Continuum Mech. Thermodyn. (2000) 12: 151–184

Tales of Thermodynamics and Obscure Applications of the Second Law

Wolfgang Dreyer[1], **Wolfgang H. Müller**[2] **and Wolf Weiss**[1]

[1] Weierstraß-Institut für Angewandte Analysis und Stochastik, Mohrenstrasse 39, 10117 Berlin, Germany
(e-mail: dreyer@wias-berlin.de,weiss@wias-berlin.de)
[2] Department of Mechanical and Chemical Engineering, Heriot-Watt University, Riccarton Campus, Edinburgh EH14 4AS, UK
(e-mail: W.H.Muller@hw.ac.uk)

Received January 20, 1997

Science is searching
for a perpetuum mobile.
It has found it now:
Science itself is the
perpetuum mobile.

VICTOR HUGO (1802-1885)

1 On the History of Thermodynamics

The fundamental concepts of thermodynamics are temperature, heat, and entropy. However, because these concepts have also long been used in an intuitive way outside of thermodynamics, meanings are frequently attributed to them which lead to involuntary metamorphoses of the original notions.

Before we start a tour de force through the history of these concepts, let us consider the contemporary interpretation.

Today, firmly based on statistical mechanics, everything appears to be totally simple and clear. A macroscopic body, for example a gas, a piece of iron, or a rubber band, consists of microscopic particles that constantly perform a more or less irregular motion. In a gas these micro-particles consist of atoms or molecules that irregularly traverse the space that is at their disposition. Molecules can additionally vibrate and rotate. In iron, the iron atoms are embedded regularly in a crystal lattice but vibrate around their assigned lattice sites with variable amplitudes. And in rubber's long chain structure, isoprene molecules play the role of chain links and perform a macroscopically invisible, irregular motion that constantly leads to new configurations.

The microscopic constituents that take part in the irregular motion are called "particles," irrespective of whether they are gas atoms, gas molecules, or isoprene links. Knowing this we may interpret:

Temperature: a measure of the mean kinetic energy of a particle.

Heat: a synonym for the total energy of the irregular motion, also known as internal energy.

Entropy: a measure for the degree of disorder of the particles.

Dedicated to Ingo Müller on the occasion of his 60th birthday

1.1 Temperature

Als ich vor etwa zehn Jahren in der Geschichte der Wissenschaften der königlichen Gesellschaft zu Paris gelesen hatte, der berühmte Amontons *habe mittels eines von ihm erfundenen Thermometers entdeckt, dass Wasser bei einer bestimmten Temperatur koche, hegte ich sogleich den Wunsch, solch ein Thermometer mir selbst anzufertigen, um diese schöne Naturerscheinung meinen Augen vorzuführen und von der Richtigkeit dieses Versuches mich selbst zu überzeugen.*[1]

D.G. Fahrenheit, Versuche über den Siedepunkt einiger Flüssigkeiten

Before the statistical interpretation was available, temperature was simply a measure for *warm* or *cold*. Exactly where and when *warm* and *cold* were quantified for the first time by means of the concept of temperature is hidden in the darkness of history. As far back as ancient Greece, philosophers attempted to explore the essence of *warm* and *cold*. It is therefore presumed by some that the word *temperature* is derived from the Latin word *temperamentum* (temperament).

C. Galenus

There is, however, yet another tale [1], according to which the notion of temperature originates from the Greek physician Claudius Galenus (130-201). Galenus measured the temperature of diseased gladiators with a scale of eight steps (degrees). This scale was "calibrated" by means of a mixture of boiling water and ice. Thus, according to this version, it is from the Latin word *temperatura* (for blending and mixing) that the notion of temperature emerged.

The temperature of a body is determined by contacting it with a thermometer. A thermometer correlates the temperature of the body to an essentially arbitrary physical phenomenon of the thermometer substance, provided it changes monotonically with the kinetic energy of the particles of the substance. Among other phenomena, this may be the thermal expansion of a gas or a fluid.

Nowadays temperature is measured, at least in physics, according to the absolute Kelvin scale. This scale is identical to the Celsius scale except for its point zero. The Kelvin scale starts at 0 K= -273.15°C. From a microscopic point of view, this is the temperature at which there is no more motion of the micro-particles; phenomenologically, 0 K corresponds to a state where a heat reservoir can gain an arbitrary amount of heat from any other heat reservoir that is at a higher temperature.

A. F. Reaumur

A. Celsius

The construction of modern thermometers dates back to 1724. In that year the instrument maker Daniel Gabriel Fahrenheit (1686-1736) from Danzig attempted to establish a universal standard for temperature measurements. He was followed in this endeavor a few years later by the nobleman René Antoine Ferchault de Reaumur (1683-1757) and finally, in 1742, by the Swedish professor of astronomy Anders Celsius (1701-1744). Of course, working independently, each of them created his own private scale and his own fixed points. During the 16th century at least nineteen scales were known.

Fahrenheit and Celsius chose mercury to be the thermometer substance, while Reaumur preferred spirit of wine. To fix the scale, Fahrenheit used three, Celsius two, and Reaumur a single fixed point [2].

Reaumur defined the degree of freezing water as zero, and reported that if he brings his thermometer in contact with boiling water, the spirit of wine extends its volume from 1000 to 1080 and, consequently, he divided this interval into 80 parts. Clearly, the reproducibility of the Reaumur scale relies on the precise determination of the concentration of the alcohol in the spirit of wine. This was not an easy task during

[1] *Approximately ten years ago, after having read in the History of Sciences of the Royal Society of Paris that the famous* Amontons *had discovered, by means of a self-invented thermometer, that water boils at a certain temperature, I had the desire to fabricate such a thermometer for myself, in order to present this beautiful natural phenomenon to my own eyes and to convince myself of the correctness of this experiment.* D.G. Fahrenheit, Experiments Regarding the Boiling Point of Several Liquids.

Reaumur's days. Apparently for this reason Reaumur hardly trusted his figures of measurement, so that instead of reporting temperature in °R he rather paraphrases it by *a summer temperature pleasant to the Parisians*.

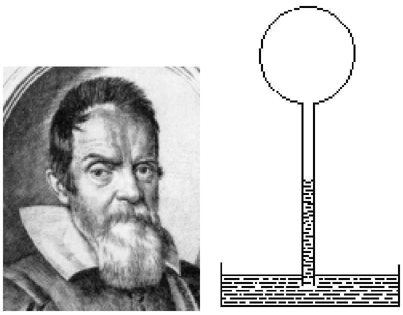
On another occasion he says ([2]):

The degree of heat of the cellars was found to be 10 1/4 degrees above the freezing point of a thermometer, the compressed volume of the water of which, during artificial freezing, was equal to 1000 and, in the boiling heat of the water, expanded to 1080 or, what is the same, the volume reduced by a factor of 1000 during freezing of the water corresponds to 1010 1/4 in the caves of the observatory.

In a nutshell: the specification 10 1/4 °R would have been sufficient. Celsius related his zero point to boiling water, declared the degree of freezing water to be 100, and divided the space in between into 100 parts. A few years later his successor at the observatory in Uppsala revised the scale, so that now the freezing point of water is at 0 °C and the boiling point is at 100 °C.

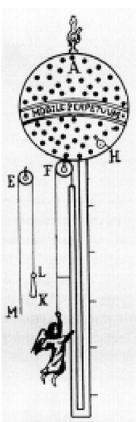

O. Rømer

For what reason, however, did Fahrenheit require three fixed-points? In the year 1724, he mentions [3] that the idea for the construction of his scale originated from a conversation with the Danish astronomer and discoverer of the figure for the speed of light, Ole Rømer. Rømer had informed him of a plan to proceed as follows. Mark two positions which correspond to the heights of a column of mercury which is brought into contact, first, with a mixture of ice and water and, second, with the armpit of a healthy man. In order to determine the zero-point, half of the resulting distance should now be added below the mark characterizing the ice-water mixture. Finally Rømer planned to divide the interval between zero and the body temperature of the healthy man into 22.5 degrees. However, in this respect Fahrenheit did not follow his mentor. Instead he subdivided 1 °Rømer into four parts and, a few years later, he multiplied this by 16/15 to obtain the figures 32 °F and 98 °F for the temperatures of an ice/water mixture and of the body of a healthy man, which are still known today.


G. Galilei and his Thermometer

For obvious reasons we skip the other 16 scales mentioned previously, although these scales were in everyday use during the 16th century, and turn directly to the ancestor of thermometry. This is presumably Galileo Galilei (1564-1642), who in 1592 constructed the thermometer shown opposite. It is left to the reader to explore its mode of operation and to eventually come to the conclusion that it should rather be used as a barometer than a thermometer.

If we ask ourselves which applications of thermometry existed during Galileo's days, medicine and meteorology come immediately to mind. However, there is another less profane application which, until today, has not sufficiently been explored. In other words, the discussion will now, of necessity, become a little speculative.


Flor. Therm.

In 1588 Galileo gave two lectures commissioned by the Florentine Academy regarding the location, shape, and size of hell according to Dante's Divine Comedy [4]. Presumably during the geometrical computations required for this purpose, which were very diligently performed by Galileo, a question regarding the temperature of hell also went through his head. In order to find an answer to this question, an empirically based clue is required — one which is found not in the Divine Comedy but rather in the Book of Books — and for its evaluation, a thermometer is needed. Could this have been the reason why Galileo drew up plans for the construction of a thermometer a few years later?

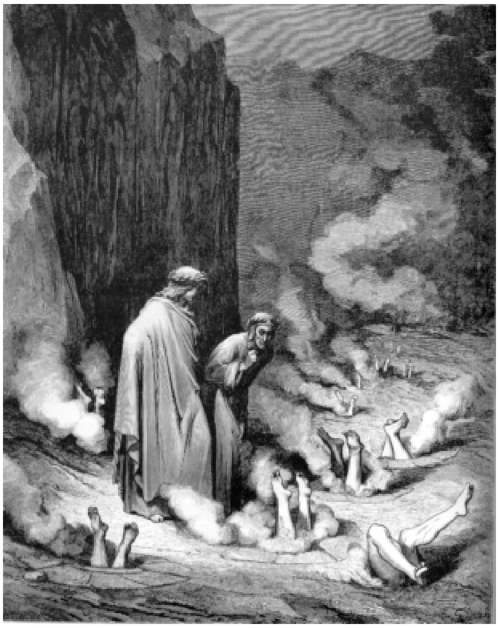
The aforementioned clue to the temperature of hell can be found in the Bible, where we learn in the Revelations of John, Chapter 21, Verse 8 [5, 6]:

But the fearful, and unbelieving, and the abominable, and murderers, and whoremongers, and sorcerers, and idolaters, and all liars, shall have their part in the lake which burneth with fire and brimstone: which is the second death.

Thus, from today's perspective, and on the basis of the work performed by FAHRENHEIT, REAUMUR, and CELSIUS, the problem is solved. The temperature of boiling sulfur turns out to be 444.6 °C and, consequently, the temperature of hell cannot be less than this value.

In GALILEO's days there was an enormous interest not only in the temperature of hell but also in the temperature of heaven. This interest is evidenced by the example of a Florentine thermometer on which an angel indicates the heavenly temperature. And once again, the Bible offers a clue to obtaining an otherworldly temperature [7]. In MARTIN LUTHER's edition we find in Jesaja, Chapter 30, Verse 26 [5]:

Und des Mondes Schein wird sein wie der Sonne Schein, und der Sonne Schein wird siebenmal heller sein denn jetzt, zu der Zeit, wenn der Herr den Schaden seines Volkes verbinden und seine Wunden heilen wird.[2]



DANTE's Hell

DANTE's Heaven

From this we conclude that the radiation density in the heaven of Protestants, e_H^P, is related to the radiation density of the earth, e_E, as follows:

$$e_H^P = (1 + 7)\, e_E\,. \tag{1}$$

If we assume that the STEFAN BOLTZMANN law, $e{\sim}T^4$, is also valid within heavenly spheres, we obtain for the temperature in Protestant heaven:

$$T_H^P = 216\ ^{\mathrm{o}}\mathrm{C}. \tag{2}$$

Therefore it is considerably colder in the heaven of Protestants than in hell. However, it remains to be asked as to whether this is also the case for the heaven of the Roman Catholics. Here the KING JAMES version is appropriate to use, and in Isaiah, Chapter 30, Verse 26 [6] we learn:

Moreover the light of the moon shall be as the light of the sun, and the light of the sun shall be seven fold, as the light of seven days, in the day that the LORD bindeth up the breach of his people, and healeth the stroke of their wound.

[2] *And the light of the moon is as bright as the light of the sun; the light of the sun, however, is sevenfold brighter, in the day that the Lord bindeth up the breach of his people, and healeth the stroke of their wound.*

Thus the radiation density in the Roman Catholic heaven, e_H^{RC}, is related to the radiation density of the earth according to:

$$e_H^{RC} = (1 + 7 \cdot 7)\, e_E\,. \tag{3}$$

As calculated before, we now obtain for the temperature in Roman Catholic heaven:

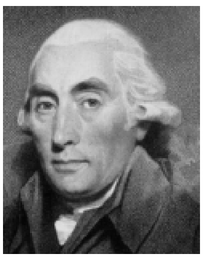
$$T_H^{RC} = 501\ ^{\mathrm{o}}\mathrm{C}, \tag{4}$$

and this is considerably hotter than hell. However, it is unknown to us which temperature is comfortable for an angel.[3]

1.2 Heat and Energy

Das Gebiet der Wissenschaften
ist bereits übergroß genug,
und daher ist eine Erweiterung
desselben keineswegs wünschenswert.[4]

Anonymous mathematician to Julius Robert Mayer.



J. Black

As early as 1760, the Scottish chemist Joseph Black (1728-1799) was concerned with the determination and quantification of amounts of heat. In other words, he tried to answer the question of how much "heat" (in those days, a vague term) is required to raise the temperature of a body a certain number of degrees.

Even though in Black's day a given number of degrees was only a subjective specification of temperature, many qualitative statements could, nevertheless, already be made. For example, Black was astonished by the fact that, despite a continuous heat supply, the temperature of a mixture of ice and water starts to increase only after all the ice has melted.

Black is also the creator of the terms *heat capacity* and *latent heat*, both of which suggest that heat is a substance which, to certain amount, is naturally present within a body. The term heat capacity establishes Black's point of view that bodies possess the capability to store "heat substance." Thus Black's concept supported didactically the theory of heat substance which was already available at his time [8].

This theory is an incorrect precursor of the conservation law of energy. It originated from the desire of several chemists and physicians to systematize various diverse phenomena of chemistry.

G. Stahl

The theory of heat substance was formulated in 1718 by Georg Ernst Stahl (1660-1734), Physician in Ordinary of the King of Prussia Friederich Wilhelm I (and, until 1710, a professor for theoretical medicine at the University of Halle). In essence, the theory of heat substance postulates:

Heat is a massless fluid, which can neither be created nor destroyed. Rather, if the occasion arises, it flows from one place to another.

This idea was originally developed in connection with oxidation and reduction reactions. Stahl believed that sulfurous acid, which results from burning sulfur, *is* sulfur deprived of its combustible principle, namely of the heat substance. The massless heat substance was called *phlogiston* and, later, also *caloric*. This concept is clearly demonstrated by means of a comparison. The following equation describes a simple reaction:

$$2\mathrm{Na} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{Na}_2\mathrm{O}. \tag{5}$$

[3] For example, at a wetness of 0.01 the temperature of the air in a sauna can be 136 °C and, nevertheless, the body temperature will only be 40 °C.

[4] *The field of sciences is already much too large, and therefore its further expansion is by no means desirable.*

M. A. P. & A. L. LAVOISIER

In modern language, this equation describes the combustion of sodium to create sodium oxide. In contrast to this, phlogiston theory interprets this process as follows:

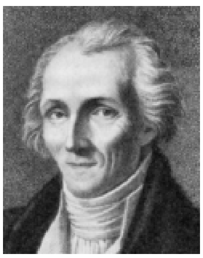
$$\text{multicomponent matter Na} \;\rightarrow\; \text{single matter Na}_2\text{O} \\ \qquad\qquad +\text{escaping phlogiston.} \qquad (6)$$

It was the French chemist and tax-collector ANTOINE LAURENT LAVOISIER (1743-1794) who integrated phlogiston into his system of elements, an equal alongside such substances as sulfur and mercury. By virtue of his authority, the theory of heat substance subsequently became an irrefutable doctrine.

From today's point of view (knowing as we do, for example, that light is a form of *massless* matter), this first part of Lavoisier's doctrine, which assumes that heat is a massless fluid, seems to be a courageous vision.

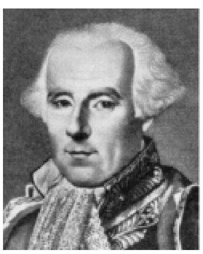
However, his first part is just as wrong as his second, which refers to the capability of bodies to act as reservoirs of heat substance. The fallacy of this supposition was already known to LAVOISIER's contemporary, COUNT RUMFORD (1753-1814), who for a certain while was engaged in manufacturing canons. In 1798, COUNT RUMFORD noticed, during the drilling of canon barrels in a foundry in Munich, that it is possible to withdraw an indefinite amount of heat from the barrel provided only that the drill is blunt enough. Moreover, COUNT RUMFORD already seemed to have a hunch as to what the true nature of heat is, namely:

Heat is a form of disordered motion of the atomic particles, which constitute a body.



COUNT RUMFORD

However, by 1777 (when the role of oxygen during combustion processes was established), even LAVOISIER knew that the phlogiston theory had become untenable. Presumably he became deeply ashamed of his former promotion of phlogiston, and it was for that reason that he and his wife, MARIA ANNA PIERETTE LAVOISIER (1758-1836), brought a farce to the stage wherein they presented a public trial of the caloric theory in which, finally, MADAME LAVOISIER (in the role of a High Priestess) consigned the caloric theory to the flames. It may be, however, that LAVOISIER had the last laugh over his rival. COUNT RUMFORD, who apparently considered this scientific victory over LAVOISIER as insufficient proof of his own superiority, later married LAVOISIER's widow (the great man having been guillotined during the French revolution, due to his second profession as a tax-collector). Ironically, in the end, RUMFORD strongly regretted his marriage.



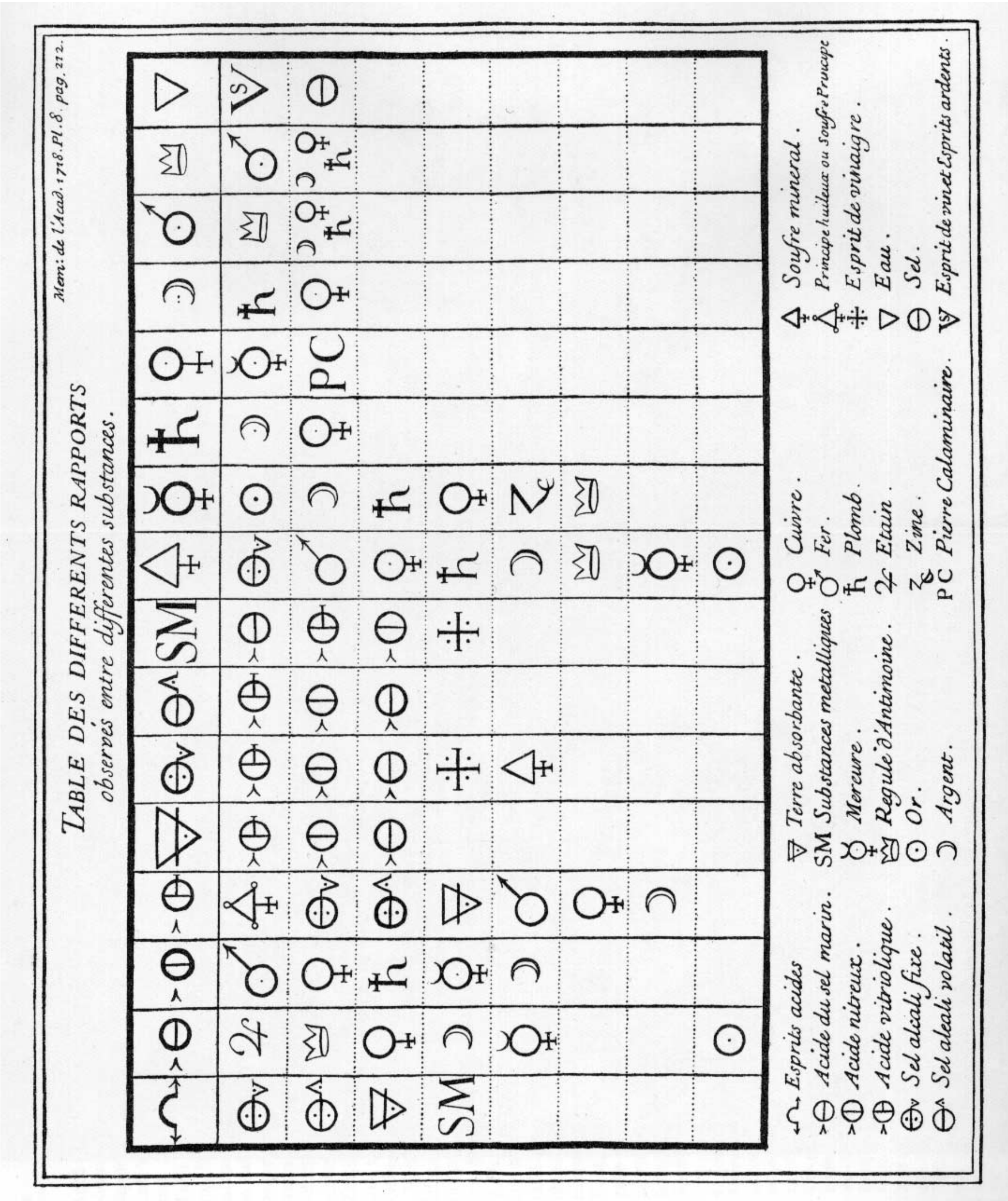
P. S. LAPLACE

J. B. FOURIER

However, the phlogiston theory could not be defeated by a mere *autodafé*. It continued to serve COUNT PIERRE SIMON DE LAPLACE (1749-1827), who used it to derive a formula for the speed of sound [9] which, while based on a flawed theory, nevertheless turned out to be correct. Moreover, JEAN BAPTISTE JOSEPH BARON DE FOURIER (1768-1830) based his theory of heat conduction (which continues to stay technically important until today) on phlogiston [10]. Finally, NICOLAS LEONARD SADI CARNOT (1796-1832) made phlogiston the basis of his famous law on the maximally obtainable work from a heat engine [11]. Thus, despite LAVOISIER's early recanting, it was not until 1842 that the theory of phlogiston started noticeably to decline and finally be superseded by the conservation law of energy.

	Noms nouveaux.	*Noms anciens correſpondans.*
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Lumière..........	Lumière.
	Calorique........	Chaleur.
		Principe de la chaleur.
		Fluide igné.
		Feu.
		Matière du feu & de la chaleur.
	Oxygène..........	Air déphlogiſtiqué.
		Air empiréal.
		Air vital.
		Baſe de l'air vital.
	Azote............	Gaz phlogiſtiqué.
		Mofete.
		Baſe de la mofete.
	Hydrogène........	Gaz inflammable.
		Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre...........	Soufre.
	Phoſphore........	Phoſphore.
	Carbone..........	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique .	Inconnu.
	Radical boracique,.	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine........	Antimoine.
	Argent...........	Argent.
	Arſenic..........	Arſenic.
	Biſmuth..........	Biſmuth.
	Cobolt...........	Cobolt.
	Cuivre...........	Cuivre.
	Etain............	Etain.
	Fer..............	Fer.
	Manganèſe........	Manganèſe.
	Mercure..........	Mercure.
	Molybdène........	Molybdène.
	Nickel...........	Nickel.
	Or...............	Or.
	Platine..........	Platine.
	Plomb............	Plomb.
	Tungſtène........	Tungſtene.
	Zinc.............	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux............	Terre calcaire, chaux.
	Magnéſie.........	Magnéſie, baſe du ſel d'Epſom.
	Baryte...........	Barote, terre peſante.
	Alumine..........	Argile, terre de l'alun, baſe de l'alun.
	Silice...........	Terre ſiliceuſe, terre vitrifiable.

LAVOISIER's Periodic System (1789)



System of Elements (“Table of Relations”) According to Etienne-Francois Geoffry, the Elder from 1718, which Contains the Phlogiston [8]

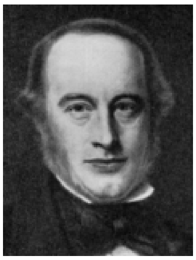
Three men accomplished this deed:

R. J. Mayer

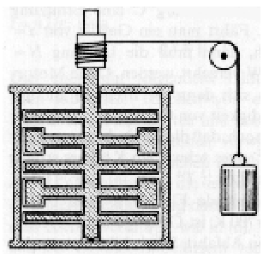
The physician Robert Julius Mayer (1814-1878) from Heilbronn drowned his findings on the conservation law of energy in a verbal ocean of sibylic notions. Nevertheless, he was the first to have distinct insight into the equivalence of all imaginable forms of energy, which includes mechanical energy, energy of heat, chemical energy and, in particular, physiological energy. The following quotations may serve as an illustration of Mayer's style of writing:
Ex nihilo nil fit. Nil fit at nihilum.[5]
Kräfte sind Ursachen. Die Wirkung ist gleich der Ursache. Die Wirkung der Kraft ist wiederum Kraft.[6]

Expressed in Mayer's words, the conservation law of energy reads:
... die Erschaffung oder die Vernichtung einer Kraft liegt außer dem Bereiche menschlichen Denkens und Wirkens.[7]

The correlation between heat and mechanical energy is expressed by the so-called *mechanical heat equivalent*. This quantity determines by how many meters a mass of 1 g can be raised by means of the energy required to increase the temperature of of water by 1°C. Mayer used calorimetry to determine this height to be 367 m [12].



J. P. Joule



Joule's Calorimeter

The degree of accuracy of Mayer's figure for the mechanical heat equivalent was improved by the English private scholar James Prescott Joule (1818-1889). Joule determined, through precise measurements, the amount of heat which results through friction of water in a vessel (shown in the picture) if the water is set into motion by means of a wheel that acts in a manner similar to that of a turbine [13].[8]

Joule recognized the universality of the conservation of energy through a further experimental study on the correspondence between the heat generated by an electric current and the mechanical energy needed for its creation.

Mayer's main results were published in the years 1842 and 1845. Joule ultimately summarized his results in 1847, and in the same year the Prussian military physician Hermann Helmholtz (1821-1894) released a publication entitled *Über die Erhaltung der Kraft* [14].

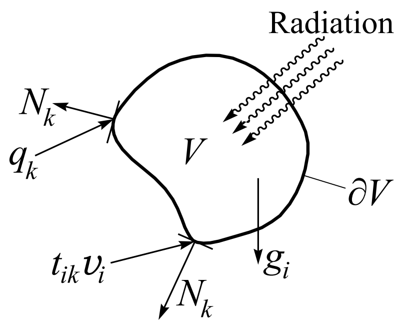
H. v. Helmholtz

In his work, Helmholtz first considers a system of mass points, which interact by central forces, and rederives the previously well-established conservation law of energy of analytical mechanics. Then he considers phenomena for which analytical mechanics provides no energy conservation law, such as the inelastic impact of mass points, and the creation of heat by friction and by an electric current. Acknowledging that in these cases the firm ground of analytical mechanics must be left for the shakier soil of phenomenological argument, Helmholtz then states the universal principle of the conservation of energy.

To illustrate the contemporary version of the energy law, we consider the body shown opposite, which contains the energy, E, in its volume, V, which is enclosed by the surface, ∂V. The law of conservation of energy states:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \text{power of the forces + heat supply} \tag{7}$$

[5] *Nothing is created out of nothing. Nothing created turns into nothing.*
[6] *Forces are causes. The action is equal to the cause. The action of a force is again a force.*
[7] *... the creation and annihilation of force* [energy] *is beyond human thought and capability.*
[8] According to modern measurements, the accurate figure of the equivalent of heat is 4.18 J, by means of which a mass of 1 g can be raised by 455.3 m.



The energy, E, is decomposed into internal energy, U, which refers to the total energy of the disordered motion of the atomic particles of the body, and into the kinetic energy, which is formed by the macroscopic velocity, υ_i, of a mass element, $\varrho \mathrm{d}V$, where ϱ denotes the mass density.

At its surface the body is subjected to surface forces, which are represented by the scalar product of the stress tensor, t_{ik}, and the surface normal, N_k. The body can gain energy by an external force, $\varrho \mathrm{d}V\, g_i$, which directly affects the mass elements within its interior such as, for example, gravitational force. In addition, the body can gain or lose energy by conduction of heat across its surface, which is represented by the scalar product of the heat flux vector, q_k, and the surface normal. Finally, the body may gain or lose energy by radiation, $\varrho \mathrm{d}Vr$. Radiation acts, just as gravity does, directly within the interior of a body. In full, then, the conservation law of energy reads [15]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(U + \int_V \frac{\varrho}{2}\upsilon^2 \mathrm{d}V\right) = \oint_{\partial V} t_{ik}\upsilon_i N_k \mathrm{d}A + \int_V \varrho g_i \upsilon_i \mathrm{d}V - \oint_{\partial V} q_k N_k \mathrm{d}A + \int_V \varrho r \mathrm{d}V\,. \tag{8}$$

If we now neglect the kinetic energy as well as radiation and gravity and, furthermore, assume that the stress tensor at the surface is represented by an overall constant pressure, p, according to $t_{ik} = -p\delta_{ik}$, and if we finally abbreviate the supply of heat by $\dot{Q} = -\oint q_k N_k \mathrm{d}A$, then the conservation law of energy reduces to the simple form:

$$\dot{Q} = \frac{\mathrm{d}U}{\mathrm{d}t} + p\frac{\mathrm{d}V}{\mathrm{d}t}. \tag{9}$$

In this form the conservation law of energy is also called the *First Law of Thermodynamics*.

At this point we want to revisit an aspect of the phlogiston theory, which can most excellently be demonstrated here. If we assume that internal energy and pressure are related in a material-dependent manner to the temperature, T, and to the volume, V, according to $U = \hat{U}(T,V)$ and $p = \hat{p}(T,V)$, we obtain a representation for the First Law the way it was used by all of the 19th century users of phlogiston theory (except for its notation):

$$\dot{Q} = C_V\frac{\mathrm{d}T}{\mathrm{d}t} + \Lambda_V\frac{\mathrm{d}V}{\mathrm{d}t} \quad \text{with} \quad C_V = \frac{\partial U}{\partial T} \quad \text{and} \quad \Lambda_V = \frac{\partial U}{\partial V} + p. \tag{10}$$

C_V and Λ_V represent *heat capacity* and *latent heat*, respectively. Phlogiston theory also assumed [16] that there exists a function $H_V(T,V)$, so that:

$$C_V = \frac{\partial H_V}{\partial T} \quad , \quad \Lambda_V = \frac{\partial H_V}{\partial V} \quad \text{and therefore} \quad \dot{Q} = \frac{\mathrm{d}H_V}{\mathrm{d}t}. \tag{11}$$

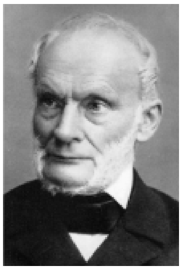
Accordingly, the First Law would become a conservation law for the phlogiston substance, the amount of which is described by the function $H_V(T,V)$. However, calorimetric measurements show that this is erroneous.

1.3 Entropy

In den Kreis der Symbole des Niederganges
gehört nun vor allem die Entropie,
bekanntlich das Thema des zweiten Hauptsatzes
der Thermodynamik.

O. SPENGLER, Der Untergang des Abendlandes[9]

S. CARNOT



R. CLAUSIUS

In 1865, the concept of entropy was introduced quite unspectacularly by the academic RUDOLF JULIUS EMMANUEL CLAUSIUS (1822-1888) as an auxiliary quantity to assess the efficiency of heat engines. This fact, however, represents already the final point of the development of the classical form of the Second Law of Thermodynamics, a development that had been set into motion many years before, in 1824, by the paper *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* [11]. The author of this seminal work was NICOLAS LEONARD SADI CARNOT (1796-1832), a former officer of the Grand Armée who, after retirement from the army, led the life of a private scholar.

Through theoretical study of steam engines, which were increasingly coming into use in those days, CARNOT recognized their insufficient use of the supplied heat. He says:

Malgré les travaux de tous genres entrepris sur les machines à feu, malgré l'état satisfaisant ou elles sont aujourd'hui parvenues, leur théorie est fort peu avancée, et les essais d'amélioration tentes sur elles sont encore diriges presque au hasard.[10]

Further on, he continues:

Pour envisager dans toute sa généralité le principe de la production du mouvement par la chaleur, il faut le concevoir indépendamment d'aucun mécanisme, d'aucun agent particulier; il faut établir des raisonnements applicables, non seulement aux machines à vapeur, mais à toute machine à feu imaginable, quelle que soit la substance mise en oeuvre et quelle que soit la manière dont on agisse sur elle.[11]

CARNOT begins these reflections with the important conclusion:

... il ne suffit pas, pour donner naissance à la puissance motrice, de produire de la chaleur: il faut encore se procurer du froid; sans lui la chaleur serait inutile.[12]

Starting from this important thought, CARNOT considered a warm body at a temperature T_+ and a cold body at a temperature T_-. As an orthodox believer in phlogiston theory, CARNOT naturally assumed that the amount of heat, Q_+, which leaves the warm body, enters the cold body as Q_-, and accomplishes work during its "fall" from warm to cold, without being consumed by itself. He says:

La production de la puissance motrice est donc due, dans les machines à vapeur, non à une consommation réelle du calorique, mais à son transport d'un corps chaud a un corps froid.[13]

This is a consequence of the equation for the conservation of phlogiston $(11)_3$, which implies that, in a cyclic process:

$$Q_+ + Q_- = 0. \tag{12}$$

[9] *Among the symbols of decline there is, in particular, the entropy which is notably the subject of the Second Law of Thermodynamics.* O. SPENGLER, The Decline of the West.

[10] *Despite all of the work undertaken on heat engines, and despite the satisfying state which they have reached up to today, their theory is much less advanced and the attempts for their improvement are still almost driven by pure accident.*

[11] *In order to envisage the principle of the production of motion from heat in its full generality, it is necessary to conceive it independently of any mechanism and any particular agent; it is necessary to establish a way of thinking that does not only apply to steam engines but to all heat engines imaginable, independent of the substance used to perform work and independent of the way one acts on it.*

[12] *... in order to give birth to the motive force, it does not suffice to produce heat: it is also necessary to provide coldness, without which heat would be useless.*

[13] *The creation of motive power in steam engines is thus not due to a real consumption of the heat substance, but by its transport from a warm to a cold body.*

Although this equation is wrong, CARNOT notes correctly:

La puissance motrice de la chaleur est indépendante des agents mis en uvre pour la réaliser; sa quantité est fixée uniquement par les températures des corps entre lesquels se fait en dernier résultat le transport du calorique.[14]

On another occasion he wrote that

... le maximum de puissance motrice résultant de l'emploi de la vapeur est aussi le maximum de puissance motrice réalisable par quelque moyen que ce soit.[15]

This holds under the condition

... qu'il ne se fasse dans les corps employés a réaliser la puissance motrice de la chaleur aucun changement de température qui ne soit du à un changement de volume.[16]

Here CARNOT was referring to a special cyclic process (today called the CARNOT process) that is performed such that the heat of the fire, Q_+, is supplied isothermally, at a temperature T_+, to the working medium, i.e., the steam, and is also removed isothermally, at a temperature T_-, in the condenser. In this case, the utilization of the supplied heat is maximum and independent of the properties of the working medium. In modern notation this means:

$$A_{\circlearrowleft} = f\left(T_+, T_-\right) Q_+, \quad \text{where} \quad f \quad \text{is a universal function.} \tag{13}$$

No other process that operates between T_+ and T_- produces more work, $A_{\circlearrowleft}$, than a CARNOT process would provide.

Many years after CARNOT's pioneering work, RUDOLF CLAUSIUS took up these thoughts. In 1850, he replaced the phlogiston formula $Q_+ + Q_- = 0$ with his own:

$$Q_+ + Q_- + A_{\circlearrowleft} = 0. \tag{14}$$

Moreover, CLAUSIUS was looking for a simple phenomenon on which the maximum property of a CARNOT process and the statement (13) could be based. He discovered it in the natural law [17], that

Wärme ... überall das Bestreben zeigt, vorkommende Temperaturdifferenzen auszugleichen und also aus den wärmeren Körpern in die kälteren überzugehen.[17]

Four years later, CLAUSIUS demonstrated that, in CARNOT processes, $Q_+ + Q_- = 0$ does not hold but that:

$$\frac{Q_+}{T_+} + \frac{Q_-}{T_-} = 0 \tag{15}$$

does [18]. CLAUSIUS pondered anew the fundamental principle, which he then rephrased as follows:

Die Wärme kann nicht von selbst aus einem kälteren in einen wärmeren Körper fließen.[18]

However, CLAUSIUS deemed the term "by itself" to be imprecise, and he considered that an explanation was necessary:

Die hierin vorkommenden Worte „von selbst", welche der Kürze wegen angewandt sind, bedürfen, um vollkommen verständlich zu sein, noch einer Erläuterung, welche ich in meinen Abhandlungen an verschiedenen Orten gegeben habe. Zunächst soll darin ausgedrückt sein, dass durch Leitung und Strahlung die Wärme sich nie in dem wärmeren Körper auf Kosten des kälteren noch mehr anhäufen kann. ... Ferner soll der Satz sich auch auf solche Prozesse beziehen, die aus meheren verschiedenen Vorgängen zusammengesetzt sind, wie z.B. Kreisprocesse. ... Durch einen solchen Process kann allerdings (...) *Wärme aus einem kälteren in einen*

---

[14] *The motive power of heat is independent of the agent that is used for its realization, and its amount is exclusively determined by the temperatures of the bodies between which the transfer of the heat substance takes finally place.*

[15] *... the maximum motive power that results from the application of steam is the same as the maximum motive power that results from any other means.*

[16] *... that the bodies that serve to realize motive power from heat do not suffer a change of temperature that is not due to a change of their volumes.*

[17] *... everywhere, heat ... has the tendency to compensate existing temperature differences and thus flows from the warmer bodies to the colder ones.*

[18] *Heat cannot flow by itself from a colder body into a warmer body.*

wärmeren Körper übertragen werden; unser Satz soll aber ausdrücken, dass dann gleichzeitig mit diesem Wärmeübergange aus dem kälteren in den wärmeren Körper entweder ein entgegengesetzter Wärmeübergang aus einem wärmeren in einen kälteren Körper stattfinden oder irgend eine sonstige Veränderung eintreten muss, welche die Eigenthümlichkeit hat, dass sie nicht rückgängig gemacht werden kann, ohne ihrerseits, sei es unmittelbar oder mittelbar, einen solchen entgegengesetzten Wärmeübergang zu veranlassen. Dieser gleichzeitig stattfindende entgegengesetzte Wärmeübergang oder die sonstige Veränderung, welche einen entgegengesetzten Wärmeübergang zur Folge hat, ist dann als **Compensation** *jenes Wärmeüberganges von dem kälteren zum wärmeren Körper zu betrachten, und unter Anwendung dieses Begriffes kann man die Worte „***von selbst***“ durch die Worte „„***ohne Compensation***“ ersetzen. ...*[19]

After this remarkable effort of clarification, it took eleven more years before CLAUSIUS found — by the introduction of the concept of *entropy* — a satisfying mathematical form for his principle, which by that time already existed in three different representations.

CLAUSIUS considered the case of heat reservoirs, which exchange heat with a system and, in so doing, perform mechanical work [20]. If we apply his thoughts to the body in the figure for the law of energy, and if we, like CLAUSIUS, additionally neglect radiation, his result can be transferred as follows: a new quantity, S, which CLAUSIUS calls *entropy*, is attributed to the body. If the body has the same (absolute) temperature, T, across its surface, then CLAUSIUS’ law reads in modern mathematical notation:

$$\frac{\mathrm{d}S}{\mathrm{d}t} \geqq \frac{\dot{Q}}{T}. \tag{16}$$

If the process that leads to a change in entropy can be reversed, i.e., is *reversible*, then the equality sign holds in this equation. Otherwise the process is *irreversible* and the change in entropy is greater as expressed by the right hand side of the inequality. This is the original form of the *Second Law of Thermodynamics*.

When radiation is also considered, the inequality above must be modified. The explicit form of the radiation term can be derived in different ways [20] and leads finally to:

$$\frac{\mathrm{d}S}{\mathrm{d}t} \geqq \frac{\dot{Q}}{T} + \int\limits_V \frac{\varrho r}{T} \mathrm{d}V. \tag{17}$$

If the body is adiabatically sealed, i.e., it can neither by conduction nor by radiation take in or provide heat, the Second Law implies the statement:

The entropy of an adiabatic body cannot decrease.

In particular, CLAUSIUS concludes [20]:

1. *Die Energie der Welt ist konstant.*
2. *Die Entropie der Welt strebt einem Maximum zu.*[21]

Thus, Clausius had recognized that the Second Law is not only significant for heat engine designers, but that beyond this it makes a tremendous statement regarding the temporal development of things within the largest adiabatic body we know, the universe [20]:

Der Wärmetod des Universums ist unausweichlich![22]

[19] *The words “by itself,” occurring in here, which are used for shortness, still require, in order to be perfectly understandable, an explanation, which I have given in my treatises at various places. First, they are supposed to express that, by conduction and radiation, heat can never accumulate in the warmer body at the expense of the colder one. ... Moreover, the statement shall also refer to such processes as are composed of several different processes, such as, for example, cyclic processes. ... Indeed, by such a process (...) heat can be transferred from a colder into a warmer body; but our statement is supposed to express that then, simultaneously with this heat transfer from the colder into the warmer body, either an opposite heat transfer from a warmer into a colder body must occur, or any other change must take place, the peculiarity of which is that it cannot be reversed without giving rise, directly or indirectly, to another such opposite heat transfer. This simultaneously occurring opposite heat transfer, or the other change, which results in such an opposite heat transfer, is then to be considered as a* **compensation** *of that heat transfer from the colder to the warmer body, and by application of this terminology one may replace the words “***by itself***” with the words “***without compensation***.” ...*

[20] In 1978, I. Müller presented a very elegant method for the derivation of the radiation term [19].

[21] *1. The energy of the world is constant. 2. The entropy of the world approaches a maximum.*

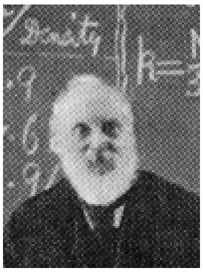
[22] *The heat death of the universe is inevitable!*

O. Spengler

Obviously this statement is extremely frightening to people who believe in progress and, naturally, proved itself to be explosively controversial. An outcry was heard from the philosophers and Sunday pundits alike and, for a period of time, the Second Law was torn from the hands of engineers and scientists to be disputed instead in coaches, clubs, and drawing rooms throughout the cultured world. The originally simple statement on the direction of the flow of heat was recast into new forms over and over and, finally, reads in the words of Oswald Spengler (1880-1936) [21, 22]:

Das Weltende als Vollendung einer innerlich notwendigen Entwicklung — das ist die Götterdämmerung; das bedeutet also, als letzte, als irreligiöse Fassung des Mythos, die Lehre von der Entropie.[23]

However, even among scientists the Second Law and its implications were not uncontroversial, and new formulations arose there as well, although these are less difficult to comprehend than Spengler's version.



Lord Kelvin

As early as 1851 the Scottish physicist Lord Kelvin of Largs (1824-1907), when he still carried the ordinary name William Thomson, wrote [23]:

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

Thomson also provides for the first time a formula for the universal efficiency, e_C, of a Carnot process that operates between the upper and lower temperature levels, T_+ and T_-, respectively:

$$e_C = 1 - \frac{T_-}{T_+}. \tag{18}$$

A consequence of Thomson's axiom is:

$$e < e_C, \tag{19}$$

for the efficiencies, e, of all processes that operate between T_- and T_+, and that are not Carnot processes. To further explain this result, Thomson states [23]:

If this axiom be denied for all temperatures, it would have to be admitted that a self-acting machine might be set to work and produce mechanical effect by cooling the sea or earth, with no limit but the total loss of heat from the earth and sea, or, in reality, from the whole material world.

This would then be a *Perpetuum Mobile* of the Second Kind.

C. Caratheodory M. Planck

For Max Born (1882-1970), an icon of the famous Göttingen physics group, the aforementioned contraptions were not aesthetically pleasing enough, and so he inspired the mathematician Constantin Caratheodory (1873-1950) to approach the problem without any reference to heat engines. As a result, Caratheodory replaced Lord Kelvin's axiom by the following [24]:

In jeder beliebigen Umgebung eines willkürlich vorgeschriebenen Anfangszustandes gibt es Zustände, die durch adiabatische Zustandsänderungen nicht beliebig approximiert werden können.[24]

Max Planck (1858-1947), the German physicist and discoverer of the quantum mechanics constant that carries his name, made the criticism that, in comparison to the Clausius/Kelvin principles, the experimental validation of Caratheodory's axiom is much more difficult to realize. In this context, Planck offers his version of the Second Law [25]:

[23] *The end of the world as the completion of an intrinsically necessary development — this is the twilight of the gods; which therefore means, as the final, as the irreligious form of the mythos, the lore of the entropy.*

[24] *In every arbitrary neighborhood of an arbitrarily prescribed initial state, there are states that cannot be arbitrarily approximated by adiabatic processes.*

Die Wärmeerzeugung durch Reibung ist irreversibel [25]

We realize that the number of possible alternatives to CLAUSIUS' principle is probably almost identical to the number of scientists interested in it. What is important to note is that, of the five alternatives mentioned, all five always lead to the inequality represented in (16), although, to be sure, CARATHEODORY's principle is restricted to adiabatic bodies [24]. By focusing on CLAUSIUS' formulation of the Second Law and by listing possible alternative versions, we have slightly confused the chronology of events. Note that, while CLAUSIUS' principle originates from the year 1850, the concept of entropy and, consequently, (16) were not introduced by him until 1865. LORD KELVIN's axiom, on the other hand, was already formulated in 1851. CARATHEODORY's work was published a significant time later, in 1909, and PLANCK's critique, including his alternative version, does not find print until 1926. Finally, it should also be noted that by 1822 the concept of the heat death of the universe was already implicitly contained in FOURIER's famous differential equation regarding the development of temperature in space and time [10].

J. C. MAXWELL

L. BOLTZMANN

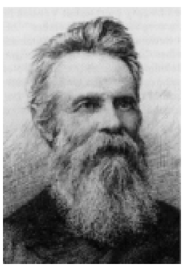
Now we move to the years 1871 and 1872, when JAMES CLERK MAXWELL (1831-1879), who lived as a private scholar on the manor of his old Scottish family, and LUDWIG BOLTZMANN (1844-1906), the professor of mathematical physics, published their pioneering papers on the molecular constitution of bodies and on the statistical interpretation of temperature, energy, and entropy [26, 27]. Both scholars had realized that the macro-state of a body which, for example, is given by temperature and energy, has many realizations from the perspective of its atomic constituents.

For gases, LUDWIG BOLTZMANN proved the H-theorem, which, among other things, predicts the increase of entropy. BOLTZMANN based his proof on a statis- tical interpretation of entropy [27], according to which this quantity is a measure for the degree of disorder of the atomic constituents of a body. In mathematical terms we write:

$$S = k_B \ln W . \tag{20}$$

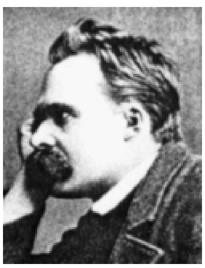
$k_B = 1.38062 \cdot 10^{-23}$ JK^{-1} is a universal constant, the BOLTZMANN constant, and W denotes the number of possible microscopic realizations of a given macro-state. In this form, (20) is due to PLANCK and, in spite of that, formed BOLTZMANN's epitaph.

By means of the H-theorem, it had been proven anew that the heat death of the universe is inevitable and, as a consequence, the discussions and speculations, which were still ongoing, were rekindled. In addition BOLTZMANN, by the way he presented his proof, created a new battlefield. Now it was the mechanics scientists and the mathematicians who engaged in fierce fights with BOLTZMANN, since due to his statistical interpretation, the determinism of the mechanically based laws of nature was endangered.



J. LOSCHMIDT

H. POINCARE



F. NIETZSCHE

For his part, MAXWELL, in order to outwit the principle according to which *heat cannot flow by itself from a colder body into a warmer body*, established a creature with such extraordinary abilities that, soon after its birth, it was called MAXWELL's demon. JOSEPH LOSCHMIDT (1821-1895) formulated the *Umkehreinwand* [26] and HENRI POINCARÉ (1854-1912) the *Wiederkehreinwand* [27], and, before that, even FRIEDRICH NIETZSCHE (1844-1900) became engaged in the debate [50, 28, 29].

[25] *The creation of heat by friction is irreversible.*
[26] *The reversibility objection.*
[27] *The recurrence objection.*

The *Umkehreinwand* states that the molecular processes are reversible. In other words: they are symmetric in time. As a result, there can be no growth of entropy since this would lead to an asymmetry in time.

The *Wiederkehreinwand* states that once a mechanical system is started it will return in due course of time infinitely often to the immediate neighborhood of its initial state. The conclusion is that this contradicts the Second Law, which enforces the approach of a closed system into an equilibrium state with a maximum of disorder.

NIETZSCHE had already effectively expressed the point of POINCARE's *Wiederkehreinwand* in the intuitive words of a philosopher: *Kann der Mechanismus der Consequenz eines Finalzustandes nicht entgehen, so ist damit der Mechanismus widerlegt.*[28] Moreover, he argued:

Wenn die Welt als bestimmte Größe von Kraft und als bestimmte Zahl von Kraftcentren gedacht werden darf — und jede andere Vorstellung bleibt unbestimmt und folglich unbrauchbar — so folgt daraus, daß sie eine berechenbare Zahl von Combinationen im großen Würfelspiel ihres Daseins durchzumachen hat. In einer unendlichen Zeit würde jede Combination irgendwann einmal erreicht sein; mehr noch, sie würde unendliche Male erreicht sein. ... [29]

Both of these objections were refuted by BOLTZMANN [30]. Regarding the *Umkehreinwand*, he retorts [31]:

Ja es ist klar, dass jede einzelne gleichförmige Zustandsvertheilung, welche bei einem bestimmten Anfangszustande nach Verlauf einer bestimmten Zeit entsteht, gerade so unwahrscheinlich ist wie eine einzelne noch so ungleichförmige Zustandsvertheilung, ... Nur daher, dass es viel mehr gleichförmige als ungleichförmige Zustandsvertheilungen gibt, stammt die grössere Wahrscheinlichkeit, dass die Zustandsvertheilung mit der Zeit gleichförmig wird.[30]

For the *Wiederkehreinwand*, explicit calculations can be carried out that show that there is indeed a recurrence. However, even a simple system that consists of only one hundred atoms requires more than 10^{10} more time for its recurrence than our universe had time to exist. We will return to this topic later. Therefore, within the framework of a description of nature, the *Wiederkehreinwand* should be considered refuted. Most likely it was viewed that way by the majority of scientists. Initially, however, it was not seen as such by MAX PLANCK who, at this time, struggled fiercely with himself as to whether he should keep or abandon the axiomatic thermodynamic interpretation of the Second Law, which had become so dear to him [32].

E. ZERMELO

Until approximately 1900, PLANCK rejected vigorously the statistical interpretation of the Second Law and, through his assistant ERNST ZERMELO (1871-1951), ordered a "deputy war" to be fought against BOLTZMANN on its behalf [32]-[36].

However, by the turn of the century, conflicts over these issues were growing fewer, not only because the involved parties had arrived at a consensus (PLANCK needed BOLTZMANN's interpretation of entropy for the derivation of his famous radiation law), but also because of natural loss of the disputants. The designers of heat engines could finally make use of entropy again without being distracted. Also a new species had appeared, ringing in the next epoch of the Second Law: the *materials scientists*.

These scientists recognized that the Second Law was capable of making very concrete statements regarding the behavior of wildly different materials. It explains, for example, why rubber contracts during heating whereas iron expands. Also the Second Law dictates how processes that on first glance have nothing to do with the propagation of heat must run. For instance, osmosis (i.e., the capability of water to ascend in plants against the force of gravity) is a consequence of the Second Law [37].

Materials scientists also recognized the Second Law could address another class of problems they routinely faced. Sometimes, in order to describe a material, a materials scientist develops a system of differential

[28] *If the mechanism cannot escape the consequence of a final state, then the mechanism is refuted.*

[29] *If the world may be thought to consist of a certain amount of force and a certain number of force centers — and any other conception remains vague and, consequently, useless — it follows that it must live through a computable number of combinations during the grand game of dice of its existence. Within an infinite time any combination would be encountered sometime; even more, it would be encountered infinitely many times. ...*

[30] *Yes, it is clear that any single uniform distribution of state that, for a certain initial state, results after a certain time has elapsed is just as unlikely as a single distribution of state, as non-uniform as it may want to be, ... Only because there are many more uniform than non-uniform distributions of state, the greater probability results that the distribution of state becomes uniform over time.*

equations that has several solutions. In this case, entropy and the Second Law frequently select which of the possible solutions is actually realized by the material [38].

The reader might now be left with the impression that, after initial turmoil, entropy and the Second Law have finally turned into important and versatile tools in science, engineering, and mathematics, the applicability and validity of which require no further discussion. To a great extent, this is indeed so. Nevertheless, heated discussions regarding their applicability still continue in the realm of exotic materials.

Yea verily, in recent times, the sky over the palace of the universal validity of the Second Law has indeed been darkened sporadically by black clouds. Many of these clouds arise from the study of black holes — quite arguably the most exotic materials in the universe. Here the question (which has not yet completely been answered) arises: Is gravity a carrier of entropy?

But there are other cloud makers: problems of everyday life also lead, under certain circumstances, to another type of question regarding the validity and applicability of the Second Law.

Clearly, no serious scientist doubts the validity of the inequality demonstrated in (16). However, it so happens that this inequality, just like the law of energy conservation (8), makes only a global statement for a given body, and for many questions this is insufficient. One would also like to perform calculations in local points of the body and, to this end, local forms of (8) and (16) are required. In the case of the energy conservation law, the local form in regular points reads without a doubt:

$$\frac{\partial\left(\varrho u+\frac{\varrho}{2}\upsilon^2\right)}{\partial t}+\frac{\partial}{\partial x_k}\left(\left(\varrho u+\frac{\varrho}{2}\upsilon^2\right)\upsilon_k+q_k-t_{ik}\upsilon_i\right)=\varrho g_i\upsilon_i+\varrho r. \tag{21}$$

This form is predicated on the assumption that the internal energy, U, can be written as a volume integral of the density of the internal energy, ϱu. Therefore it is additive and, in the global energy balance, no quantities outside of integrals occur.

However, in the case of CLAUSIUS' inequality (16), the temperature is outside the surface integral and, consequently, the mathematical techniques by means of which a global equation is turned into a local one fail. The question, more specifically asked, becomes: What is the form of the local entropy flux?

Again, if we assume that the entropy, S, can be written as a volume integral over the entropy density, ϱs, then, at least, the local form of the inequality (17) results:

$$\frac{\partial\varrho s}{\partial t}+\frac{\partial}{\partial x_k}\left(\varrho s\upsilon_k+\Phi_k\right)-\frac{\varrho r}{T}\geqq 0. \tag{22}$$

However, in this equation the specific form of the local entropy flux vector, Φ_k, is not known. In analogy to the global form, $\dot{Q}/T$, and in view of the radiation term, $\varrho r/T$, the majority of thermodynamicists usually assumes [39] that:

$$\Phi_k=\frac{q_k}{T}. \tag{23}$$

For ideal gases, on the other hand, it follows from the kinetic gas theory of MAXWELL and BOLTZMANN that, near equilibrium [40]:

$$\Phi_k=\frac{q_k}{T}-\frac{2}{5pT}q_i t_{ik}. \tag{24}$$

There is also a kinetic theory to describe heat conduction in crystals at temperatures close to absolute zero. In this case it follows that, near equilibrium [41]:

$$\Phi_k=\frac{q_k}{T}\left(1-\frac{3}{32c_D^2a^2T^8}q_iq_i\right), \tag{25}$$

where a denotes the phonon radiation constant, and c_D is the DEBYE velocity. At very low temperatures, the deviation from the q_k/T law becomes extremely important. However, the corrections to the q_k/T law are not always additive; rather, they can be multiplicative as well. For example, the entropy flux of a bundle of black radiation reads [42]:

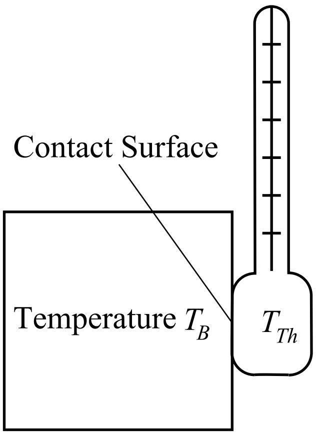
$$\Phi_k=\frac{4}{3}\frac{q_k}{T}, \tag{26}$$

where T is the temperature of the surface that emits the black radiation.

I. MÜLLER

We conclude that the entropy flux depends on the heat flux and other thermodynamic quantities, in a material-dependent manner. Fictitious contradictions to the Second Law can always arise if this conclusion is not seriously taken into account. It is the distinction of the thermodynamicist INGO MÜLLER (1936-Present) from Berlin to have clearly recognized this point and to have revised it in thermodynamics.

Presumably the reader who is not confronted daily with thermodynamics will ask himself at this point whether the form of the entropy flux has an immediate, practical meaning. Indeed, it has: whenever, for a temperature reading, a thermometer is brought into contact with the to-be-measured body. At the point of contact, the following laws, (27) and (28), apply. The energy that the body gains from or supplies to the thermometer is conserved. In other words, the normal component of the heat flux vector, q_k, at the contact surface has the same numerical value on the side of the thermometer as on the side of the body.



Moreover, a thermometer is constructed such that there is no entropy being produced at the contact surface. Thus, the normal component of the entropy flux, Φ_k, has the same numerical value on both sides of the contact surface. This is expressed:

$$(q_k N_k)_{\mathrm{B}} = (q_k N_k)_{\mathrm{Th}}\,, \tag{27}$$

$$(\Phi_k N_k)_{\mathrm{B}} = (\Phi_k N_k)_{\mathrm{Th}}\,. \tag{28}$$

If the equation $\Phi_k = q_k/T$ holds, then this implies immediately that:

$$T_{\mathrm{B}} = T_{\mathrm{Th}}. \tag{29}$$

However, if $\Phi_k = q_k/T$ does not hold, the thermometer ("Th") does not show the temperature of the body ("B") and the form of the entropy flux is required in order to suitably correct the reading on the thermometer scale [15].

2 Obscure Applications of the Second Law

Die Wissenschaften zerstören sich auf doppelte Weise selbst: Durch die Breite, in die sie gehen, und durch die Tiefe, in die sie sich versenken.

GOETHE, Maximen und Reflexionen[31]

Die exakte Wissenschaft geht der Selbstvernichtung durch Verfeinerung ihrer Fragestellungen und Methoden entgegen.

SPENGLER, Der Untergang des Abendlandes[32]

2.1 Prologue

Nowhere else in science is there, or has there ever been, such an extreme and sometimes absurd struggle over models, concepts, interpretations, and fictitious problems as in thermodynamics. The following — naturally, incomplete — list presents the most famous controversies.

Already classic are the controversies over:

- the phlogiston / caloric theory,
- the heat death of the universe,
- the statistical interpretation of entropy,
- the reversibility and the recurrence objections,
- MAXWELL's demon, and
- the Second Law in the physics of animated matter.

[31] *The Sciences destroy themselves in a twofold way: by the breadth into which they go and by the depth in which they drown.* W. VON GOETHE, Maximes and Reflections.

[32] *Exact science moves toward self-destruction by refinement of its questions and methods.* O. SPENGLER, The Decline of the West.

Almost fallen into oblivion are the controversies over:

- the stratification of temperature of the Earth's atmosphere and LOSCHMIDT's devices,
- WIEN's paradox,
- the entropy in the processes of refraction, reflection, and interference, and
- the temperature of bodies which move almost at the speed of light — the PLANCK-OTT imbroglio.

And, after 1945 controversies originated over:

- the paradox of heat conduction,
- GABOR's *Perpetuum Mobile* of the Second Kind,
- the Principle of Material Objectivity,
- the apparent contradiction of the Second Law in rotational flows of highly polymerized matter, and
- the entropy of black holes.

The next chapters present a small selection of these controversies which, above all, are related to an eventual contradiction of the Second Law.

For a first taste of these controversies, the reader is reminded of three sessions of the Committee for Housing and Settlement of the Bavarian Parliament in 1950. The debates at these three sessions centered around Petition No. 16515, which requested a change in heating and cooling techniques. The Bavarian Parliament had invited as expert witnesses several gentlemen from the TÜV (the Agency for Technical Supervision) as well as the successor to SOMMERFELD's Chair, Professor Dr. F. BOPP, from the University of Munich. The three sessions were devoted to not more nor less than an examination as to whether Mr. ROBERT C. GROLL (the petitioner) had refuted the Second Law, and whether the machine he had conceived could be used on a large industrial scale or not. After one of the experts, Baurat GRÜNBECK, had illustrated to the deputies how a *Perpetuum Mobile* (that is, a perpetual motion machine) of the Second Kind works, he continued to say [43]:

Die Praxis und die Erfindungen eilen erfahrungsgemäß der Wissenschaft voraus. Man sollte unbedingt den Gedanken von Groll fördern. Wissenschaftler sollten gemeinsam mit Praktikern ein Kuratorium bilden, das die Frage weiter erörtert. Hierzu müssen auch die erforderlichen Mittel bereit gestellt werden. Die noch bestehenden kleinen [!] *wissenschaftlichen Differenzen dürfen kein Hinderungsgrund sein.*[33]

2.2 Fluctuations

Dort in der Ewigkeit geschieht alles zugleich,
es ist kein Vor noch Nach wie hier im Zeitenreich.

ANGELUS SILESIUS, Der Cherubinische Wandersmann[34]

If we consider classical mechanics to be the foundation of thermodynamics, it seems odd on first glance that the macroscopic equations are *irreversible*, whereas microscopic equations are *reversible*. The most known formulations of this circumstance are expressed by LOSCHMIDT's *reversibility objection* [50] and POINCARE / ZERMELO's *recurrence objection* [28, 33], both of which were described before. Here we are concerned with the *recurrence objection* and explicitly show that the time periods necessary for a recurrence become extremely large as the numbers of particles increase. Consequently, one would have to wait for an extremely long time in order to observe macroscopic reversibility.

First, we consider N gas particles within an adiabatically insulated container of volume, V. Furthermore, in this case, we restrict ourselves to a strongly rarefied, ideal gas, so that, practically speaking, the particles interact with only the container walls. The gas is supposed to be in thermodynamic equilibrium at a temper-

[33] *By experience, practice and inventions run ahead of science. One should unconditionally support Groll's thought. Scientists and men of practice should form a board of trustees to further discuss the question. To this end the necessary funds also need to be provided. The remaining minor* [sic] *scientific differences cannot be a reason for impedance.*

[34] *There in eternity everything happens simultaneously, there is no Before nor After as here in the realm of times.* ANGELUS SILISIUS, The Cherubic Wanderer.

ature, T. Then all the other macroscopic quantities are determined. For example, the mean values, $\bar{N}_L$ and $\bar{N}_R$, of the particles in the left and right halves of the container are given by $N/2$.

Now we ask for the amount of time, t_r, that passes on average until the current number of particles in the left half of the container has increased by ΔN and, consequently, in the right half has decreased by the same amount.

Since the particles traverse the container basically free of interaction at an average speed, $\bar{c}$, the average duration of their stay, τ, in one half of the container is of the order:

$$\tau \approx \frac{V^{1/3}}{\bar{c}} \qquad \text{with} \qquad \bar{c} = \sqrt{\frac{8}{\pi}\frac{k_B}{\mu}T}, \tag{30}$$

where k_B denotes BOLTZMANN's constant and μ is the mass of a gas particle.

Now we consider the case where there are N_L particles in the left and $N_R = N - N_L$ in the right half of the container. From combinatorics it follows for the number, w, of microscopic realizations of this distribution that:

$$w(N_L) = \frac{N!}{N_L!N_R!} = \frac{N!}{N_L!\,(N - N_L)!}. \tag{31}$$

The total number of all microscopic realizations becomes:

$$W = \sum_{N_L=0}^{N} w\,(N_L) = 2^N. \tag{32}$$

The number of possibilities to realize $N_L \geq \frac{N}{2} + \Delta N$ is given by:

$$W\,(\Delta N) = \sum_{N_L=\frac{N}{2}+\Delta N}^{N} w\,(N_L). \tag{33}$$

Now we shall assume that the time of transition between two micro-states is of the order of the time τ. Hence, on the average, all micro-states are run through within the time $W\tau$. During this time, the situation $N_L \geq \frac{N}{2} + \Delta N$ is encountered on the average $W\,(\Delta N)$-times. Consequently, we obtain for the average time, t_r, between two successive compressions such that $N_L \geq \frac{N}{2} + \Delta N$:

$$t_r \approx \left(\frac{W}{W\,(\Delta N)} - 1\right)\tau. \tag{34}$$

For $N \gg 1$ and $\Delta N < N$ it follows, because of the Law of Large Numbers, that:

$$t_r \approx \left(\frac{2}{1 - \operatorname{erf}\left(\sqrt{\frac{2}{N}}\Delta N\right)} - 1\right)\tau. \tag{35}$$

For a 1 m^3 container filled with argon at $T = 300$ K, the recurrence times, t_r, are presented in the table for $\Delta N = \bar{N}_L/100 = \left(N/2\right)/100$ and for various particle numbers, N.

Average time between two successive compressions

N	t_r in s
10^2	0.0054
10^3	0.0066
10^4	0.0158
10^5	3.2062
10^6	$3.2934 \cdot 10^{20}$
10^7	$2.7948 \cdot 10^{216}$

We conclude that the average time between two succesive compressions, for which the change in particle numbers differs by only 1% from the mean value, increases enormously with the total number of particles, N, in the container. For one million particles, the time to recurrence, t_r, is already large compared to the age of the universe, which is roughly $6.3 \cdot 10^{17}$s.

This example clearly shows in which sense reversible microscopic mechanics does not contradict the macroscopic experience of irreversibility. In order to experience a phenomenon such as the compression described before, the time for observation that is at our disposal is much too short [44].

It could now be argued that, indeed, the average waiting time for one such experiment is very large but, on the other hand, we are surrounded by many similar "experiments." Each accumulation of several million particles, for example in a small water droplet, constitutes such an experiment, and what happens rarely during a single experiment may happen frequently during many such experiments.[35]

Consider that in a lottery game it is very unlikely for one person to predict the proper six out of 49 possible numbers. However, since the game is played every week and by many people, there is usually always a first prize winner, and often there are several.

Why then do we not observe every now and then a spontaneous compression or the spontaneous vaporization of a small water droplet? This answer can also be found in the table shown above. According to an estimate by EDDINGTON, the universe consists of roughly 10^{79} electrons and protons. If we imagine the universe to be distributed into containers with 10^7 particles each, whereby the container walls are neglected, then the average time between two successive compressions of a 1% increase in particle number in any one of the $10^{79}/10^7 = 10^{72}$ containers is still approximately $10^{216}/10^{72} = 10^{144}$s. Consequently, it is thus extremely unlikely to observe such a compression. However, for relatively small particle numbers, such fluctuations *can* be observed, for example during light scattering experiments [45].

2.3 Entropy and Gravity

Liegt der Irrtum nur erst
wie ein Grundstein im Boden,
immer baut man darauf,
nimmermehr kommt er an [den] *Tag.*[36]

GOETHE and SCHILLER, Xenien

An interesting possibility for violating the Second Law goes back to the work of MAXWELL and LOSCHMIDT. In 1866, MAXWELL submitted a paper to the Royal Society in London [46] in which he calculated the temperature of an atmosphere in equilibrium. The following briefly recapitulates MAXWELL's calculation in today's nomenclature.

We first write out the balance of momentum:

$$\frac{\partial \varrho \upsilon_i}{\partial t} + \frac{\partial}{\partial x_k}\left(\varrho \upsilon_i \upsilon_k + p\delta_{ik} + p_{\langle ik\rangle}\right) = \varrho g_i\,. \tag{36}$$

Here the mass density is denoted by ϱ, velocity by υ_i, and pressure by p, while $p_{\langle ik\rangle}$ is the pressure deviator and $g_i = (0, 0, -g)$ is the gravitational force.

We consider a stationary equilibrium process, during which all quantities are independent of time and depend only on one spatial coordinate, z. Moreover, the pressure deviator vanishes in equilibrium, and we obtain:

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -\varrho g. \tag{37}$$

The pressure of an ideal gas can be calculated from the thermal equation of state:

$$p = \varrho\frac{k_B}{\mu}T. \tag{38}$$

However, (37) and (38) are not yet sufficient to calculate the temperature in the atmosphere, since they connect three unknown quantities, ϱ, p, and the temperature T. MAXWELL derived another equation for the heat flux, q_i, which reads in modern form [46]:

$$q_i = A\left(\frac{1}{2}\frac{\partial}{\partial x_k}\left(\overline{C^2 C_i C_k}\Big|_E\right) - \frac{5}{2}\frac{p}{\varrho}\frac{\partial p}{\partial x_i}\right), \tag{39}$$

[35] The average calculated lifetime of a proton is 1031 years. For an aggregate of 1031 protons, one proton decay should be observed, on the average, per year. For this reason several tons of iron are brought together in order to observe several decays within one year.

[36] *Once the error is based like a foundation stone in the ground, everything is built thereupon, nevermore it returns to light.*

with:

$$\left.\overline{C^2 C_i C_k}\right|_E = \frac{\mu}{\varrho} \int_{-\infty}^{\infty} C^2 C_i C_k f_M \, \mathrm{d}\mathbf{C}. \tag{40}$$

In (39), A denotes a relaxation time, C_i is the thermal velocity of the particles, and f_M is the MAXWELLian distribution function:

$$f_M = \frac{\varrho}{\mu} \sqrt{\frac{\mu}{2\pi k_B T}}^{\,3} \exp\left(-\frac{\mu}{2k_B T} C^2\right). \tag{41}$$

Now we also restrict (39) to a one-dimensional, stationary equilibrium process and, since q_i vanishes in equilibrium, it follows that:

$$\frac{1}{2} \frac{\mathrm{d}}{\mathrm{dz}} \left(\varrho \left.\overline{C^2 C_z C_z}\right|_E\right) - \frac{5}{2} \frac{p}{\varrho} \frac{\mathrm{d}p}{\mathrm{dz}} = 0. \tag{42}$$

In the next step, MAXWELL calculated:

$$\left.\overline{C^2 C_z C_z}\right|_E = \underbrace{\frac{m}{\varrho} \int_{-\infty}^{\infty} C_x^2 C_z^2 f \, \mathrm{d}\mathbf{C}}_{\left.\overline{C_x^2 C_z^2}\right|_E = \frac{k_B^2}{\mu^2} T^2} + \underbrace{\frac{m}{\varrho} \int_{-\infty}^{\infty} C_y^2 C_z^2 f \, \mathrm{d}\mathbf{C}}_{\left.\overline{C_y^2 C_z^2}\right|_E = \frac{k_B^2}{\mu^2} T^2} + \underbrace{\frac{m}{\varrho} \int_{-\infty}^{\infty} C_z^4 f \, \mathrm{d}\mathbf{C}}_{\left.\overline{C_z^4}\right|_E = \frac{k_B^2}{\mu^2} T^2} = 3 \frac{k_B^2}{\mu^2} T^2, \tag{43}$$

and in doing so he made a mistake, since the integral $\left.\overline{C_z^4}\right|_E$ in (43) does not yield $\frac{k_B^2}{\mu^2} T^2$ but rather $3 \frac{k_B^2}{\mu^2} T^2$. Due to this wrong result, (42) turns into:

$$\frac{3}{2} \frac{k_B^2}{\mu^2} \frac{\mathrm{d}}{\mathrm{dz}} \left(\varrho T^2\right) - \frac{5}{2} \frac{p}{\varrho} \frac{\mathrm{d}p}{\mathrm{dz}} = 0, \tag{44}$$

or after using the thermal equation of state (38):

$$\frac{3}{2} \frac{k_B}{\mu} p \frac{\mathrm{d}T}{\mathrm{dz}} - \frac{k_B}{\mu} T \frac{\mathrm{d}p}{\mathrm{dz}} = 0. \tag{45}$$

From this it follows that in equilibrium the temperature gradient is proportional to the pressure gradient. After elimination of the latter by means of (37), it follows that:

$$\frac{3}{2} \frac{k_B}{\mu} p \frac{\mathrm{d}T}{\mathrm{dz}} + \frac{k_B}{\mu} T \varrho g = 0. \tag{46}$$

This equation can easily be integrated and we obtain, with $T(z = 0) = T_0$ for the temperature distribution in equilibrium, the following stratification which, in particular, is dependent of the mass, μ, of the gas atoms:

$$T(z) = T_0 - \frac{2}{3} \frac{\mu g}{k_B} z. \tag{47}$$

Of course this result is wrong since the integral $\left.\overline{C_z^4}\right|_E$ in (43) was calculated erroneously. Using the correct integration, which is $\left.\overline{C_z^4}\right|_E = 3 \frac{k_B^2}{\mu^2} T^2$, instead of the integration shown in (43), it follows that:

$$\left.\overline{C^2 C_z C_z}\right|_E = 5 \frac{k_B^2}{\mu^2} T^2, \tag{48}$$

and using this instead of (45), we obtain the known result:

$$\frac{\mathrm{d}T}{\mathrm{dz}} = 0, \quad \text{i.e.,} \quad T = \text{constant} \tag{49}$$

in an atmosphere which is in equilibrium.

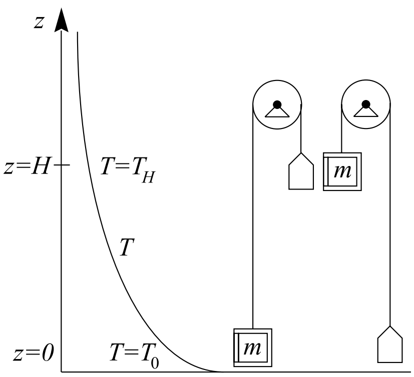
MAXWELL realized very early that he had made a mistake. In a supplement [47] to his paper [46] he wrote:

...When I first attempted this investigation, I overlooked the fact that $\overline{C_z^4}\Big|_E$ *is not the same as* $\overline{C_z^2}\Big|_E \overline{C_z^2}\Big|_E$*, ... The result as now given is, that temperature in gases, when in thermal equilibrium, is independent of height, ...*

However, it was too late. The message that the temperature of an atmosphere in equilibrium changes with height had already reached the ears of other scholars and, due to the possibilities associated with it, it has not lost its fascination up through today since, if an inhomogeneous distribution of temperature in equilibrium were realized in nature, this would imply a violation of the Second Law.

MAXWELL described this possibility (and problem) as follows [47]:

In fact, if the temperature of any substance, when in thermic equilibrium, is a function of the height, that of any other substance must be the same function of height. For if not, let equal columns of two substances be enclosed in cylinders impermeable to heat, and put in thermal communication at the bottom. If, when in thermal equilibrium, the tops of the two columns are at the same temperatures, an engine might be worked by taking heat from the hotter and giving it up to the cooler, and the refuse heat would circulate round the system till it was all converted into mechanical energy, which is in contradiction to the second law of thermodynamics.



However, even if the temperature distribution were universal, i.e., the temperature was of the same form for all substances, an interesting device could be conceived. Such a device consists essentially of an elevator. Its adiabatic cabin contains a mass, m, that can absorb or emit heat, depending on whether the cabin door is closed or not. This cabin is held in mechanical equilibrium by a counterweight so that an up or down movement of the cabin becomes possible without providing mechanical work. Initially let the temperature of the atmosphere at the bottom be at level T_0 and the height at $T_H = T(z = H) < T_0$. Let the temperature of the mass in the cabin be T_m where $T_H < T_m < T_0$. If the elevator is at the ground, the cabin door is opened and, due to $T_0 > T_m$, heat flows from the atmosphere to the mass, m. During this process, mechanical work could be gained by means of a heat engine. After the mass, m, has reached the temperature $T_m + \Delta T$, the cabin door is closed and the elevator is brought to the height, H, without provision of mechanical work, and without changing the temperature of the mass, m. There the cabin door is opened again and now, due to $T_m + \Delta T > T_H$, heat flows from the mass, m, into the atmosphere. Also during this process a part of the energy can be converted into mechanical work by means of a heat engine. If the temperature of the mass, m, is back to the level T_m, the cabin is closed and the whole process is repeated.

Consequently, a single heat reservoir, i.e., the atmosphere, would be cooled here as well, and by doing so mechanical work could be gained, thus violating the Second Law. However, in equilibrium a homogeneous temperature field is realized in the atmosphere and, therefore, such a device will not function.

Of course, since an inhomogeneous temperature distribution of the atmosphere would open fantastic possibilities, it is not surprising that it found many supporters once it had been put into this world by MAXWELL. Moreover, the temperature in our atmosphere does indeed decrease with height. This, however, happens because our atmosphere is not in equilibrium. At different heights, radiation is absorbed and emitted and, in addition to that, there is airflow. The actual inhomogeneous temperature profile was known by virtue of 380 balloon rides performed by ADOLF WAGNER [54].

However, in those days, the assumption was made that the atmosphere *is* in equilibrium. Consequently, it is not surprising that there was a desire to calculate this decrease in temperature — a desire which resulted in a long controversy regarding the temperature of an atmosphere in equilibrium. This controversy is comparable to the controversy of the irreversibility of the macroscopic equations, and it is still ongoing until this very day. However, because the late 19th century dispute between BOLTZMANN and LOSCHMIDT is representative of the entire debate on the temperature profile, in what follows we will give an impression of it.

To begin with, it is interesting to note that LOSCHMIDT presumably had two problems with the Second Law. On the one hand there is his recurrence objection and, on the other, there is his fascination with the idea that cooling the atmosphere of the earth would place an inexhaustible source of energy at mankind's disposal. Neither concept is acceptable under the Second Law. Thus LOSCHMIDT hoped to eliminate several unpleasant consequences of the Second Law by its refutation [50] (p. 135):

Damit wäre auch der terroristische Nimbus des zweiten Hauptsatzes zerstört, welcher ihn als vernichtendes Princip des gesammten Lebens des Universums erscheinen lässt, und sogleich würde die tröstliche Perspective eröffnet, dass das Menschengeschlecht betreffs der Umsetzung von Wärme in Arbeit nicht einzig auf die Intervention der Steinkohle oder der Sonne angewiesen ist, sondern für alle Zeiten einen unerschöpflichen Vorrath verwandelbarer Wärme zur Verfügung haben werde.[37]

Now on to the debate. In October 1875, BOLTZMANN wrote [48] (p.443):

... folgt, daß trotz der Wirksamkeit der äußeren Kräfte für die Richtung der Geschwindigkeit irgend eines der Moleküle jede Richtung im Raume gleich wahrscheinlich ist, ferner dass in jedem Raumelemente des Gases die Geschwindigkeitsvertheilung des Gases genau ebenso beschaffen ist, wie in einem Gase von gleicher Temperatur, auf das keine Aussenkräfte wirken. Der Effect der äusseren Kräfte besteht blos darin, dass sich die Dichte im Gase von Stelle zu Stelle verändert und zwar in einer Weise, welche schon aus der Hydrostatik bekannt ist .[38]

This sybilic sentence probably states the constancy of temperature. However, LOSCHMIDT doubted the results presented by MAXWELL and BOLTZMANN that led to a constant temperature in the equilibrium atmosphere. In February 1876, LOSCHMIDT wrote [50] (p. 136):

Den ... Nachweis für die Ausdehnung des [2. Haupt-] *Satzes auf alle Substanzen findet Maxwell in der nach seinem Ermessen unzulässigen Consequenz der gegentheiligen Annahme, dass es dann nämlich möglich sein würde, unausgesetzt Wärme in Arbeit umzusetzen. Wie schon bemerkt, vermag ich in dieser Folgerung keine Absurdität zu erkennen.*[39]

and (p. 137): *... Man ist ... nicht berechtigt, ein Vertheilungsgesetz, welches unter der Supposition der Abwesenheit äusserer Kräfte , speciell der Schwerkraft, abgeleitet ist, bei einem Probleme in Anwendung zu bringen, bei welchem es sich geradezu um die Feststellung des Einflusses dieser Schwerkraft handelt.*[1]

[1]*Beanständet wird ...* $f_1(a) f_2(b) = f_1\left(a'\right) f_2\left(b'\right)$*... der Maxwell'schen Abhandlung.*[40]

LOSCHMIDT's footnote "[1]" obviously refers to a relation for the distribution function, f, in equilibrium, which also follows from BOLTZMANN's Stoßzahlansatz. Therefore, LOSCHMIDT's remark is also of importance to BOLTZMANN.

In March of the same year, LOSCHMIDT wrote [51] (p. 367):

Ich habe nun in einer vorhergehenden Abhandlung: Sitzb. der k. Akad. Feb. 1876 [50] *den Nachweis geliefert, dass der ursprüngliche Beweis von C. Maxwell nicht auf den Fall anwendbar ist, wo äussere Kräfte, in unserem Falle die Schwerkraft, berücksichtigt werden müssen. In der vorliegenden Arbeit will ich nun zeigen, dass nicht nur jener Beweis des Satzes, sondern auch der Satz selber für diesen Fall zurückzuweisen ist.*[41]

---

[37] *Thereby the terroristic nimbus of the Second Law would also be destroyed, which makes it look like a destructive principle of the whole life of the universe and, at the same time, the comforting perspective would be offered that, in order to transform heat into work, the human race does not depend on the intervention of bituminous coal or on the sun alone, but will have for all times an inexhaustible stock of convertible heat at its disposal.*

[38] *... it follows that, despite the presence of external forces, each direction in space is equally probable for the direction of the velocity of any one of the molecules, moreover, that in each volume element of the gas, the distribution of velocities of the gas is of the same form as in a gas of the same temperature on which no external forces act. The effect of the external forces consists only in a variation of the density in the gas from point to point, and namely in a way that is already known from hydrostatics.*

[39] *The ... proof of extension of the* [Second] *Law to all substances finds Maxwell in the consequence of the opposite assumption, which is inadmissible in his opinion, that it would then become possible to convert heat into work without any restriction. As has been mentioned already, I cannot see any absurdity in this conclusion.*

[40] *One is ... not entitled to apply a distribution law that has been derived under the assumption of the absence of external forces, especially gravity, to a problem that is specifically devoted to the statement of the influence of that gravitational force*[1]. ([1]Objected is ... $f_1(a) f_2(b) = f_1\left(a'\right) f_2\left(b'\right)$ ... of the treatise by Maxwell.)

[41] *In a previous treatise: Sitzb. der k. Akad. Feb. 1876, I have provided evidence that C. Maxwell's original proof is not applicable to the case where external forces, in our case gravitational force, have to be taken into account. In the present paper I shall demonstrate now that not only that proof but also the proposition itself have to be rejected for this case.*

Although BOLTZMANN is not attacked here directly at all, he picked up the gauntlet and wrote in December 1876 [49] (p. 522):

Die Bemerkung, welche Loschmidt, Sitzber. Vol. 73, S. 137 in der Anmerkung macht, trifft ebenso wie die Maxwell'sche auch meine Abhandlung.[42]

(p. 513):

... Wir haben somit einen directen Beweis geliefert, dass die ...[Gleichgewichts-] *Zustandsvertheilung durch den Einfluss der Schwere auf die Bewegung der Gasmolecüle nicht gestört wird.*[43]

On that LOSCHMIDT replied in February 1877 [52]. He wrote (p.292):

Bis heute ist übrigens für die behauptete Temperaturgleichheit der verschiedenen Schichten einer verticalen Luftsäule noch in keinem Falle ein stichhältiger Beweis erbracht, ...[44]

And also in another paper from July of the same year [53] (p. 210):

Und desshalb ist es von Wichtigkeit, dass der Widerstreit zweier diametral entgegengesetzter Thesen präcis formulirt, und wenigstens innerhalb des Gebietes des gasförmigen Aggregationszustandes zur Entscheidung gebracht werde.[45]

However, the case was not yet settled. MAXWELL, BOLTZMANN, and LOSCHMIDT were not the only scholars who dealt with this problem. Also S. H. BURBURY and R. C. NICHOLS contributed to the debate, and in 1923, the nobleman RICHARD VON DALLWITZ-WEGNER submitted a paper with the title:

Die atmosphärische Temperaturabnahme nach oben und ähnliche Erscheinungen als Wirkung der Schwerkraft, der Sama-Zustand der Materie [46]

VON DALLWITZ-WEGNER wrote [54]:

In meiner Arbeit: „Der Zustand der oberen Schichten der Atmosphäre" [55] *führte ich aus, daß die atmosphärische Temperaturabnahme nach oben wohl nur eine Folge der adiabatischen Expansion der Atmosphäre nach oben sein kann. Bei näherem Zusehen stellt sich aber heraus, daß das nicht richtig ist, daß vielmehr die Temperaturabnahme dt/dh ganz allein eine Folge der Schwerkraft, der Anziehungskraft der Erde sein kann, und zwar nicht in dem Sinne, daß ja durch die Schwerkraft erst eine Expansion der nach oben strebenden Luft bewirkt wird, sondern in einem gleichsam statischen Sinne, indem die molekulare Schwingungsgeschwindigkeit der Luftmolekeln, deren Maß ja die Temperatur ist, nach oben infolge der Wirkung der Schwerkraft abnimmt, wie die Steiggeschwindigkeit einer nach oben geschossenen Flintenkugel aus diesem Grunde bis Null abnimmt.*[47] [48]

The state of the atmosphere, in which the temperature is inhomogeneous and, nevertheless, the heat flux vanishes, is particularly important to von DALLWITZ-WEGNER:

---

[42] *The remark that Loschmidt, Sitzber. Vol. 73, p. 137, made in the footnote concerns my own treatise as well as Maxwell's.*

[43] *... We have thus provided a direct proof that the ...* [equilibrium] *distribution of states is not affected by the influence of gravity on the motion of the gas molecules.*

[44] *By the way, until today there has been no sound proof for the equality of temperatures, as claimed, in different layers of a vertical column of air, ...*

[45] *And for that reason it is of importance that the conflict between two diametrically opposite theses is formulated precisely, and at least within the field of the gaseous state of aggregate, brought to a decision.*

[46] *The atmospheric decrease of temperature with increasing height and similar phenomena as a result of the force of gravity, the sama-state of matter.*

[47] *In my paper: "The state of the upper layers of the atmosphere," I explained that the atmospheric decrease of temperature with increasing height could only be a consequence of the adiabatic expansion of the atmosphere with increasing height. However, at a closer inspection, it turns out that this is not right, but rather that the decrease of temperature dt/dh is exclusively a consequence of the force of gravity, but not in the sense that the force of gravity initiates an expansion of the ascending air but rather in an almost static sense, where the molecular vibrational velocity of the air molecules, a measure of which after all is the temperature, decreases upwards due to the influence of gravity, such as the climbing velocity of a bullet shot straight up into the air decreases, for that reason, to zero.*

[48] These reasonings also led PAUL EHRENFEST to a nice study, which contains yet another proof of the non-existence of temperature layers [56].

Es gibt also zur Wärmeleitung untaugliche Temperaturgefälle. Um den eigenartigen Zustand der Materie kurz zu kennzeichnen, möchte ich ihn den Sama-Zustand nennen, (Sama=derselbe, in Esperanto), weil die Zunahme an potentieller Energie prinzipiell immer eine gleich große Abnahme an Wärmeenergie entspricht.[49]

As we shall see later, the *sama state* really exists, but only if relativistic effects are taken into account.

Even today a paper on this topic can be found in a contemporary medium, the internet. It is from the keyboard of the lawyer Andreas Trupp [57] and is titled:

Energy, Entropy — On the occasion of the 100th anniversary of Josef Loschmidt's death:
Is Loschmidt's greatest discovery still waiting for its discovery?

However, we dare say that nowadays the majority of scholars is convinced of a homogeneous temperature in an equilibrium atmosphere.

So far all of our studies were non-relativistic. However, relativistic thermodynamics enforces in equilibrium an inhomogeneous temperature distribution in the atmosphere. In this case (39) for the heat flux, q_i, no longer holds but rather [58, 59]:

$$q_i = -\frac{\kappa}{\sqrt{g_{00}}}\frac{\partial}{\partial x_i}\left(T\sqrt{g_{00}}\right), \tag{50}$$

where κ is the heat conductivity, and g_{00} denotes the time component of the metric tensor. For a non-self-gravitating atmosphere in a gravitational field with radial symmetry that is created by a mass, M, the Schwarzschild solution holds outside of M, and in particular:

$$\sqrt{g_{00}} = \sqrt{1 - \frac{2GM}{c^2 r}}, \tag{51}$$

where G denotes Newton's gravitational constant, c is the speed of light, and r indicates the radial distance from the center of the mass, M. Consequently, in equilibrium, it follows from (50) and (51):

$$T(r)\sqrt{1 - \frac{2GM}{c^2 r}} = \text{constant}, \tag{52}$$

and from this equation we obtain for the temperature distribution in an atmosphere:

$$T(r) = T_0 \frac{\sqrt{1 - \frac{2GM}{c^2 R}}}{\sqrt{1 - \frac{2GM}{c^2 r}}}, \tag{53}$$

where T_0 is the temperature at the surface, $r = R$, of the gravitating mass.

This is the *sama state* of the atmosphere.

However, this is a universal law, i.e., valid for all substances, so that we cannot violate the Second Law by using the two columns as described by Maxwell. While at first glance it seemed that we might potentially succeed by means of the elevator described above, now we must consistently take into account that the elevator, including its contents, is also subject to relativistic effects.

When we discussed the principle of the elevator in non-relativistic thermodynamics before, we assumed correctly that the mass of the cabin and of the counterweight are independent of temperature and height. However, now this is no longer true. As before, let the cabin at the beginning be at the ground and the counterweight at a height, $r = H$. Let the atmosphere at the ground be at a temperature T_0, and the cabin at a temperature T_m, with $T_m < T_0$, respectively. The masses of the cabin and of the counterweight shall be equal at the beginning so that mechanical equilibrium is guaranteed. If we now open the cabin door, heat flows from the atmosphere into the cabin since $T_m < T_0$, which increases its energy by ΔE. However, because of $E = mc^2$, the mass of the cabin will also increase by $\Delta m = \Delta E/c^2$ and the system is no longer

[49] *Thus there are there are unsuitable temperature profiles for heat conduction. In order to characterize that peculiar state of matter, I shall call it the sama state (sama = the same, in Esperanto) since an increase in potential energy principally always corresponds to a decrease of heat energy of the same amount.*

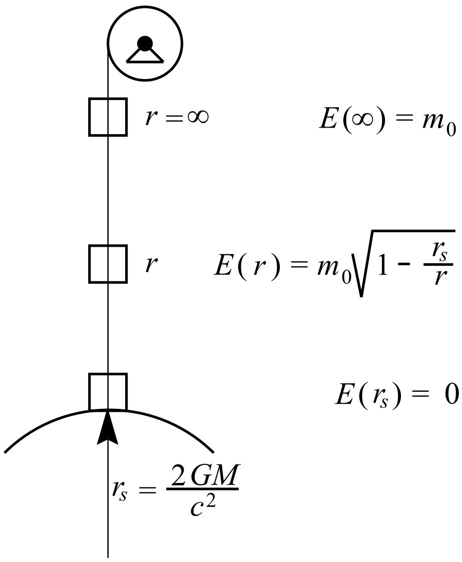
in mechanical equilibrium since now the cabin is heavier than the counterweight and cannot be moved back to the height H without doing work.

Hence, the device described above will not function and, consequently, the Second Law will not be violated.

Nevertheless, the idea of using gravity in order to violate the Second Law is fascinating, and it is therefore not surprising that another attempt in this direction has already been undertaken.

In December 1971, the relativist RICHARD GEROCH reported during a colloquium at Princeton on the following process, which we consider to be abstruse [60]. In summary, he argued:

Let $r_S = 2GM/c^2$ be the SCHWARZSCHILD radius of a black hole of mass, M. At an infinite distance from the black hole, a cable winch is installed that is coupled to an electric generator. A box filled with black body radiation of mass, m_0, falls towards the SCHWARZSCHILD radius because of its weight, which powers the generator.



For the operator at the cable winch, the mass in the SCHWARZSCHILD field, $m(r)$, varies as follows:

$$m(r) = m_0\sqrt{1 - \frac{r_S}{r}}. \tag{54}$$

Thus the work gained to lower the box to reach the SCHWARZSCHILD radius is given by:

$$W_{\infty\to r_S} = \{m(\infty) - m(r_S)\}\,c^2 = m_0c^2. \tag{55}$$

Now the box is opened for a short while so that some radiation of an equivalent mass, Δm, is emitted toward the black hole. Then the box is closed and pulled up again. But now it holds that:

$$m(r) = (m_0 - \Delta m)\sqrt{1 - \frac{r_S}{r}}, \tag{56}$$

and the work to be performed by the generator is given by:

$$W_{r_S\to\infty} = \{m(r_S) - m(\infty)\}\,c^2 = -(m_0 - \Delta m)\,c^2. \tag{57}$$

The efficiency, e, for the complete process is calculated according to:

$$e = \frac{\text{profit}}{\text{effort}} = \frac{|W_{\infty\to r_S} + W_{r_S\to\infty}|}{\Delta mc^2} = 1, \tag{58}$$

and, consequently, is at its maximum. In any case, it is greater than the CARNOT efficiency, no matter how the latter could be determined. Is, therefore, the Second Law violated?

JACOB BEKENSTEIN, who was a physics student at Princeton during those days, offered a response to GEROCH's assumption. His argument, in summary, is as follows [60]:

GEROCH's reasoning presupposes that the box has no extension and, consequently, is able to completely reach the SCHWARZSCHILD radius. However, a box filled with black body radiation of temperature, T, must at least have a linear extension, $\lambda_{\max}$, where $\lambda_{\max}$ can be calculated from WIEN's law, $\lambda_{\max}T = b$, where $b = 2.8978 \cdot 10^{-3}$Km is WIEN's constant. Therefore, the center of the box can, at most, be lowered down to the height $r_S + \Delta r(\lambda_{\max})$, since energy or matter that pass the SCHWARZSCHILD radius will never return.

Now we calculate the two required amounts of work again:

$$W_{\infty\to r_S+\Delta r} = \{m(\infty) - m(r_S + \Delta r)\}\,c^2 = m_0c^2\left(1 - \sqrt{1 - \frac{r_S}{r_S + \Delta r}}\right), \tag{59}$$

$$W_{r_S+\Delta r\to\infty} = \left\{(m_0 - \Delta m)\sqrt{1 - \frac{r_S}{r_S + \Delta r}} - (m_0 - \Delta m)\right\}c^2. \tag{60}$$

After BEKENSTEIN's correction of GEROCH's argument, the efficiency reads:

$$e = \frac{|W_{\infty\to r_S+\Delta r} + W_{r_S+\Delta r\to\infty}|}{\Delta mc^2} = 1 - \sqrt{1 - \frac{r_S}{r_S + \Delta r}} < 1. \tag{61}$$

Now this efficiency is definitely less than one. The question is whether it is also less than or, at most, equal to a CARNOT efficiency, $e_C = 1 - T_-/T_+$ (18). What, however, are the temperatures T_- and T_+ pertinent to (61)?

We are interested in the maximum value of e. Since the efficiency becomes large for small Δr, we expand (61) under the condition $\Delta r << r_S$, and obtain:

$$e = 1 - \sqrt{\frac{\Delta r}{r_S}}. \tag{62}$$

Clearly, the box emits the radiation at the temperature, $T_B = b/\lambda_{\max}$. The wavelength, $\lambda_{\max}$, however, is related to Δr by:

$$\int\limits_{r_S}^{r_S+\Delta r} \frac{\mathrm{d}r}{\sqrt{1-\frac{r_S}{r}}} = \lambda_{\max}. \tag{63}$$

In order to easily calculate this integral, we even assume that $\lambda_{\max} << r_S$, and in this case we obtain from (63):

$$\Delta r = \frac{\lambda_{\max}^2}{4r_S} = \frac{b^2}{4r_S T_B^2}. \tag{64}$$

Consequently, we can replace the distance, Δr, in (62) by the temperature, T_B, of the box. We obtain:

$$e = 1 - \frac{\left(\frac{b}{2r_S}\right)}{T_B}, \tag{65}$$

and conclude that the upper temperature, T_+, must be identified with the temperature of the box, T_B. The recipient of the radiation, i.e., the black hole, should therefore be the carrier of the temperature, $T_{BH} = T_-$. Consequently, the temperature of the black hole, T_{BH}, must be a function of r_S.

And indeed, BEKENSTEIN has motivated equations according to which the thermodynamic quantities temperature and entropy are connected to the mass, M, and to the surface area, A, of the event horizon of a black hole according to [60, 61]:

$$T_{BH} = \frac{hc^3}{16\pi^2 k_B G}\frac{1}{M}, \qquad S_{BH} = \frac{\pi k_B c^3}{2Gh}A. \tag{66}$$

For a black hole with a SCHWARZSCHILD metric it holds that:

$$M = \frac{c^2 r_S}{2G}, \qquad A = 4\pi r_S^2. \tag{67}$$

Consequently, the efficiency from (65) reads:

$$e = 1 - C\frac{T_{BH}}{T_B}, \qquad \text{where} \qquad C = \frac{4\pi^2 b k_B}{hc} = 7.949\ldots, \tag{68}$$

which for $T_{BH} < T_B$ is always less than the CARNOT efficiency.[50]

However, the other equivalent aspect of the Second Law is satisfied, according to which the entropy of a closed system cannot decrease. The body emits radiation energy, Δmc^2, at the temperature T_B. Consequently, its change of entropy is:

[50] Since a black hole at temperature T_{BH} does not emit heat by radiation of this very temperature, the described device would eventually also operate if $T_{BH} >> T_B$. Whether the Carnot efficiency could be exceeded in this case needs to be decided by means of a careful analysis without the approximations that led to (62) and (64). In this connection we would also like to point out the fact that the temperature of a black hole decreases if energy is provided [61].

$$\Delta S_B = -\frac{\Delta mc^2}{T_B}. \tag{69}$$

The black hole of mass, M, absorbs this energy, which results in a change of its entropy of:

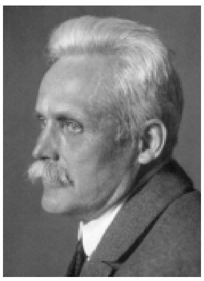
$$\Delta S_{BH} = \frac{8\pi^2 k_B G}{hc} M^2 \left(1 - \left(1 + \frac{\Delta m}{M}\right)^2\right) > \frac{16\pi^2 k_B G}{hc^3} M \,\Delta mc^2 = \frac{\Delta mc^2}{T_{BH}}. \tag{70}$$

Therefore, the total change of entropy of the whole system reads:

$$\Delta S_{\text{tot}} = \Delta S_B + \Delta S_{BH} > \left(\frac{1}{T_{BH}} - \frac{1}{T_B}\right) \Delta mc^2 > 0. \tag{71}$$

3 Entropy and Radiation

Die Entropie des Gesamtsystems
ist also gleich der Summe
der Entropien ihrer verschiedenen
Bestandteile.[51]
C. Caratheodory

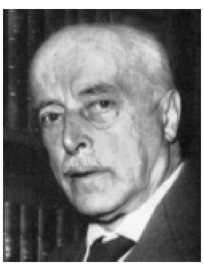


W. Wien

By now the reader might be left with the impression that all attempts to violate the Second Law can be defeated after a careful analysis. However, this is not so. By means of the following examples we want to demonstrate that there are problems that must be taken seriously, the mechanisms of which are, even today, not clearly understood. To this end we turn to the thermodynamics of radiation.

Wilhelm Wien (1864-1928), the discoverer of the displacement law that is named after him, was the first in 1896 to point out an apparent violation of the Second Law, which became known as Wien's paradox [62]. Wien studied the radiation of heat exchanged between two bodies that are at the same temperature. In the path of the heat rays, Wien put two Nicol prisms and a magnetic field in order to initiate the Faraday effect. Using this setup, Wien believed to be able to show that two bodies, initially in equilibrium, are forced to emit and to absorb different amounts of energy, so that, after a certain while, they are no longer in equilibrium. According to the Second Law, this is a process that is not allowed. However, the Second Law was rehabilitated shortly after, when Planck found a simple mistake in Wien's calculations [63]. Instead of expressing his thanks to his colleague, Wien dropped his old idea without further comment and conceived a new device in order to reestablish his paradox [64]. Hereto Planck remarked [65]:

Allein auch die neue Deduction erweist sich bei näherer Überlegung als unzulänglich ...[52]



M. v. Laue

However, the solution to the following problems, which address scattering, refraction, and interference of light, is still in the dark. These problems were investigated and intensely discussed in 1906 and 1907 by the physicist and founder of X-ray spectroscopy, Max von Laue (1879-1960), in two papers [67, 68] that were far ahead of their time. Von Laue was, in those days, Planck's assistant.

For preparation we consider, first, a non-polarized bundle of rays with direction, n_i, and frequencies, ν, in the range $[\nu, \nu + \mathrm{d}\nu]$. Let the rays consist of non-polarized photons, and let $f\,\mathrm{d}\mathbf{k}$ be their number density with wave vectors, $\mathbf{k}$, taken from the interval $[\mathbf{k}, \mathbf{k}+\mathrm{d}\mathbf{k}]$. In spherical coordinates we have $\mathrm{d}\mathbf{k} = \mathbf{k}^2 \mathrm{d}k\,\mathrm{d}\Omega$, with $\mathrm{d}\Omega$ being the surface element of the unit sphere, and the magnitude of the wave vector, k, being related to the frequency by $k = \frac{2\pi}{c}\nu$. It follows that the photons which, during the

[51] *The entropy of the whole system is therefore equal to the sum of the entropies of its different constituents.*
[52] *But even the new deduction is, at a closer inspection, insufficient ...*

time, $\mathrm{d}t$, cross a surface element, $\mathrm{d}A$, with unit normal, N_i, of a warm body transport in the direction $n_i = k_i/k$ the amount of energy $\mathrm{d}t \cdot \mathrm{d}A \cdot n_i N_i \cdot \mathrm{d}\Omega \cdot \frac{2}{c^2}\nu^3 \left(\frac{1}{y}f\right)\mathrm{d}\nu$, where $y = \frac{2}{(2\pi)^3}$.

Now it is crucial to assume that, for all the cases considered below, the state of the photons can be described by means of the PLANCK distribution, f, which reads:

$$f = \frac{y}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}, \tag{72}$$

where $h = 6.63 \cdot 10^{-34}$Js is PLANCK's constant. In this case the spectral decomposition of the energy density, u, and of the entropy density, s, may be written as:

$$u = \int_0^\infty u_\nu \mathrm{d}\nu \quad \text{and} \quad s = \int_0^\infty s_\nu \mathrm{d}\nu, \tag{73}$$

where the spectral densities of both quantities read:

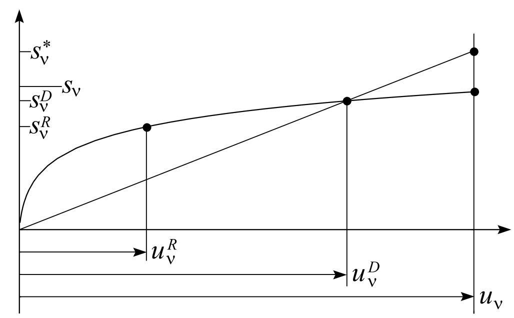
$$u_\nu(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{y}f \quad \text{and} \quad s_\nu(\nu, T) = \frac{8\pi k_B \nu^2}{c^3}\left(\left(1 + \frac{1}{y}f\right)\ln\left(1 + \frac{1}{y}f\right) - \frac{1}{y}f\ln\left(\frac{1}{y}f\right)\right). \tag{74}$$

In view of the statement of the Second Law according to which the entropy cannot decrease in an adiabatically closed system, we shall now study various processes with ray bundles.

First, we investigate a narrow bundle that propagates toward a thin diathermal[53] plate and, thereby, splits into a reflected and a transmitted ray. We ask by how much the initial spectral entropy density will change. Energy is conserved in diathermal plates, and this is expressed by:

$$u_\nu = u_\nu^R + u_\nu^T, \tag{75}$$

where , u_ν, u_ν^R and u_ν^T denote the spectral energies of the initial, reflected, and transmitted ray bundle, respectively.



The figure shows the entropy density, s_ν, as a function of the energy density according to the change of the spectral energy density, u_ν, from (74). In addition, the entropy densities that correspond to the different ray bundles are also indicated in the graph. As is obvious by inspection of the figure we obtain the relations $s_\nu^*/u_\nu = s_\nu^T/u_\nu^T < s_\nu^R/u_\nu^R$, and because of (75), the inequalities:

$$s_\nu < s_\nu^* < s_\nu^R + s_\nu^T \tag{76}$$

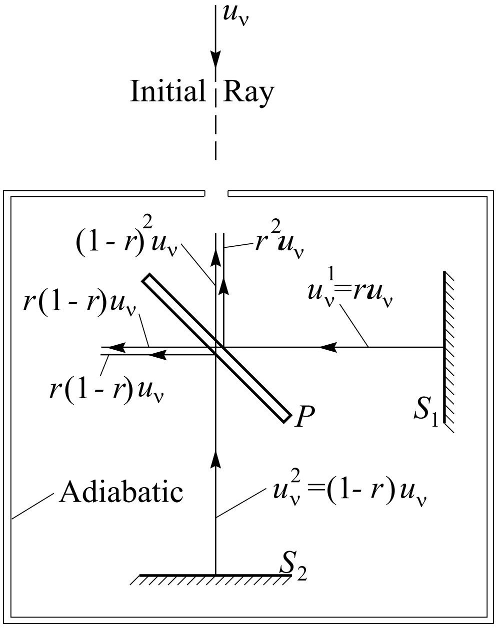
must hold.

Thus, the sum of the entropy densities of the reflected and the transmitted ray bundles turns out to be larger than the entropy density of the initial ray bundle. Does this mean that we have just studied an irreversible process? PLANCK, who posed this question in 1907, had precisely this opinion [66]. In contrast to PLANCK, VON LAUE argued as follows [67]: The process of reflection and transmission of rays can be inverted by means of a properly adjusted device of concave mirrors and, therefore, the process under consideration is obviously reversible.

However, if VON LAUE's lines of reasoning were right, we have a problem since, undoubtedly, entropy did increase during this process.

Before we discuss this any further let us consider another process. By reflection and diffraction of a ray of the described type, new rays are created which, subsequently, are brought together so that interference phenomena will appear.

[53] i.e., not absorbing heat radiation.



Again we ask for the change of entropy in this process that is realized in the device shown on the left, which was conceived by VON LAUE. The interference is initiated by the ray, which enters the chamber from the top. The chamber contains two ideal reflecting mirrors, S_1 and S_2, and the thin diathermal plate, P, where initially the ray is split into a transmitted and a reflected part. After that, the initial ray is no longer needed and will be shielded. The new rays propagate to the mirrors, S_1 and S_2, where they are completely reflected so that they return to the plate, P. There the rays will be partially reflected and transmitted.

The process of interest to us is as follows. The two rays coming from the mirrors create new two pairs of rays at the plate. The corresponding partner rays interfere and give rise to two new bundles, which propagate to the left and to the top of the chamber.

Usually the reflection coefficient, r, of a diathermal plate that is partially permeable depends on the angle of incidence and on the wavelength. However, in optics it is shown that both dependencies can be neglected if the plate is only sufficiently thin.

Now let us denote by u_ν, $u_\nu^1 = ru_\nu$, and $u_\nu^2 = (1-r)\,u_\nu$ the spectral energy densities of the initial ray (which was shielded in the meantime) and the two rays coming from the mirrors, S_1 and S_2, respectively, which are approaching the plate, P. After transition through P, the pair of rays that runs to the left carries the spectral energy densities:

$$u_\nu^{L1} = ru_\nu^1 = (1-r)\,ru_\nu \qquad \text{and} \qquad u_\nu^{L2} = ru_\nu^2 = r\,(1-r)\,u_\nu, \tag{77}$$

while the pair that propagates upwards has energy densities:

$$u_\nu^{U1} = ru_\nu^1 = r^2 u_\nu \qquad \text{and} \qquad u_\nu^{U2} = (1-r)\,u_\nu^2 = (1-r)^2\,u_\nu. \tag{78}$$

The rays that go to the left experience the same, one transmission and one reflection each. Consequently, their phase difference, δ_L, is zero. The rays that go up are treated differently: ray 1 undergoes two reflections and ray 2 two transmissions. After interference, both pairs lead to energies u_ν^L and u_ν^O as follows

$$u_\nu^L = u_\nu^{L1} + u_\nu^{L2} + 2\sqrt{u_\nu^{L1}}\sqrt{u_\nu^{L2}}\cos(\delta_L) \quad \text{and} \quad u_\nu^U = u_\nu^{U1} + u_\nu^{U2} + 2\sqrt{u_\nu^{U1}}\sqrt{u_\nu^{U2}}\cos(\delta_U). \tag{79}$$

The conservation law of energy, i.e.:

$$u_\nu^L + u_\nu^U = u_\nu^1 + u_\nu^2 = u_\nu \tag{80}$$

implies after a short calculation that $\delta_U = \pi$. Then (79) yield:

$$u_\nu^L = 4r\,(1-r)\,u_\nu \quad \text{and} \quad u_\nu^U = (1-2r)^2\,u_\nu. \tag{81}$$

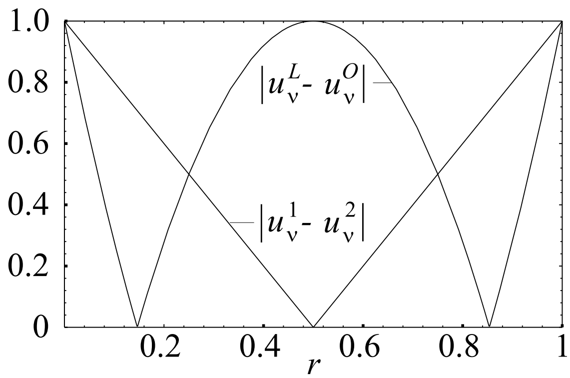
Next we form:

$$\left|u_\nu^1 - u_\nu^2\right| = |2r-1|\,u_\nu \quad \text{and} \quad \left|u_\nu^L - u_\nu^U\right| = \left|8r - 1 - 8r^2\right|u_\nu, \tag{82}$$

which is depicted in the graph shown on the left, from which we read off:

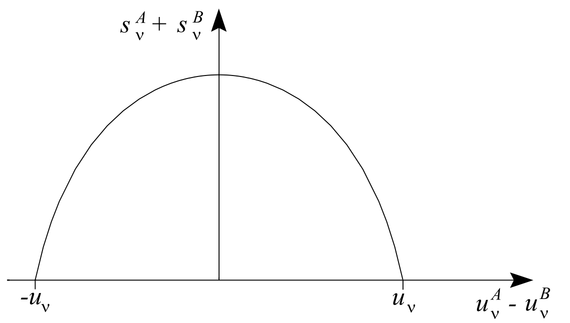
$$\left|u_\nu^L - u_\nu^U\right| \geqq \left|u_\nu^1 - u_\nu^2\right| \qquad \text{if} \qquad 1/4 \leqq r \leqq 3/4. \tag{83}$$

In summary, if we choose the reflection coefficient, r, from the interval $[0.25, 0.75]$, then the energy difference of the ray bundles, L and U, increases when compared to that of the initial bundles, 1 and 2.



Finally, we note that, according to the assumed additivity of the entropy, the total spectral entropy of two ray bundles, A and B, is given by s_ν^A and s_ν^B, respectively, where A and B may either represent L and U or 1 and 2. On the other hand, the conservation law of energy, (75) implies that $s_\nu^A + s_\nu^B$ is only a function of $u_\nu^A - u_\nu^B$. This dependence can be read off from the figure.

We conclude that if the reflection coefficient, r, lies between 0.25 and 0.75, then the spectral entropy density of the new ray bundles, L and U, is lower than the spectral entropy of the initial ray bundles, 1 and 2. Since we consider an adiabatic system, this constitutes a violation of that aspect of the Second Law according to which the entropy in an adiabatic system can never decrease.



In summary and for the record: Reflection and diffraction have led to an increase of entropy and, consequently, were considered by PLANCK to be irreversible processes. Furthermore, there are phenomena of interference that lead to a decrease of entropy. However, since these can be reversed by a suitable arrangement of concave mirrors, we are seemingly faced with a contradiction. It should be noted that VON LAUE's device already represents such an arrangement if a plate, P, with reflection coefficient $r = 1/2$ is chosen.

But now what is VON LAUE's summary? He says, expressed in our words, that the entropy of a system of coherent ray bundles loses the property of additivity. This proposition is an immediate consequence of BOLTZMANN's famous definition $S = k_B \ln(W)$, which relates the entropy, S, of a system to the number of its possible microstates, W. If the system consists of two parts, 1 and 2, having the entropies, $S_1 = k_B \ln(W_1)$ and $S_2 = k_B \ln(W_2)$, then the total entropy is given by the sum $S = S_1 + S_2$ only if $W = W_1 W_2$ holds. However, this relation presupposes that the micro-states of the systems 1 and 2 can be realized independently of each other, which is not possible in coherent ray bundles.

4 Epilogue

Felix, qui potuit rerum cognoscere causas.[54]

VERGIL, Georgica

We have seen that – up to today – the Second Law of thermodynamics has stimulated many obscure investigations. So why does this seem to happen, in particular, in the field of thermodynamics? In fact, obscure investigations are pertinent to all studies concerned with the definition of concepts that do not allow for an immediate intuitive interpretation, such as entropy, and consequences that can be deduced on the basis of these concepts, such as the maximum limit of efficiencies, that are likewise beyond an immediate understanding.

Another example is offered by the special theory of relativity where the concept of the non-existence of signals with infinite speeds inevitably leads to the strange phenomenon of time dilatation.

Nevertheless, we agree with the words of a sage who once said: ”*To overshoot a goal is just as bad as doing nothing at all*.”

[54] *Lucky is who can get insight into the causes of things.*

Acknowledgement. We would like to thank Sheryl Adams-Siebenborn for her invaluable help in making this project a reality.

References

1. Smorodinsky YA, *Temperature*, MIR Publishers Moscow
2. Fahrenheit DG, de Reaumur RAF, Celsius A (1894) *Abhandlungen über Thermometrie*, Editor von Oettingen AJ, Ostwald's Klassiker der Exakten Wissenschaften Nr. 57, Leipzig
3. Dingel H (1952) *The Scientific Adventure* (S. 27), Pitman & Sons, London
4. Galilei G (1890-1909) *Le Opere di Galileo Galilei*, Editor Favaro A, Edizione Nationale, IX, 32
5. Luther M (1937) *Die Bibel oder die ganze Heilige Schrift*, Privilegierte Würtembergische Bibelanstalt, Stuttgart
6. Hamp V, Stenzel M, Kürzinger J (1962) *Die Heilige Schrift des Alten und Neuen Testamentes*, Vom II. Vatikanischen Konzil genehmigter Text, Pattloch Verlag, Würzburg
7. Anonymus letter to the Editor (1972) *Heaven is hotter than hell*, Applied Optics, Vol. 11, Nr. 8, Anhang 14
8. Bugge G (1955) *Das Buch der großen Chemiker*, Verlag Chemie Weinheim
9. Laplace PS (1823) *Traité de Méchanique Céleste*, in Œuvres Complètes de Laplace, Tome 5 (8182)
10. Fourier J (1822) *The analytical theory of heat*, Cambridge University Press (1877)
11. Carnot S (1996) *Betrachtungen über die Bewegende Kraft des Feuers* (1824), Ostwald's Klassiker der Exakten Wissenschaften Nr. 37, Frankfurt a. M.
12. Mayer R (1911) *Die Mechanik der Wärme*, Editor von Oettingen AJ, Ostwald's Klassiker der Exakten Wissenschaften Nr. 180, Leipzig
13. Joule JP (1845) *On the existence of an equivalent relation between heat and the ordinary forms of mechanical power*, in Joules Scientific Papers, Vol. I, p. 202 (1887)
14. Helmholtz H (1889) *Über die Erhaltung der Kraft*, Ostwald's Klassiker der Exakten Wissenschaften Nr. 1, Leipzig
15. Müller I (1985) *Thermodynamics*, Pitman London
16. Truesdell C (1980) *The tragicomical history of thermodynamics 1822-1854*, Springer Berlin
17. Clausius R (1921) *Über die Bewegende Kraft der Wärme* (1850), Ostwald's Klassiker der Exakten Wissenschaften Nr. 99, Leipzig
18. Clausius R (1854) *Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie*, Poggendorf's Annalen **93**, 481
19. Müller I (1978) *Thermodynamics and statistical mechanics of fluids and mixtures of fluids*, Lecture Notes of a Sommer School in Bari, Italy 1976, published as Quaderno Consiglio Nazionale delle Ricerche
20. Clausius R (1865) *Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie*, Poggendorff's Annalen 2, **125**, 353
21. Brusch SG (1986) *Die Temperatur der Geschichte*, Vieweg Braunschweig
22. Spengler O (1917) *Der Untergang des Abendlandes*, Beck'sche Verlagsbuchhandlung, München
23. Thomson W (1851) *On the dynamical theory of heat, with numerical results deduced from Mr. Joule's equivalent of a thermal unit, and M. Regnault's observations on steam*,Trans. R. S. Edinburgh **20**, 261
24. Caratheodory C (1909) *Untersuchungen über die Grundlagen der Thermodynamik*, Math. Annalen, **67**
25. Planck M (1926) *Über die Begründung des zweiten Hauptsatzes der Thermodynamik*, Sitzungsberichte der Preußischen Akademie der Wissenschaften der mathematisch-physikalischen Klasse, p. 453-463, included in Planck M (1958) *Physikalische Abhandlungen und Vorträge*, Vol. II, S. 618-628, Vieweg Braunschweig
26. Maxwell JC (1871) *Theory of Heat*, Longmans Green & Co, London
27. Boltzmann L (1872) *Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen*, Wien. Sitzungsber. II **66**, 275
28. Poincaré H (1890) *Sur le problème des trois corps et les équations de dynamique*, in Acta math. **13**
29. Nietzsche W (1926) *Die Ewige Wiederkunft*, in *Der Wille zur Macht*, Gesammelte Werke Nr. 19, München
30. Boltzmann L, Vorlesungen über Gastheorie II Teil, J. A. Barth, Leipzig (1898)
31. Boltzmann L, Bemerkungen über einige Probleme der mechanischen Wärmetheorie, Wien. Sitzungsber. II, **75**, 62 (1877)
32. Planck M (1968) *Das Gesetz der schwarzen Strahlung*, Dokumente der Naturwissenschaft, Bd. 9, Editor Hermann A, Battenberg München
33. Zermelo E (1896) *Über einen Satz der Dynamik und die mechanische Wärmelehre*, Wied. Ann. **57**, 485
34. Zermelo E (1897) *Über mechanische Erklärungen irreversibler Vorgänge. Eine Antwort auf Hrn. Boltzmann's "Entgegnung"*, Wied. Ann. **60**, 392
35. Boltzmann L (1896) *Entgegnung auf die Wärmetheoretischen Betrachtungen des Hrn. E. Zermelo*, Wied. Ann. **57**, 773
36. Boltzmann L (1897) *Zu Hrn. Zermelos Abhandlung "Über mechanische Erklärungen irreversibler Vorgänge"*, Wied. Ann. **60**, 776
37. Müller I (1994) *Grundzüge der Thermodynamik*, Springer Berlin
38. Müller I, Ruggeri T (1993) *Extended thermodynamics*, Springer Tracts in Natural Philosophy Vol. 37, Springer Berlin
39. Colemann BD, Noll W (1963) *The thermodynamics of elastic materials with heat conduction and viscosity*, Arch. Rational Mech. Anal., **13**
40. Grad H (1958) *Principles of the kinetic theory of gases*, Handbuch der Physik, XII, Springer Berlin
41. Dreyer W, Strehlow P (1993) *Quantenthermodynamik und ihre Bedeutung für thermische Präzisionsmessungen*, Mitteilungen für die Physikalisch Technische Bundesanstalt
42. Planck M (1912) *Theorie der Wärmestrahlung*, J. A. Barth, Leipzig (1966)
43. Witt A (1993) *Unterdrückte Entdeckungen und Erfindungen* , Ullstein Book Nr. 34942, Berlin
44. Müller I (1962) *Durch eine äußere Kraft erzwungene Bewegung der mittleren Masse eines linearen Systems von N durch Federn verbundenen Massen*, Diploma thesis, Inst. f. Th. Physik, TH Aachen
45. Weiss W, Müller I (1995) *Light scattering and extended thermodynamics*, Continuum Mech. Thermodyn. **7**, 1-55

46. Maxwell C (1866) *On the dynamical theory of gases*, Philosophical Transactions, Vol. CLVII
47. Maxwell C, *Final equilibrium of temperature*, supplement to [46], dated December 7, 1866
48. Boltzmann L (1876) *Über das Wärmegleichgewicht von Gasen, auf welche äußere Kräfte wirken*, Wien. Sitzungsber. II **72**, 427
49. Boltzmann L (1876) *Über die Aufstellung und Integration der Gleichungen, welche die Molecularbewegung in Gasen Bestimmen*, Wien. Sitzungsber. II **74**, 503
50. Loschmidt J (1876) *Über den Zustand desWärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft I*, Wien. Sitzungsber. II, **73**, 128
51. Loschmidt J (1876) *Über den Zustand desWärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft II*, Wien. Sitzungsber. II, **73**, 366
52. Loschmidt J (1877) *Über den Zustand desWärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft III*, Wien. Sitzungsber. II, **75**, 287
53. Loschmidt J (1877) *Über den Zustand desWärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft IV*, Wien. Sitzungsber. II, **76**, 209
54. von Dallwitz-Wegner R (1923) *Die atmosphärische Temperaturabnahme nach oben und ähnliche Erscheinungen als Wirkung der Schwerkraft, der Sama-Zustand der Materie*, Z. Physik **15**, 280
55. von Dallwitz-Wegner R (1923) *Der Zustand der oberen Schichten der Atmosphäre*, Z. Physik **14**, 296
56. Ehrenfest P (1923) *Ein alter Trugschluß betreffs des Wärmegleichgewichtes eines Gases im Schwerefeld*, Z. Physik **17**, 421
57. Trupp A (1996) *Energy, Entropy - On the occasion of the 100th anniversary of Josef Loschmidt's death: Is Loschmidt's greatest discovery still waiting for its discovery?*, Internet, http://users.aol.com/atrupp/
58. Tolman RC, Ehrenfest P (1930) *Temperature equilibrium in a static gravitational field*, Phys. Rev. **36**, 1791
59. Eckart C (1940) *The thermodynamics of irreversible processes III: Relativistic theory of the simple fluid*, Phys. Rev. **58,** 919
60. Bekenstein JD (1973) *Black holes and entropy*, Phys. Rev. D, **7**, 2333
61. Davis PCW (1977) *The thermodynamic theory of black holes*, Proc. R. Soc. Lond. A., **353**, 499
62. Wien W (1894) *Temperatur und Entropie der Strahlung*, Wied. Ann. **52**, 132
63. Planck M (1900) *Ein vermeintlicher Widerspruch des magnetooptischen Faraday-Effektes mit der Thermodynamik*, Verh. d. Deutsch. Phys. Ges. **2**, 206
64. Wien W (1900) *Zur Theorie der Strahlung schwarzer Körper*. Kritisches, Ann. d. Phys **3**, 530
65. Planck M (1900) *Kritik zweier Sätze des Hrn. W. Wien*, Ann. d. Phys. **3**, S 764
66. Planck M (1900) *Entropie und Temperatur strahlender Wärme*, Ann. d. Physik **1**, 719
67. von Laue M (1906) *Zur Thermodynamik der Interferenzerscheinung*, Ann. d. Phys. **20**, S.365
68. von Laue M (1907) *Die Entropie von partiell kohärenten Strahlenbündeln*, Ann. d. Phys. **23**, S.1