal{F}}{\partial \lambda} = L.$$

.

We assume that the actions $A, B, \ldots, L$ sustain a potential Ω, which will be a function of $\alpha, \beta, \ldots, \lambda$, but not of ϑ (Section 9.5), and in conformity with Equation (1), we put $\Phi = \mathcal{F} + d\Omega$. The preceding equations can be written

$$\frac{\partial \Phi}{\partial \alpha} = 0, \quad \frac{\partial \Phi}{\partial \beta} = 0, \quad \ldots, \quad \frac{\partial \Phi}{\partial \lambda} = 0. \tag{5}$$

Solving for $\alpha, \beta, \ldots, \lambda$, these equations become

$$\alpha = \alpha(\vartheta), \quad \beta = \beta(\vartheta), \quad \ldots, \quad \lambda = \lambda(\vartheta).$$

At the temperature $(\vartheta + d\vartheta)$, under the actions of the same external bodies, a new state of equilibrium will be established in which the normal variables defining the state of the system will have the new values

$$\begin{aligned} \alpha' &= \alpha(\vartheta) + \frac{d\alpha(\vartheta)}{d\vartheta} d\vartheta, \\ \beta' &= \beta(\vartheta) + \frac{d\beta(\vartheta)}{d\vartheta} d\vartheta, \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \lambda' &= \lambda(\vartheta) + \frac{d\lambda(\vartheta)}{d\vartheta} d\vartheta. \end{aligned}$$

Differentiating the equations of equilibrium (5) with respect to ϑ yields [266] the system of equations

$$\left\{\begin{array}{l}\dfrac{\partial^2\Phi}{\partial\alpha\,\partial\vartheta}+\dfrac{\partial^2\Phi}{\partial\alpha^2}\,\dfrac{d\alpha}{d\vartheta}+\dfrac{\partial^2\Phi}{\partial\alpha\,\partial\beta}\,\dfrac{d\beta}{d\vartheta}+\ldots+\dfrac{\partial^2\Phi}{\partial\alpha\,\partial\lambda}\,\dfrac{d\lambda}{d\vartheta}=0,\\ \dfrac{\partial^2\Phi}{\partial\beta\,\partial\vartheta}+\dfrac{\partial^2\Phi}{\partial\beta\,\partial\alpha}\,\dfrac{d\alpha}{d\vartheta}+\dfrac{\partial^2\Phi}{\partial\beta^2}\,\dfrac{d\beta}{d\vartheta}+\ldots+\dfrac{\partial^2\Phi}{\partial\beta\,\partial\lambda}\,\dfrac{d\lambda}{d\vartheta}=0,\\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,\\ \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\vartheta}+\dfrac{\partial^2\Phi}{\partial\lambda\,\partial\alpha}\,\dfrac{d\alpha}{d\vartheta}+\dfrac{\partial^2\Phi}{\partial\lambda\,\partial\beta}\,\dfrac{d\lambda}{d\vartheta}+\ldots+\dfrac{\partial^2\Phi}{\partial\lambda^2}\,\dfrac{d\lambda}{d\vartheta}=0.\end{array}\right. \tag{6}$$

We multiply the two sides of the first of these equations by $d\alpha\big/d\vartheta$, the two sides of the second by $d\beta\big/d\vartheta$, ... , and the two sides of the last by $d\lambda\big/d\vartheta$. Adding the results obtained yields the following equation

$$\left\{\begin{array}{l}\dfrac{\partial^2\Phi}{\partial\alpha\,\partial\vartheta}\,\dfrac{d\alpha}{d\vartheta}+\dfrac{\partial^2\Phi}{\partial\beta\,\partial\vartheta}\,\dfrac{d\beta}{d\vartheta}+\ldots+\dfrac{\partial^2\Phi}{\partial\lambda\,\partial\vartheta}\,\dfrac{d\lambda}{d\vartheta}+\dfrac{\partial^2\Phi}{\partial\alpha^2}\left(\dfrac{d\alpha}{d\vartheta}\right)^2\\ \quad+\dfrac{\partial^2\Phi}{\partial\beta^2}\left(\dfrac{d\beta}{d\vartheta}\right)^2+\ldots+\dfrac{\partial^2\Phi}{\partial\beta^2}\left(\dfrac{\lambda}{d\vartheta}\right)^2+2\sum\dfrac{\partial^2\Phi}{\partial\mu\,\partial\nu}\,\dfrac{d\lambda}{d\vartheta}\,\dfrac{d\mu}{d\vartheta}=0.\end{array}\right. \tag{7}$$

In this equation, the symbol $\sum\dfrac{\partial^2\Phi}{\partial\mu\,\partial\nu}\,\dfrac{d\lambda}{d\vartheta}\,\dfrac{d\mu}{d\vartheta}$ should be attributed the following meaning:

All the values distinct from one another of the quantity $\dfrac{\partial^2\Phi}{\partial\mu\,\partial\nu}\,\dfrac{d\lambda}{d\vartheta}\,\dfrac{d\mu}{d\vartheta}$ that can be obtained by replacing μ and ν by two letters, distinct from one another, taken from the collection $\alpha,\beta,\ldots,\lambda$, are considered and their sum taken.

By hypothesis, the values of $\alpha,\beta,\ldots,\lambda$ defined by Equations (5) give to Φ a minimum value amongst all those which it can take at the temperature ϑ. Consequently, if these values are ascribed to $\alpha,\beta,\ldots,\lambda$, then the quadratic form

$$\frac{\partial^2\Phi}{\partial\alpha^2}\,a^2+\frac{\partial^2\Phi}{\partial\beta^2}\,b^2+\ldots+\frac{\partial^2\Phi}{\partial\lambda^2}\,l^2+2\sum\frac{\partial^2\Phi}{\partial\mu\,\partial\nu}\,mn$$

is [267] positive, whatever the values, different from 0, that are attributed to the quantities $a,b,\ldots,l$.

This will be the case, in particular, if

$$a=\frac{d\alpha}{d\vartheta},\qquad b=\frac{d\beta}{d\vartheta},\ldots,l=\frac{d\lambda}{d\vartheta}$$

Therefore,

$$\frac{\partial^2\Phi}{\partial\alpha^2}\left(\frac{d\alpha}{d\vartheta}\right)^2+\frac{\partial^2\Phi}{\partial\beta^2}\left(\frac{d\beta}{d\vartheta}\right)^2+\ldots+\frac{\partial^2\Phi}{\partial\lambda^2}\left(\frac{\lambda}{d\vartheta}\right)^2+2\sum\frac{\partial^2\Phi}{\partial\mu\,\partial\nu}\,\frac{d\lambda}{d\vartheta}\,\frac{d\mu}{d\vartheta}>0$$

This equation, together with Equation (7), yields the inequality

$$\frac{\partial^2\Phi}{\partial\alpha\,\partial\vartheta}\,\frac{d\alpha}{d\vartheta}+\frac{\partial^2\Phi}{\partial\beta\,\partial\vartheta}\,\frac{d\beta}{d\vartheta}+\ldots+\frac{\partial^2\Phi}{\partial\lambda\,\partial\vartheta}\,\frac{d\lambda}{d\vartheta}<0.$$

We put

$$d\alpha=\frac{d\alpha}{d\vartheta}\,d\vartheta,\qquad d\beta=\frac{d\beta}{d\vartheta}\,d\vartheta,\ldots,d\lambda=\frac{d\lambda}{d\vartheta}\,d\vartheta.$$

The inequality that we have just obtained can be stated in the following way. The quantity

$$\frac{\partial^2\Phi}{\partial\alpha\,\partial\vartheta}\,d\alpha+\frac{\partial^2\Phi}{\partial\beta\,\partial\vartheta}\,d\beta+\ldots+\frac{\partial^2\Phi}{\partial\lambda\,\partial\vartheta}\,d\lambda$$

has the opposite sign to that of $d\vartheta$.

The external actions $A, B, \ldots, L$ equal, except for sign, to the partial derivatives of the function Ω with respect to $\alpha, \beta, \ldots, \lambda$, are independent of the temperature ϑ. It therefore follows that

$$\frac{\partial^2\Omega}{\partial\alpha\,\partial\vartheta}=0,\qquad\frac{\partial^2\Omega}{\partial\beta\,\partial\vartheta}=0,\qquad\ldots,\qquad\frac{\partial^2\Omega}{\partial\lambda\,\partial\vartheta}=0.$$

Consequently, in virtue of Equation (1), the result that we have just obtained can be stated thus:
The quantity

$$\frac{\partial^2\mathcal{F}}{\partial\alpha\,\partial\vartheta}\,d\alpha+\frac{\partial^2\mathcal{F}}{\partial\beta\,\partial\vartheta}\,d\beta+\ldots+\frac{\partial^2\mathcal{F}}{\partial\lambda\,\partial\vartheta}\,d\lambda\tag{8}$$

has the opposite sign to that of $d\vartheta$.

In [268] virtue of Equation (5a) of Chapter 9, the quantity (8) can be written

$$-\,E\,F'(\vartheta)\left(\frac{\partial S}{\partial\alpha}\,d\alpha+\frac{\partial S}{\partial\beta}\,d\beta+\ldots+\frac{\partial S}{\partial\lambda}\,d\lambda\right)$$

In virtue of Equations (3) of the same chapter, this becomes

$$-\,\frac{E\,F'(\vartheta)}{F\,(\vartheta)}\,\big(R_\alpha\,d\alpha+R_\beta\,d\beta+\ldots+R_\lambda\,d\lambda\big)$$

Since the quantity $F'(\vartheta)\big/F\,(\vartheta)$ is certainly positive, the quantity

$$R_\alpha\,d\alpha+R_\beta\,d\beta+\ldots+R_\lambda\,d\lambda$$

clearly has the same sign as $d\vartheta$, which is expressed by the following law:

> *Consider a system subject to actions which sustain a potential. The system is at equilibrium at a given temperature. If this temperature is raised, it establishes an equilibrium different from the first; the normal variables which characterise the state of the system undergo*

certain variations; if they undergo the same variations at constant temperature, the virtual change imposed on the system entails an absorption of heat.

This law, which was glimpsed by Lavoisier and Laplace, was stated by J.-H. van 't Hoff.

12.4 Isothermal Displacement of Equilibrium

A system is subject to the constant actions $A, B, \ldots, L$ and has a temperature ϑ. It adopts a certain stable equilibrium state which renders the thermodynamic potential a minimum under the constant actions $A, B, \ldots, L$. The normal variables $\alpha, \beta, \ldots, \lambda$ have values defined as functions of $A, B, \ldots, L$ by the equations

$$\frac{\partial \mathcal{F}}{\partial \alpha} = A, \quad \frac{\partial \mathcal{F}}{\partial \beta} = B, \quad \ldots, \quad \frac{\partial \mathcal{F}}{\partial \lambda} = L. \tag{9}$$

Letting the temperature have the value ϑ and giving the actions [269] $A, B, \ldots, L$ new values close to the preceding ones, $(A+dA), (B+dB), \ldots, (C+dC)$, the system adopts a new state of equilibrium defined by the values $(\alpha+d\alpha), (\beta+d\beta), \ldots, (\lambda+d\lambda)$ of the normal variables $\alpha, \beta, \ldots, \lambda$, putting for the sake of brevity

$$\begin{aligned}
d\alpha &= \frac{\partial \alpha}{\partial A}\,dA + \frac{\partial \alpha}{\partial B}\,dB + \ldots + \frac{\partial \alpha}{\partial L}\,dL, \\
d\beta &= \frac{\partial \beta}{\partial A}\,dA + \frac{\partial \beta}{\partial B}\,dB + \ldots + \frac{\partial \beta}{\partial L}\,dL, \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\
d\lambda &= \frac{\partial \lambda}{\partial A}\,dA + \frac{\partial \lambda}{\partial B}\,dB + \ldots + \frac{\partial \lambda}{\partial L}\,dL.
\end{aligned}$$

Differentiating Equations (9) gives us

$$\begin{aligned}
&\frac{\partial^2 \mathcal{F}}{\partial \alpha^2}\,d\alpha + \frac{\partial^2 \mathcal{F}}{\partial \alpha\,\partial \beta}\,d\beta + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \alpha\,\partial \lambda}\,d\lambda = dA, \\
&\frac{\partial^2 \mathcal{F}}{\partial \beta\,\partial \alpha}\,d\alpha + \frac{\partial^2 \mathcal{F}}{\partial \beta^2}\,d\beta + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \beta\,\partial \lambda}\,d\lambda = dB, \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\
&\frac{\partial^2 \mathcal{F}}{\partial \lambda\,\partial \alpha}\,d\alpha + \frac{\partial^2 \mathcal{F}}{\partial \lambda\,\partial \beta}\,d\beta + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2}\,d\lambda = dL.
\end{aligned}$$

Multiplying the first of these equations by $d\alpha$, the second by $d\beta$, ... , the last by $d\lambda$, and adding the results obtained, we find

$$\begin{cases} \dfrac{\partial^2 \mathcal{F}}{\partial \alpha^2}(d\alpha)^2 + \dfrac{\partial^2 \mathcal{F}}{\partial \beta^2}(d\beta)^2 + \ldots + \dfrac{\partial^2 \mathcal{F}}{\partial \lambda^2}(d\lambda)^2 + 2\sum \dfrac{\partial^2 \mathcal{F}}{\partial \mu\, \partial \nu}\, d\mu\, d\nu \\ \quad = dA\, d\alpha + dB\, d\beta + \ldots + dL\, d\lambda. \end{cases} \tag{10}$$

We now propose to determine the sign of the left-hand side of Equation (10). Consider the thermodynamic potential under the constant actions $A, B, \ldots, L$.

$$\Phi = \mathcal{F}(\alpha, \beta, \ldots, \lambda, \vartheta) - (A\alpha + B\beta + \ldots + L\lambda). \tag{11}$$

By [270] hypothesis, the values of $\alpha, \beta, \ldots, \lambda$ defined by the Equations (9) lead to a minimum value of this potential taken amongst all those that it can take at the temperature ϑ. Therefore, if $\alpha, \beta, \ldots, \lambda$ are given these values, the quadratic form

$$\frac{\partial^2 \Phi}{\partial \alpha^2} a^2 + \frac{\partial^2 \Phi}{\partial \beta^2} b^2 + \ldots + \frac{\partial^2 \Phi}{\partial \lambda^2} l^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu\, \partial \nu} mn$$

will be positive whatever the non-zero values that are attributed to the quantities $a, b, \ldots, l$. It will be, in particular, if we put

$$a = d\alpha, \qquad b = d\beta, \ldots, l = d\lambda.$$

We will therefore have[2]

$$\frac{\partial^2 \Phi}{\partial \alpha^2}(d\alpha)^2 + \frac{\partial^2 \Phi}{\partial \beta^2}(d\beta)^2 + \ldots + \frac{\partial^2 \Phi}{\partial \lambda^2}(d\lambda)^2 + 2\sum \frac{\partial^2 \Phi}{\partial \mu\, \partial \nu}\, dm\, dn > 0$$

But since the actions $A, B, \ldots, L$ figuring in the expression (11) of Φ are constants, we have

$$\frac{\partial^2 \Phi}{\partial \alpha^2} = \frac{\partial^2 \mathcal{F}}{\partial \alpha^2}, \quad \frac{\partial^2 \Phi}{\partial \beta^2} = \frac{\partial^2 \mathcal{F}}{\partial \beta^2}, \quad \ldots, \quad \frac{\partial^2 \Phi}{\partial \lambda^2} = \frac{\partial^2 \mathcal{F}}{\partial \lambda^2}, \quad \frac{\partial^2 \Phi}{\partial \mu\, \partial \nu} = \frac{\partial^2 \mathcal{F}}{\partial \mu\, \partial \nu}$$

and consequently,

$$\frac{\partial^2 \mathcal{F}}{\partial \alpha^2}(d\alpha)^2 + \frac{\partial^2 \mathcal{F}}{\partial \beta^2}(d\beta)^2 + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2}(d\lambda)^2 + 2\sum \frac{\partial^2 \mathcal{F}}{\partial \mu\, \partial \nu}\, d\mu\, d\nu > 0.$$

Equation (10) therefore leads us to the inequality

$$dA\, d\alpha + dB\, d\beta + \ldots + dL\, d\lambda > 0,$$

which is expressed by the following proposition:

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[2] [In its original form, the following equation has $(da)^2$ instead of $(d\alpha)^2$, $(db)^2$ instead of $(d\beta)^2$, and $(dl)^2$ instead of $(d\lambda)^2$.]

A system is at equilibrium at a given temperature under certain external actions. To these external actions certain infinitesimal perturbational actions are added while the temperature remains the same, the initial equilibrium is disturbed, and a new [271] *state of equilibrium is established. In the passage from the old state of equilibrium to the new, the perturbational actions always effect positive work.*

A special case of this law has been stated by H. Le Chatelier.

12.5 Isentropic Stability of the Equilibrium

A change in which the entropy of the system remains the same is called, following Gibbs, an isentropic change. During such a change the variations $d\alpha, d\beta, \ldots, d\lambda, d\vartheta$ of the normal variables are connected by the relation

$$\frac{dS}{d\alpha}\,d\alpha + \frac{dS}{d\beta}\,d\beta + \ldots + \frac{dS}{d\lambda}\,d\lambda + \frac{dS}{d\vartheta}\,d\vartheta = 0. \tag{12}$$

Isentropic changes are interesting to consider because if the system describing an isentropic change is at equilibrium at each instant under the action of external bodies, the isentropic change that it describes is what we have called a *reversible adiabatic change*. Conversely, a reversible adiabatic change is isentropic.

We consider a system subject to external actions which sustains a potential Ω, and suppose that the system is at equilibrium. We have

$$\frac{\partial(\mathcal{F}+\Omega)}{\partial\alpha} = 0, \quad \frac{\partial(\mathcal{F}+\Omega)}{\partial\beta} = 0, \ \ldots, \ \frac{\partial(\mathcal{F}+\Omega)}{\partial\lambda} = 0.$$

These equalities can be written

$$\left\{\begin{array}{l} E\,\dfrac{\partial U}{\partial\alpha} + E\,F(\vartheta)\,\dfrac{\partial S}{\partial\alpha} + \dfrac{\partial\Omega}{\partial\alpha} = 0, \\ E\,\dfrac{\partial U}{\partial\beta} + E\,F(\vartheta)\,\dfrac{\partial S}{\partial\beta} + \dfrac{\partial\Omega}{\partial\beta} = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ E\,\dfrac{\partial U}{\partial\lambda} + E\,F(\vartheta)\,\dfrac{\partial S}{\partial\lambda} + \dfrac{\partial\Omega}{\partial\lambda} = 0. \end{array}\right. \tag{13}$$

We add [272] the identity

$$\frac{\partial U}{\partial\vartheta} - F(\vartheta)\,\frac{\partial S}{\partial\vartheta} = 0$$

which, since Ω can always be chosen independently of ϑ, can also be written as

$$E\,\frac{\partial U}{\partial\vartheta} - E\,F(\vartheta)\,\frac{\partial S}{\partial\vartheta} + \frac{\partial\Omega}{\partial\alpha} = 0. \tag{13a}$$

Multiplying the two sides of the first Equation of (13) by $d\alpha$, the two sides of the second by $d\beta$, ... , the two sides of the last by $d\lambda$, and the two sides of the Equation (13a) by $d\vartheta$, then $d\alpha, d\beta, \ldots, d\lambda, d\vartheta$ define an isentropic change. Adding the left and right hand sides of the results obtained and taking into account Equation (12) yields

$$d(E\,U + \Omega) = 0. \tag{14}$$

Thus, *all isentropic changes undergone by a system starting in a state of equilibrium conform to Equation* (14). Moreover, this equation simply expresses that the change at issue is adiabatic.

Recall the general equality (Chapter 10, Equation (11))

$$d\mathfrak{F} - \frac{\partial \mathfrak{F}}{\partial \vartheta}\,d\vartheta + d\Omega = -d\mathfrak{T} + f_\alpha\,d\alpha + f_\beta\,d\beta + \ldots + f_\lambda\,d\lambda.$$

It can be written

$$\begin{aligned} &E\left(\frac{\partial U}{\partial \alpha}\,d\alpha + \frac{\partial U}{\partial \beta}\,d\beta + \ldots + \frac{\partial U}{\partial \lambda}\,d\lambda\right) \\ &-E\,F\,(\vartheta)\left(\frac{\partial S}{\partial \alpha}\,d\alpha + \frac{\partial S}{\partial \beta}\,d\beta + \ldots + \frac{\partial S}{\partial \lambda}\,d\lambda\right) + d\Omega \\ &= -d\mathfrak{T} + f_\alpha\,d\alpha + f_\beta\,d\beta + \ldots + f_\lambda\,d\lambda \end{aligned}$$

and the identity

$$\frac{\partial U}{\partial \vartheta} - F\,(\vartheta)\,\frac{\partial S}{\partial \vartheta} = 0$$

allows [273] it to be transformed into

$$d\,(E\,U + \Omega) - E\,F\,(\vartheta)\;dS = -d\mathfrak{T} + f_\alpha\,d\alpha + f_\beta\,d\beta + \ldots + f_\lambda\,d\lambda.$$

For an isentropic change, this equality reduces to

$$d\,(E\,U + \Omega) = -d\mathfrak{T} + f_\alpha\,d\alpha + f_\beta\,d\beta + \ldots + f_\lambda\,d\lambda. \tag{15}$$

Since the quantity

$$f_\alpha\,d\alpha + f_\beta\,d\beta + \ldots + f_\lambda\,d\lambda$$

can never be positive, a demonstration like that of Lejeune-Dirichlet can be constructed from Equations (14) and (15) to obtain the following theorem:

> *The equilibrium of a system is certainly stable for any isentropic changes it may be subject to if the quantity $d(E\,U + \Omega)$ has a minimum value amongst all those that it can take without changing the value of the entropy.*

This theorem has been stated by J.-W. Gibbs. It can be said with him that if the quantity $(\mathfrak{F} + \Omega)$ is the thermodynamic potential at constant temperature, the quantity $(EU + \Omega)$ is the *thermodynamic potential at constant entropy*.

Consider a system at equilibrium. If the equilibrium of this system is stable for all the isothermal changes that can be imposed on it, is it also stable for all isentropic changes? In other words, if it is stable when the system is supposed encompassed by sources of heat which maintain the temperature constant, is it still stable when the system is supposed surrounded by a wall impermeable to heat?

In order to answer this question, it is necessary for us to invoke a fundamental postulate which we will call *Helmholtz's Postulate*, H. von Helmholtz being the only physicist, to our knowledge, who has explicitly stated it.[3] This postulate is the following:

> HELMHOLTZ'S POSTULATE.—*When* [274] *a system is described with normal variables, the calorific capacity of the system is positive.*

This postulate is expressed by the inequality

$$C > 0, \tag{16}$$

which the equalities

$$\begin{aligned} C &= \frac{\partial U}{\partial \vartheta}, \\ C &= F(\vartheta)\, \frac{\partial S}{\partial \vartheta}, \\ C &= \frac{F(\vartheta)\, F''(\vartheta)}{E\left[F'(\vartheta)\right]^2}\, \frac{\partial \mathfrak{F}}{\partial \vartheta} - \frac{F(\vartheta)}{EF'(\vartheta)}\, \frac{\partial^2 \mathfrak{F}}{\partial \vartheta^2} \end{aligned}$$

allow us to rewrite in any of the following three forms

$$\begin{cases} \dfrac{\partial U}{\partial \vartheta} > 0, \\ \dfrac{\partial S}{\partial \vartheta} > 0, \\ \dfrac{F''(\vartheta)}{F'(\vartheta)}\, \dfrac{\partial \mathfrak{F}}{\partial \vartheta} - \dfrac{\partial^2 \mathfrak{F}}{\partial \vartheta^2} > 0. \end{cases} \tag{16a}$$

It should be noted that this postulate may well cease to agree with experiment if the system is not defined by normal variables. Thus, the calorific capacity of water vapour *under the pressure of the saturated vapour* is negative. This remark shows,

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[3] H. von Helmholtz, *Zur Thermodynamik chemischer Vorgänge*. I. (*Sitzungsberichte der Berliner Akademie*, 1st. semester, pp. 12 and 19; 1882).

moreover, that the preceding postulate, however natural it may appear, is neither obvious nor necessary.

Given this postulate, we will show that the isothermal stability of equilibrium entails isentropic stability.

We reserve the symbol d to designate isentropic variations and use the symbol δ to designate isothermal variations. The proposition to be deduced evidently reduces to this: *Knowing that, for a system at equilibrium, it holds that*

$$\delta^2(\mathcal{F}+\Omega) > 0, \tag{17}$$

it [275] *follows that*

$$d^2(EU+\Omega) > 0. \tag{18}$$

The inequality (17) can be written more explicitly as

$$\left\{\begin{aligned} &\frac{\partial^2(\mathcal{F}+\Omega)}{\partial\alpha^2}(\delta\alpha)^2+\dots\\ &\qquad+\frac{\partial^2(\mathcal{F}+\Omega)}{\partial\lambda^2}(\delta\lambda)^2+2\sum\frac{\partial^2(\mathcal{F}+\Omega)}{\partial\mu\,\partial\nu}\delta\mu\,\delta\nu>0\end{aligned}\right. \tag{17a}$$

During an isothermal change, the quantities $\delta\alpha, \delta\beta, \dots, \delta\lambda$ are absolutely arbitrary. The preceding inequality (17a) will therefore still hold if $\delta\alpha, \delta\beta, \dots, \delta\lambda$ are replaced by the variations $d\alpha$, $d\beta$, ..., $d\lambda$ corresponding to an isentropic change. Consequently, we will have, for any isentropic change,

$$\left\{\begin{aligned} &\frac{\partial^2(\mathcal{F}+\Omega)}{\partial\alpha^2}(d\alpha)^2+\dots\\ &\qquad+\frac{\partial^2(\mathcal{F}+\Omega)}{\partial\lambda^2}(d\lambda)^2+2\sum\frac{\partial^2(\mathcal{F}+\Omega)}{\partial\mu\,\partial\nu}d\mu\,d\nu>0.\end{aligned}\right. \tag{19}$$

On the other hand, the identity

$$\frac{dS}{d\alpha}d\alpha+\dots+\frac{dS}{d\lambda}d\lambda+\frac{dS}{d\vartheta}d\vartheta=0, \tag{12}$$

which defines an isentropic change, gives by differentiation

$$\left\{\begin{aligned} &\frac{\partial^2S}{\partial\alpha^2}(d\alpha)^2+\dots+\frac{\partial^2S}{\partial\lambda^2}(d\lambda)^2+2\sum\frac{\partial^2S}{\partial\mu\,\partial\nu}d\mu\,d\nu\\ &+\frac{dS}{d\alpha}d^2\alpha+\dots+\frac{dS}{d\lambda}d^2\lambda\\ &+\left(2\,\frac{\partial^2S}{\partial\alpha\partial\vartheta}d\alpha+\dots+2\,\frac{\partial^2S}{\partial\lambda\partial\vartheta}d\lambda+\frac{\partial^2S}{\partial\vartheta^2}d\vartheta\right)d\vartheta+\frac{\partial S}{\partial\vartheta}d^2\vartheta=0.\end{aligned}\right. \tag{20}$$

Adding left and right sides of the inequality (19) and the equality (20), having first multiplied the latter by $E\,F(\vartheta)$, and taking into account the equation

$$\mathcal{F} + EF(\vartheta)S = EU, \tag{21}$$

yields [276] the inequality

$$\left\{\begin{aligned} &\frac{\partial^2 (E\,U+\Omega)}{\partial\alpha^2}(d\alpha)^2 + \ldots + \frac{\partial^2 (E\,U+\Omega)}{\partial\lambda^2}(d\lambda)^2 \\ &+2\sum \frac{\partial^2 (E\,U+\Omega)}{\partial\mu\,\partial\nu}\,d\mu\,d\nu + E\,F(\vartheta)\left(\frac{dS}{d\alpha}\,d^2\alpha + \ldots + \frac{dS}{d\lambda}\,d^2\lambda\right) \\ &+E\,F(\vartheta)\left(2\,\frac{\partial^2 S}{\partial\alpha\partial\vartheta}\,d\alpha + \ldots + 2\,\frac{\partial^2 S}{\partial\lambda\partial\vartheta}d\lambda + \frac{\partial^2 S}{\partial\vartheta^2}d\vartheta\right)\,d\vartheta \\ &\qquad\qquad\qquad\qquad +E\,F(\vartheta)\,\frac{\partial S}{\partial\vartheta}d^2\vartheta > 0. \end{aligned}\right. \tag{22}$$

But when the system is at equilibrium,

$$\frac{\partial(\mathcal{F}+\Omega)}{\partial\alpha} = 0,\ \ldots,\ \frac{\partial\,(\mathcal{F}+\Omega)}{\partial\lambda} = 0$$

and, consequently,

$$\frac{d(\mathcal{F}+\Omega)}{d\alpha}\,d^2\alpha + \ldots + \frac{d(\mathcal{F}+\Omega)}{d\lambda}\,d^2\lambda = 0$$

which, in virtue of Equation (21), can be written

$$\begin{aligned} &\frac{\partial(E\,U+\Omega)}{\partial\alpha}\,d^2\alpha + \ldots + \frac{\partial(E\,U+\Omega)}{\partial\lambda}\,d^2\lambda \\ &= E\,F(\vartheta)\left(\frac{\partial S}{\partial\alpha}\,d^2\alpha + \ldots + \frac{\partial S}{\partial\lambda}\,d^2\lambda\right). \end{aligned}$$

Given this equation, the inequality (22) becomes

$$\left\{\begin{aligned} &\frac{\partial^2(E\,U+\Omega)}{\partial\alpha^2}(d\alpha)^2 + \ldots + \frac{\partial^2(E\,U+\Omega)}{\partial\lambda^2}(d\lambda)^2 \\ &+2\sum \frac{\partial^2(E\,U+\Omega)}{\partial\mu\,\partial\nu}\,d\mu\,d\nu + \frac{\partial(E\,U+\Omega)}{\partial\alpha}\,d^2\alpha + \ldots + \frac{\partial(E\,U+\Omega)}{\partial\lambda}\,d^2\lambda \\ &+E\,F(\vartheta)\left(2\,\frac{\partial^2 S}{\partial\alpha\partial\vartheta}\,d\alpha + \ldots + 2\,\frac{\partial^2 S}{\partial\lambda\partial\vartheta}d\lambda + \frac{\partial^2 S}{\partial\vartheta^2}d\vartheta\right)\,d\vartheta \\ &\qquad\qquad\qquad\qquad +E\,F(\vartheta)\,\frac{\partial S}{\partial\vartheta}d^2\vartheta > 0\,. \end{aligned}\right. \tag{23}$$

Noting [277] that Ω is independent of ϑ, the identity

$$\frac{\partial U}{\partial \vartheta} = F(\vartheta)\,\frac{\partial S}{\partial \vartheta}$$

can be written.

$$E\,F(\vartheta)\,\frac{\partial S}{\partial \vartheta}\,d\vartheta = \frac{\partial (E\,U+\Omega)}{\partial \vartheta}\,d\vartheta.$$

Differentiating yields

$$\begin{aligned}
&E\,F(\vartheta)\left(\frac{\partial^2 S}{\partial\alpha\partial\vartheta}\,d\alpha + \ldots + \frac{\partial^2 S}{\partial\lambda\partial\vartheta}d\lambda + \frac{\partial^2 S}{\partial\vartheta^2}d\vartheta\right)\,d\vartheta \\
&+E\,F'(\vartheta)\,\frac{\partial S}{\partial\vartheta}\,(d\vartheta)^2 + E\,F\,(\vartheta)\,\,\frac{\partial S}{\partial\vartheta}\,d^2\vartheta = \\
&\left[\frac{\partial^2(E\,U+\Omega)}{\partial\alpha\partial\vartheta}\,d\alpha + \ldots + \frac{\partial^2(E\,U+\Omega)}{\partial\lambda\partial\vartheta}d\lambda + \frac{\partial^2(E\,U+\Omega)}{\partial\vartheta^2}d\vartheta\right] \\
&\qquad d\vartheta + \frac{\partial(E\,U+\Omega)}{\partial\vartheta}\,d^2\vartheta
\end{aligned}$$

Comparing with the inequality (23), this equation allows us to write

$$\left\{\begin{aligned}
&\frac{\partial^2(E\,U+\Omega)}{\partial\alpha^2}\,(d\alpha)^2 + \ldots + \frac{\partial^2(E\,U+\Omega)}{\partial\lambda^2}\,(d\lambda)^2 \\
&+2\sum\frac{\partial^2(E\,U+\Omega)}{\partial\mu\,\partial\nu}\,d\mu\,d\nu \\
&+\left[\frac{\partial^2(E\,U+\Omega)}{\partial\alpha\partial\vartheta}\,d\alpha + \ldots + \frac{\partial^2(E\,U+\Omega)}{\partial\lambda\partial\vartheta}d\lambda + \frac{\partial^2(E\,U+\Omega)}{\partial\vartheta^2}d\vartheta\right]\,d\vartheta \\
&+\frac{\partial(E\,U+\Omega)}{\partial\alpha}\,d^2\alpha + \ldots + \frac{\partial(E\,U+\Omega)}{\partial\lambda}\,d^2\lambda + \frac{\partial(E\,U+\Omega)}{\partial\vartheta}\,d^2\vartheta \\
&+E\,F(\vartheta)\left(\frac{\partial^2 S}{\partial\alpha\partial\vartheta}\,d\alpha + \ldots + \frac{\partial^2 S}{\partial\lambda\partial\vartheta}d\lambda\right)\,d\vartheta \\
&\qquad\qquad\qquad -E\,F'(\vartheta)\,\frac{\partial S}{\partial\vartheta}\,(d\vartheta)^2 > 0.
\end{aligned}\right. \tag{24}$$

The identity

$$\frac{\partial U}{\partial \vartheta} = F(\vartheta)\,\frac{\partial S}{\partial \vartheta},$$

which [278] can be written

$$\frac{\partial(E\,U+\Omega)}{\partial\vartheta}=E\,F(\vartheta)\,\frac{\partial S}{\partial\vartheta}$$

yields the identities

$$\left\{\begin{array}{l}\dfrac{\partial^2\,(E\,U+\Omega)}{\partial\alpha\partial\vartheta}=E\,F\,(\vartheta)\,\dfrac{\partial^2 S}{\partial\alpha\partial\vartheta},\\ \dotfill,\\ \dfrac{\partial^2\,(E\,U+\Omega)}{\partial\lambda\partial\vartheta}=E\,F\,(\vartheta)\,\dfrac{\partial^2 S}{\partial\lambda\partial\vartheta}.\end{array}\right. \tag{25}$$

Given Equations (25), the inequality (24) becomes

$$\begin{aligned}&\frac{\partial^2\,(E\,U+\Omega)}{\partial\alpha^2}\,(d\alpha)^2+\ldots+\frac{\partial^2\,(E\,U+\Omega)}{\partial\lambda^2}\,(d\lambda)^2+\frac{\partial^2\,(E\,U+\Omega)}{\partial\vartheta^2}\,(d\vartheta)^2\\&+2\sum\frac{\partial^2\,(E\,U+\Omega)}{\partial\mu\,\partial\nu}\,d\mu\,d\nu+2\left[\frac{\partial^2\,(E\,U+\Omega)}{\partial\alpha\partial\vartheta}d\alpha+\ldots+\frac{\partial^2\,(E\,U+\Omega)}{\partial\lambda\partial\vartheta}d\lambda\right]d\vartheta\\&+\frac{\partial(E\,U+\Omega)}{\partial\alpha}\,d^2\alpha+\ldots+\frac{\partial(E\,U+\Omega)}{\partial\lambda}\,d^2\lambda+\frac{\partial(E\,U+\Omega)}{\partial\vartheta}\,d^2\vartheta\\&-E\,F'\,(\vartheta)\,\frac{\partial S}{\partial\vartheta}\,(d\vartheta)^2>0\,,\end{aligned}$$

or

$$d^2\ (E\,U+\Omega)-E\,\frac{F'(\vartheta)}{F(\vartheta)}\,C\,(d\vartheta)^2>0.$$

The quantities E, $F(\vartheta)$ and $F'(\vartheta)$ are essentially positive, and according to Helmholtz's postulate, the same holds for C. The preceding inequality therefore requires that we have

$$d^2\ (E\,U+\Omega)>0.$$

This is the inequality (18) that we wished to demonstrate.

12.6 Isentropic Displacement of Equilibrium

Consider a system at stable equilibrium for isothermal changes, under the constant actions $A, B, \ldots, L$. The quantity

$$\Phi=\mathcal{F}(\alpha,\beta,\,\ldots,\lambda,\vartheta)-(A\alpha+B\beta+\ldots+L\lambda),$$

in [279] which the quantities $A, B, \ldots, L$ are independent of the variables $\alpha, \beta, \ldots, \lambda$, has a minimum value amongst those that it can take at the same temperature ϑ. We have, then, in the first place

$$\frac{\partial \mathcal{F}}{\partial \alpha} - A = 0, \quad \ldots, \quad \frac{\partial \mathcal{F}}{\partial \lambda} - L = 0 \tag{26}$$

and in the second place,

$$\frac{\partial^2 \mathcal{F}}{\partial \alpha^2}(\delta\alpha)^2 + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2}(\delta\lambda)^2 + 2\sum \frac{\partial^2 \mathcal{F}}{\partial \mu\, \partial \nu}\,\delta\mu\,\delta\nu > 0 \tag{27}$$

This latter inequality holds whatever the values, not all zero, of $\delta\alpha, \delta\beta, \ldots, \delta\lambda$.

We give the actions $A, B, \ldots, L$ infinitesimal variations dA, dB, $\ldots$, dL while the system exchanges no heat with the outside. The system undergoes an isentropic change and reaches a new equilibrium state. In this state the normal variables which define the system will have the new values

$$\alpha + d\alpha, \quad \beta + d\beta, \ldots, \quad \lambda + d\lambda, \quad \vartheta + d\vartheta.$$

Since the change is isentropic, we must have the identity

$$\frac{dS}{d\alpha}\,d\alpha + \ldots + \frac{dS}{d\lambda}\,d\lambda + \frac{dS}{d\vartheta}\,d\vartheta = 0.$$

which the identity

$$E\, F'(\vartheta)\, S = -\frac{d\mathcal{F}}{d\vartheta}$$

allows us to transform into

$$\frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta}\,d\alpha + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda \partial \vartheta}\,d\lambda + \frac{\partial^2 \mathcal{F}}{\partial \vartheta^2}\,d\vartheta - \frac{F''(\vartheta)}{F'(\vartheta)}\frac{\partial \mathcal{F}}{\partial \vartheta} = 0. \tag{28}$$

On the other hand, Equations (26) yield, by differentiation,

$$\left\{\begin{array}{l}
\dfrac{\partial^2 \mathcal{F}}{\partial \alpha^2}\,d\alpha + \ldots + \dfrac{\partial^2 \mathcal{F}}{\partial \alpha \partial \lambda}\,d\lambda + \dfrac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta}\,d\vartheta = dA, \\
\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\
\dfrac{\partial^2 \mathcal{F}}{\partial \lambda \partial \alpha}\,d\alpha + \ldots + \dfrac{\partial^2 \mathcal{F}}{\partial \lambda^2}\,d\lambda + \dfrac{\partial^2 \mathcal{F}}{\partial \lambda \partial \vartheta}\,d\vartheta = dL.
\end{array}\right. \tag{29}$$

Multiplying [280] the first Equation (29) by $d\alpha$, … , the last by $d\lambda$, and adding the left and right sides of the results obtained, we find

$$\begin{aligned}
&\frac{\partial^2 \mathcal{F}}{\partial \alpha^2}(d\alpha)^2 + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2}(d\lambda)^2 + 2\sum \frac{\partial^2 \mathcal{F}}{\partial \mu\, \partial \nu}\,\delta\mu\,\delta\nu \\
&+ \left(\frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta}\,d\alpha + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda \partial \vartheta}\,d\lambda\right) d\vartheta = dA\,d\alpha + \ldots + dL\,d\lambda\,,
\end{aligned}$$

an equation which the relation (28) transforms into

$$\frac{\partial^2 \mathfrak{F}}{\partial \alpha^2}(d\alpha)^2 + \ldots + \frac{\partial^2 \mathfrak{F}}{\partial \lambda^2}(d\lambda)^2 + 2\sum \frac{\partial^2 \mathfrak{F}}{\partial \mu\, \partial \nu}\,\delta\mu\,\delta\nu$$

$$-\left[\frac{\partial^2 \mathfrak{F}}{\partial \vartheta^2} - \frac{F''(\vartheta)}{F'(\vartheta)}\frac{\partial \mathfrak{F}}{\partial \vartheta}\right](d\vartheta)^2 = dA\,d\alpha + \ldots + dL\,d\lambda\ ,$$

or into

$$\left\{\begin{aligned} & dA\,d\alpha + \ldots + dL\,d\lambda = \\ & \frac{E\,F'(\vartheta)}{F\,(\vartheta)}C\,(\delta\vartheta)^2\frac{\partial^2 \mathfrak{F}}{\partial \alpha^2}(d\alpha)^2 + \ldots + \frac{\partial^2 \mathfrak{F}}{\partial \lambda^2}(d\lambda)^2 + 2\sum \frac{\partial^2 \mathfrak{F}}{\partial \mu\, \partial \nu}\,\delta\mu\,\delta\nu\,. \end{aligned}\right. \tag{30}$$

This inequality (27) holds whatever $\delta\alpha, \delta\beta, \ldots, \delta\lambda$ might be if we put

$$d\alpha = \delta\alpha, \ldots, d\lambda = \delta\lambda.$$

We therefore have

$$\frac{\partial^2 \mathfrak{F}}{\partial \alpha^2}(d\alpha)^2 + \ldots + \frac{\partial^2 \mathfrak{F}}{\partial \lambda^2}(d\lambda)^2 + 2\sum \frac{\partial^2 \mathfrak{F}}{\partial \mu\, \partial \nu}\,\delta\mu\,\delta\nu > 0$$

On the other hand, Helmholtz' postulate gives

$$\frac{E\,F'(\vartheta)}{F(\vartheta)}C\,(\delta\vartheta)^2 > 0$$

We therefore have

$$dA\,d\alpha + \ldots + dL\,d\lambda > 0. \tag{31}$$

This [281] inequality (31) is equivalent to the following theorem:

A system is at equilibrium under certain external actions and can only undergo isentropic changes. If infinitesimal perturbations are added to the external actions, the system achieves a new state of equilibrium, and in the passage from the old equilibrium state to the new, the perturbational actions always perform positive work.

This principle of isentropic displacement from equilibrium is employed in the discussion of certain problems concerning the expansion of vapours.

12.7 Specific Heat Under Constant Actions

Consider a system maintained at equilibrium by constant external actions $A, B, \ldots, L$. It passes from a state defined by the values $\alpha, \beta, \ldots, \lambda, \vartheta$ of the normal variables to a new state defined by the values $(\alpha + D\alpha), (\alpha + D\beta), \ldots, (\lambda + D\lambda)$, $(\vartheta + D\vartheta)$ of the normal variables.

Differentiating the equations of equilibrium

$$\frac{\partial \mathcal{F}}{\partial \alpha} - A = 0, \quad \ldots, \quad \frac{\partial \mathcal{F}}{\partial \lambda} - L = 0$$

yields

$$\left\{ \begin{array}{l} \dfrac{\partial^2 \mathcal{F}}{\partial \alpha^2} D\alpha + \ldots + \dfrac{\partial^2 \mathcal{F}}{\partial \alpha \partial \lambda} D\lambda + \dfrac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta} D\vartheta = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ \dfrac{\partial^2 \mathcal{F}}{\partial \lambda \partial \alpha} D\alpha + \ldots + \dfrac{\partial^2 \mathcal{F}}{\partial \lambda^2} D\lambda + \dfrac{\partial^2 \mathcal{F}}{\partial \lambda \partial \vartheta} D\vartheta = 0. \end{array} \right. \tag{32}$$

These equations give $D\alpha, D\beta, \ldots, D\lambda$ values proportional to $D\vartheta$, the coefficient of proportionality depending on the variables $\alpha, \beta, \ldots, \lambda, \vartheta$.

Consequently, the quantity of heat absorbed in the preceding change,

$$R_\alpha D\alpha + \ldots + R_\lambda D\lambda + C D\vartheta,$$

can be written $\Gamma D\vartheta$, Γ being a function of $\alpha, \beta, \ldots, \lambda, \vartheta$.

Γ [282] is what we will call the *calorific capacity under the constant actions* $A, B, \ldots, L$. It is the calorific capacity relative to the system of non-normal variables[4] $A, B, \ldots, L, \vartheta$.

By definition, we have

$$(\Gamma - C) D\vartheta = R_\alpha D\alpha + \ldots + R_\lambda D\lambda,$$

or (Chapter 9, Equations (7a))

$$(\Gamma - C)\, D\vartheta = -\frac{F(\vartheta)}{E\, F'(\vartheta)} \left(\frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta} D\alpha + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda \partial \vartheta} D\lambda \right) \tag{33}$$

But from Equations (32) it is easy to deduce the equation

$$\frac{\partial^2 \mathcal{F}}{\partial \alpha^2} (D\alpha)^2 + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2} (D\lambda)^2 + 2 \sum \frac{\partial^2 \mathcal{F}}{\partial \mu\, \partial \nu} D\mu\, D\nu$$

$$+ \left(\frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta} D\alpha + \ldots + \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \vartheta} D\lambda \right) D\vartheta = 0\,.$$

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[4] Concerning the system of variables, see our *Mémoire sur les équations générales de la Thermodynamique*, Ch. V (*Annales de l'École Normale*, 3rd. series, vol. VII, 1891).

Comparing this equation with Equation (33) yields

$$\left\{\begin{aligned} &(\Gamma - C)\,(D\vartheta)^2 \quad = \\ &-\frac{F(\vartheta)}{E\,F'(\vartheta)}\left[\frac{\partial^2\mathfrak{F}}{\partial\alpha^2}\,(D\alpha)^2 + \ldots + \frac{\partial^2\mathfrak{F}}{\partial\lambda^2}(D\lambda)^2 + 2\sum\frac{\partial^2\mathfrak{F}}{\partial\mu\,\partial\nu}\,D\mu\,D\nu\right].\end{aligned}\right. \tag{34}$$

It the system is in stable equilibrium when the external actions $A, B, \ldots, L$ are held constant, the quantity

$$\frac{\partial^2\mathfrak{F}}{\partial\alpha^2}\,(\delta\alpha)^2 + \ldots + \frac{\partial^2\mathfrak{F}}{\partial\lambda^2}(\delta\lambda)^2 + 2\sum\frac{\partial^2\mathfrak{F}}{\partial\mu\,\partial\nu}\,\delta\mu\,\delta\nu$$

is, as we have seen in §4, positive whatever $\delta\alpha, \delta\beta, \ldots, \delta\lambda$ may be. Equation (34) therefore gives us the inequality

$$\Gamma - C > 0.$$

Consequently, [283] *if a system is in stable equilibrium when the external actions affecting it are held constant, its calorific capacity is greater when the actions A, B, ..., L are held constant than when the normal variables α, β, ..., λ are held constant.*

Suppose that the variations $D\alpha, D\beta, \ldots, D\lambda$ are imposed on the variables $\alpha, \beta, \ldots, \lambda$ while the temperature ϑ is held constant. It would be necessary to add to the external actions $A, B, \ldots, L$ the perturbing actions $\delta A, \delta B, \ldots, \delta L$. We would have, in accordance with Equation (10),

$$\left\{\begin{aligned} &\delta A\,D\alpha + \ldots + \delta L\,D\lambda = \\ &\quad\frac{\partial^2\mathfrak{F}}{\partial\alpha^2}\,(D\alpha)^2 + \ldots + \frac{\partial^2\mathfrak{F}}{\partial\lambda^2}(D\lambda)^2 + 2\sum\frac{\partial^2\mathfrak{F}}{\partial\mu\,\partial\nu}\,D\mu\,D\nu.\end{aligned}\right. \tag{35}$$

Suppose that the same variations $D\alpha, D\beta, \ldots, D\lambda$ were imposed on the variables $\alpha, \beta, \ldots, \lambda$ by an isentropic change. The temperature will then vary by an amount $d\vartheta$ defined by the equation

$$\frac{\partial S}{\partial\alpha}\,D\alpha + \ldots + \frac{\partial S}{\partial\lambda}\,D\lambda + \frac{\partial S}{\partial\vartheta}\,d\vartheta = 0. \tag{36}$$

In order to accomplish this isentropic transformation, the perturbations *dA, dB, ..., dL* must be added to the external actions and we have, in accordance with Equation (30),

$$\left\{\begin{aligned} dA\,D\alpha + \ldots + dL\,D\lambda = {}& \frac{F(\vartheta)}{E\,F'(\vartheta)}\,C\,(d\vartheta)^2 + \frac{\partial^2\mathfrak{F}}{\partial\alpha^2}\,(D\alpha)^2 \\ &+ \ldots + \frac{\partial^2\mathfrak{F}}{\partial\lambda^2}(D\lambda)^2 + 2\sum\frac{\partial^2\mathfrak{F}}{\partial\mu\,\partial\nu}\,D\mu\,D\nu\,.\end{aligned}\right. \tag{37}$$

Equations (34), (35) and (37) yield

$$\frac{E\,F'(\vartheta)}{F(\vartheta)}\;(\Gamma - C)\;(D\vartheta)^2 = \delta A\,D\alpha + \ldots + \,\delta L\,D\lambda,$$

$$\frac{E\,F'(\vartheta)}{F(\vartheta)}\,C(d\vartheta)^2 = (dA - \delta A)\;D\alpha + \ldots + (dL - \delta L)\;\;D\lambda.$$

From [284] this it can be deduced that

$$\frac{\Gamma - C}{C}\left(\frac{D\vartheta}{d\vartheta}\right)^2 = \frac{\delta A\,D\alpha + \ldots + \,\delta L\,D\lambda}{(dA - \delta A)\;D\alpha + \ldots + (dL - \delta L)\;\;D\lambda} \tag{38}$$

This relation, where $D\vartheta$ satisfies Equations (32) and $d\vartheta$ satisfies Equations (36), is the generalisation of that by which Laplace explained the experiment of Désormes and Clément.

Conclusion

Physicists who have treated thermodynamics have placed this science into two distinct positions vis-à-vis dynamics.

The founders of thermodynamics have nearly all been inclined to make this science an application of dynamics. Regarding heat as a very small and rapid motion of the particles constituting a body, the temperature as the average kinetic energy of this motion, and changes of physical state as changes of characteristic elements of this motion, they have tried to deduce the theorems of thermodynamics from the theorems of rational mechanics. Their efforts were readily crowned with success in the domain of the principle of the conservation of energy. They were less successful when they grappled with Carnot's principle. Despite the bold attempts of Clausius, Boltzmann and H. von Helmholtz, Carnot's principle has not so far been deduced in a completely satisfactory manner from the propositions of dynamics.

Many physicists have sought to render thermodynamics independent of all hypotheses about the nature of heat. They have tried the establish it, not on theorems obtained from rational mechanics, but on principles of its own. Clausius was guided in the edition of his very beautiful Memoirs by the desire to make thermodynamics an independent science. G. Kirchhoff, as witnessed by his recently published *Leçons*, has shown in his teaching that this wish could be realised. G. Lippmann, a student of Kirchhoff, has recommended [285] this approach in France, and today it dominates in the teaching in our Faculties.

We have tried in the present work to suggest a third position of dynamics in relation to thermodynamics. We have made dynamics a particular case of thermodynamics, or rather, we have constituted, under the name thermodynamics, a science which covers in shared principles all the changes of state of bodies, including both changes of position and changes in physical qualities.

The principles of this science are the experimental laws that Sadi Carnot, Mayer, Joule, Clausius, W. Thomson and Helmholtz have established or made clearer. We have put the equations of this science, first outlined by Clausius, and perfected by Massieu, Gibbs and Helmholtz, into an analytic form like that Lagrange gave to mechanics. A continuity of tradition is thus maintained in the course of the evolution of Science which assures progress.

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It seems to us that a general conclusion arises from this study. If the science of motion ceases to be the first of the physical Sciences in logical order, and becomes just a particular case of a more general science including in its formulas all the changes of bodies, the temptation will be less, we think, to reduce all physical phenomena to the study of motion. It will be better understood that change of position in space is not a more simple change than change of temperature or of any other physical quality. It will then be easier to get away from what has hitherto been the most dangerous stumbling block of theoretical physics, the search for a mechanical explanation of the Universe.

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