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José María Martín-Olalla and Alfredo Rey de Luna

Departamento de Física de la Materia Condensada, Universidad de Sevilla, Ap. Correos 1065, E-41080 Sevilla, Spain

E-mail: olalla@us.es

Abstract
We revisit the relationship between the Nernst theorem and the Kelvin–Planck statement of the second law. We propose that the exchange of entropy uniformly vanishes as the temperature goes to zero. The analysis of this assumption shows that is equivalent to the fact that the compensation of a Carnot engine scales with the absorbed heat so that the Nernst theorem should be embedded in the statement of the second law.

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1. Introduction

The classical formulation of the Kelvin–Planck statement of the second law reads: [1, p 89]

> it is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir.

Some other, essentially equivalent formulations of the law are possible—Thomson (later Lord Kelvin) [2], Clausius [3] and Carathéodory [4] statements—but, for our purpose, we will refer to the formulation posed above. Essentially the statement requires the presence of another reservoir.

The development of the law needs the concept of 'working fluid', the substance that undergoes the cyclic process. The properties of the working fluid are usually discarded because the initial and final state of the fluid coincides and 'it has done service only as a transmitting agent in order to bring about the changes in the surroundings' [1, p 68]. Nonetheless, the fluid *must* be able to do 'service' in the way required.

In this paper, we show that a general property of the matter will restrict the ability of working fluids to perform cycles, thus restricting what the Kelvin–Planck statement allows.

We show that, in fact, such a restriction follows from a comprehensive interpretation of the statement posed above.

The general property we are speaking about is nowadays known as the third law of thermodynamics. The necessity and character of this law have been a matter of discussion from the early years of the 20th century. Some chemical problems led Nernst [5, 6] to discover his *heat theorem* which reads [6, p 85]:

> in the neighbourhood of the absolute zero *all* processes proceed without alteration of entropy.

The theorem—which classically does not follow from the Kelvin–Planck statement [7, 8]—is supported by a formidable array of experimental data. We choose this older, though very valuable, version for reasons that are disclosed in section 3 but we see no particular reason for this statement to have been forgotten, other than it refers to properties of processes rather than to properties of systems as is nowadays stated [9–13].

Nernst derived the theorem from two quite general observations. The first is the so-called principle of unattainability of the zero isotherm, which recalls the fact that no process can diminish the temperature of a system to the absolute zero. The second is the fact that the specific heat of substances goes to zero as the temperature goes to zero.

It should be acknowledged that Planck [1] noticed that these observations should have led to a 'more comprehensive' conclusion: 'as the temperature diminishes indefinitely the entropy of a chemical homogeneous body of finite density approaches indefinitely to a definite value, which is independent of the pressure, the state of aggregation and of the special chemical modification.' The Planck formulation avoids the fact that $\Delta S \to 0$ while $S \to -\infty$ as $T \to 0$ and thus expresses that the absolute value of the entropy is bounded in the absolute zero.

Yet, our work is just related to the analysis of ΔS since it just deals with the analysis of the conversion of heat into work. This problem is insensitive to a translation of the value of the entropy and, thus, Planck's formulation lies out of our scope of interest. The same can be said about the vanishing of the specific heats.

Modern approaches and presentations of the third law of thermodynamics usually relate it to the microscopic properties of systems under consideration [14–18]. Some efforts have also been made to clarify its macroscopic meaning [19–25].

The goal of this paper is a revision of the mathematical description of the statement of the Nernst theorem posed above as well as its physical consequences. We study pure macroscopic observations in the field of low-temperature physics. In so doing, no hypothesis about the constitution of the systems under study will be considered.

Also, an energetic analysis of the consequences of the statement posed above is an aim of this paper. In brief, the simplest, most efficient engine contains two processes in which entropy is altered. This type of process is restricted at the neighbourhood of absolute zero by the Nernst theorem; we will prove that such a restriction will lead to a further condition that any engine must satisfy.

2. Limitations to the description of the Nernst theorem

The classical formulation of the Nernst theorem reads [9]: 'the change in entropy associated with any isothermal process between two states of a system in internal equilibrium vanishes in the limit of zero temperature,' which is usually translated into the mathematical condition:

$$\forall x_1 x_2 \in \mathcal{D} \quad \lim_{T \to 0^+} [S(T, x_1) - S(T, x_2)] = 0 \tag{1}$$
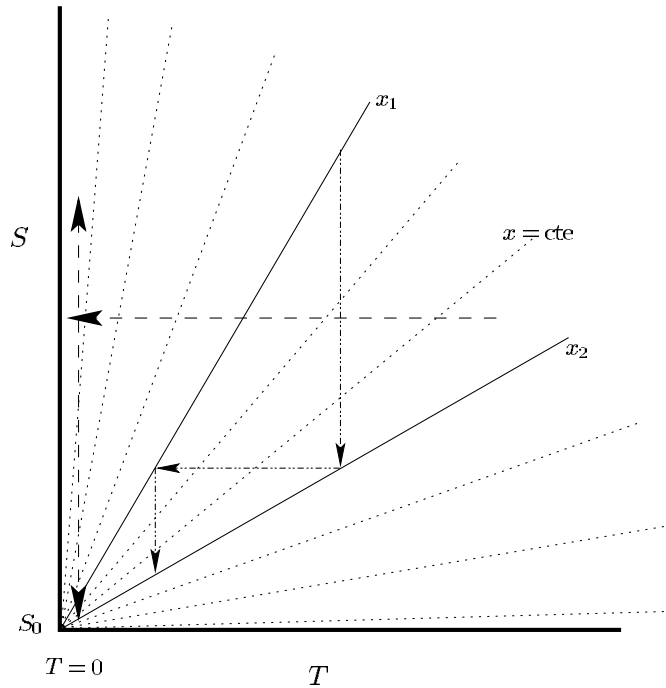
Figure 1. T–S plot for the model equation (2). Iso-x lines are depicted. The unattainability statement and equation (1) are satisfied for fixed x_1 and x_2. Yet an isentropic process (horizontal left arrow) diminishes the temperature of the system arbitrarily. Also, any alteration of entropy is possible in the neighbourhood of $T = 0$ (vertical double arrow) provided that x changes appropriately.

where x is any mechanical variable such as volume, pressure or magnetic field and $\mathcal{D} \subseteq \mathbb{R}$ is its domain of definition[1].

Landau and Lifshitz [10] showed the importance of keeping x_1, x_2 fixed in equation (1). Otherwise, they said, if, for instance, x_1 goes to infinity, the theorem may not be valid. In general, it could be said that the description works fine if the values of x are indeed fixed, but there are problems when looking for double limits of the form $T \to 0$ and $x \to \infty$.

An academic example of this problem is provided by the following naive model

$$S(T, x) = S_0 + \chi T x^g \implies S(T, x_1) - S(T, x_2) = \chi T \left(x_1^g - x_2^g\right) \tag{2}$$

with $x \in \mathbb{R}^+$. In this expression, χ is a positive constant that fits the dimensions of the model. Notice that equation (2) satisfies equation (1) but the double limit $T \to 0$, $x \to \infty$ depends on the path achieved. Figure 1 depicts a T–S plot for a system satisfying equation (2).

The model does not fulfil the unattainability statement. First, it is true that for fixed x_1 and x_2 the zero isotherm is unattainable [13]; this proposition is essentially equivalent to equation (1). Yet, there is no need to do so if we want to achieve the neighbourhood of the zero isotherm and it is also true that any isentropic path is endless for that model as, letting $g > 0$ and by increasing indefinitely the mechanical parameter, the temperature is indefinitely decreased to zero in a single step through $T x^g = \text{cte}$. The 'unattainability' of the zero isotherm would be a matter of practical limitations—how to get an infinite x—rather than a fundamental restriction posed by a law of nature; strictly speaking, the absolute zero is here attained asymptotically.

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[1] Nernst himself clothed equation (1) through the statement posed in section 1 [6, p 85].

Finally, neither does the model accomplish the words given by Nernst; see section 1. No matter how close to zero the temperature can be, *any alteration* of entropy is possible provided that the mechanical variable increases sufficiently.

The ideal gas behaves similarly to that model. A classical description of the particles leads to an entropy with no lower bound and which does not accomplish the Nernst theorem. On the contrary, a quantum description of the problem leads to [10, 15, 18] equation (2) where x is the volume and $g = 2/3$ for fermions. A deep analysis of the model shows that the quantum or classical description is driven by the condition [10, 14]

$$\frac{V}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \gg 1$$

known as the 'classical limit'. Here N is the number of particles, $\hbar$ is the Planck constant, m is the particle mass and k is the Boltzmann constant. Thus, the competition between $T \to 0$ and $V \to \infty$ is again crucial. It is likely that these contradictions are due to the fact that interactions are unavoidable at the very limit $T \to 0$ so that microscopically ideal models may not be reflecting the array of data on macroscopic systems [14].

We have shown then that a model satisfying equation (1)—the classical description of the Nernst theorem—does not lead to the unattainability statement. Even worse, it does not fit the words of Nernst. Thus, further assumptions are required for a comprehensive and accurate mathematical description of the empirical laws observed at very low temperatures.

3. The Nernst theorem as a uniform limit

The mathematical description of the statement of the Nernst theorem posed in section 1 is improved by considering the following *hypothesis I*: *the isothermal exchange of entropy is* uniformly *vanishing as the temperature goes to zero*

$$\forall \epsilon > 0 \quad \exists \delta(\epsilon) > 0 : \ T < \delta \Rightarrow |S(T, x_1) - S(T, x_2)| < \epsilon. \tag{3}$$

The key question of the 'uniform convergence' is that [26] the *same* $\delta(\epsilon)$ fits *for any* x_1, x_2 belonging to $\mathcal{D}$. It is straightforward that equation (3) matches the statement posed in section 1. We will argue that it is the best choice to express mathematically that proposition.

The Nernst theorem is classically supposed to be restricting the functional dependence of isothermal exchange of entropy $\Delta S = S(T, x_2) - S(T, x_1)$ on T so that it converges to zero at the absolute zero. The 'uniform' condition, here presented, essentially means that no value of x can challenge this convergence. That is, no accidental divergence can possibly occur for a given value of x in the neighbourhood of $T = 0$. In this way, the Nernst theorem would also restrict the functional dependence of $\Delta S(T, x)$ on x.

3.1. Role of x

If hypothesis I is taken into account, the mechanical variable plays no role in the description of the problem. This is the primary consequence of the uniform convergence since given ϵ then δ is just a property of the system under consideration regardless the value of x. The reader should notice that this is a burden in the formulation of the Nernst theorem as a law of nature which does not depend on the configuration of the system under consideration.

In the classical description of the theorem equation (1), δ is a function of ϵ, x_1, x_2 so the mechanical variable does play a role in the description of the problem. Although this role is usually discarded it is of the most importance when considering, for instance, double limits.

3.2. Existence of inaccessible regions in a T–S plot

Equation (3) ensures that $S(T, x_1) - S(T, x_2)$ is bounded in the neighbourhood of $T = 0$ so that it has a supremum:

$$\sigma(T) = \sup_{x \in \mathcal{D}}\{S(T, x_1) - S(T, x_2)\}. \tag{4}$$

The function σ exists and is a monotonically increasing function at least in the neighbourhood of $T = 0$. The function depends on the thermophysical properties of the system under consideration. In the following, we describe the relevant properties of the function in that neighbourhood.

Now, we consider a system compliant with hypothesis I whose equilibrium state is defined by a given temperature and a given mechanical configuration. The entropy of this state equals $S(T, x)$. Let us suppose that the entropy is isothermally increased, the existence of σ ensures that the final entropy cannot exceed $S(T, x) + \sigma$. The same argument applies for a process that decreases entropy. Hence, $S(T, x)$ is an upper and lower bounded function of x for a given temperature and the following functions exist:

$$S_{\max}(T) = \sup_{x \in \mathcal{D}}\{S(T, x)\} \qquad S_{\min}(T) = \inf_{x \in \mathcal{D}}\{S(T, x)\}. \tag{5}$$

Since the stability condition $(\partial S/\partial T)_x > 0$ holds in the neighbourhood of $T = 0$ (except perhaps at $T = 0$) the preceding functions are increasing functions of T so that states of the type $\{T, S > S_{\max}(T)\}$ and $\{T, S < S_{\min}(T)\}$ cannot exist. Hence, equilibrium states do not fill the plane T–S and two boundaries arises from the fulfilment of the Nernst theorem as an uniform condition.

In more detail it could be said that one of the goals of the third law is to ensure that the entropy has a single value S_0 in the neighbourhood of zero isotherm [9]. In the classical formulation of the theorem, points of the type $\{T = 0, S \neq S_0\}$ are excluded [9, figure 23.5] in a T–S plot (these points are shown by the symbol $\times$ in figure 2). From a physical point of view 'when a certain point is excluded, we must demand that the same must be true about a small region surrounding the point' [4], [27, p 236][2]. On the contrary, if a neighbourhood of $\{T = 0, S \neq S_0\}$ could be reached, the exclusion of those—isolated—points would be fictitious.

Thus, the plot T–S (see figure 2) consists in the region I of allowed values of $\{T, S\}$, and the forbidden region II. The existence of region II is a goal of hypothesis I. The boundaries, which may or may not be physically accessible, do not coincide with the axis $T = 0$. In figure 2 and in the preceding discussion we have made use of the Planck hypothesis for the purpose of clarity. The same argument would apply if S_0 comes down to $-\infty$ and, simultaneously, ΔS is vanishing.

The following issue is known, however hypothesis I enriches and clarifies its meaning.

3.3. Processes that come to an end (unattainability statement)

Let us consider the isentropic process $S = \Sigma_0$ starting at some temperature so that $S_{\min} < \Sigma_0 < S_{\max}$. The process will go on until the temperature T_1 defined by $S_{\max}(T_1) = \Sigma_0$ is attained. This temperature is non-zero.

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[2] Carathédory is here speaking about the adiabatic inaccessibility and he is preparing his celebrated axiom II. It is worth noting that the axiom literally states that '(· · ·) there exist states that cannot be approached *arbitrarily close* by adiabatic process' instead of the bare phrase, 'states that are *inaccessible* by adiabatic process.' The concept 'arbitrarily close' or 'neighbourhood' will play a leading role in the following discussion.
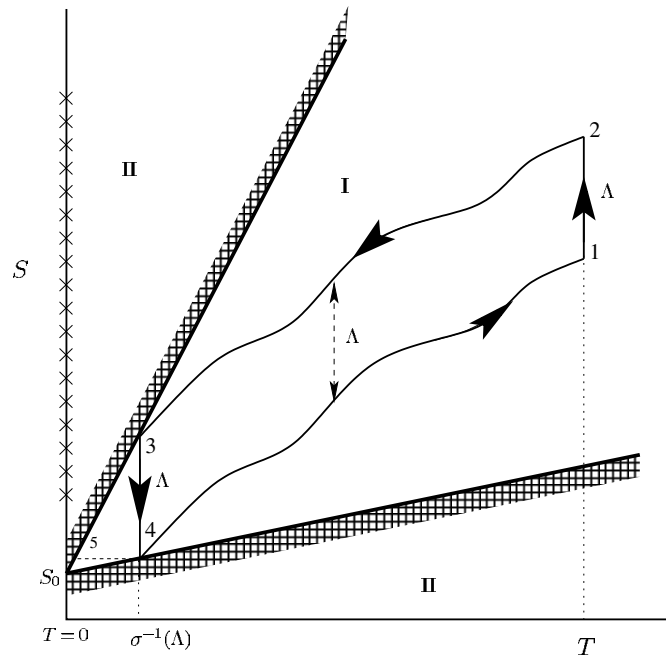
Figure 2. The T–S plot and the Nernst theorem. The symbol $\times$ represents the points classically excluded by the theorem [9, figure 23.5]. A more comprehensive analysis of the theorem reveals that there exist a region I, whose points represent equilibrium states, and a region II, which does not do so. The cycle 1–2–3–4–1 is an engine consisting of two isotherms 1–2 and 3–4, and two processes, 2–3 and 4–1, which differ just in a shift of entropy $S' = S + \Lambda$. Area 1–2–3–4–1 is equal to $\Lambda[T - \sigma^{-1}(\Lambda)]$ as in a Carnot engine. The essential of this picture is valid even if $S_0 \to -\infty$ while $\Delta S \to 0$.

Here we may decrease the entropy of the system isothermally until the condition $\Sigma_1 = \Sigma_0 - \sigma(T_1) = S_{\min}(T_1)$ is achieved. At that point, an isentropic process will cool the system down to the temperature T_2 defined by $S_{\max}(T_2) = \Sigma_1$.

The endless staircase process that goes to absolute zero is then defined.

3.4. Vanishing of the thermal expansions coefficients

The thermal coefficients are related to the derivative $(\partial S/\partial x)_T$ through Maxwell's relations [9]. From equation (3) we derive the vanishing of such a derivative since:

$$\lim_{T \to 0} \left(\frac{\partial S}{\partial x} \right)_T = \lim_{T \to 0} \lim_{x' \to x} \frac{S(T, x') - S(T, x)}{x' - x} \qquad \forall x \in \mathcal{D}.$$

If this double limit exists, it can be computed in whichever order. By taking first $T \to 0$ and invoking equation (3) we has, of necessity [9]:

$$\lim_{T \to 0} \left(\frac{\partial S}{\partial x} \right)_T = 0 \qquad \forall x \in \mathcal{D}. \tag{6}$$

Unlike the properties of sections 3.1 and 3.2, which are mathematical propositions, it should be pointed out that the properties of sections 3.3 and 3.4 are trends [6, 9] amply confirmed by experiment providing a support for the hypothesis. Yet, the most important consequence of the hypothesis relates it to the problem of the conversion of heat into work; this is considered in detail in the following section.

4. The Nernst theorem and the continuous production of work

In section 3 we have shown that the Nernst theorem forces the existence of forbidden regions in a T–S plot. We now derive the consequences for the continuous production of work, bearing in mind that the uniformity condition introduced in section 3 means that x plays no role in the problem.

Let us now consider the following question. We wish to build up an engine which produces mechanical work W by using a given working fluid that draws a given amount of heat Q from a reservoir of a given temperature T; *what is the minimal amount of heat $Q'_{\min}$ that is to be taken up to the cold reservoir?*[3]

The classical reading of the Kelvin–Planck statement would just say that the heat taken up at the cold reservoir (hereafter called 'compensation') must be non-zero $Q' \neq 0$. It then seems that, as far as this statement is concerned, a negligible Q' would suffice. Thus, $Q'_{\min} = 0^+$, i.e. arbitrarily close to zero but positive and non-zero. The answer is independent from Q, T and the working fluid and comes from the fact that we feel free to place a two-reservoir engine in a T–S plot since there happens to be no other restriction.

A machine having $Q'_{\min} = 0^+$ would result in an efficiency $\eta = W/Q$ as close to unity as desired; this most efficient engine has never been built. We now put forward the fact that this is due to fundamental properties of matter despite practical limitations to achieving such an engine.

As a general rule, σ (see equation (4)) is non-zero for non-zero temperatures and from equations (3) and (4) we obtain

$$\forall \epsilon > 0 \quad \exists \delta(\epsilon) > 0 : \quad T < \delta \implies \sigma(T) < \epsilon \tag{7}$$

i.e. $\lim_{T \to 0^+} \sigma(T) = 0$.

In equation (7) there is no need to call for absolute value delimiters since both T and σ are positive magnitudes. From equation (7) and the preceding argument, the existence of the inverse function $\sigma^{-1}(\Lambda)$ is straightforward. In fact, the inverse function is nothing else but a suitable representation for the parameter $\delta(\epsilon)$. The inverse function gives the temperature at which the width in entropy of the accessible states equals Λ. This temperature also depends on the thermophysical properties of the system under consideration.

Now, let us consider again the question posed at the beginning of this section but we now consider that the Kelvin–Planck statement and the Nernst theorem apply, as stated in section 1. Hence, the restrictions posed in section 3, shown in figure 2, are valid. The working fluid undergoes a cycle that is extracting an amount of entropy $\Lambda = Q/T$ from the hot reservoir. In doing so, it is necessary that $\Lambda < \sigma(T)$.

Now, the entropy should be being deposited into the cold reservoir which would receive an amount of heat Q'. To achieve the maximum efficiency, the temperature of the cold reservoir must be the coldest temperature able to exchange with the working fluid that amount of entropy. Following the preceding paragraphs, the minimal temperature is given by $\sigma^{-1}(\Lambda)$ which is a property of the fluid under consideration. Thus,

$$\forall Q \neq 0, T \neq 0 : \frac{Q}{T} = \Lambda < \sigma(T) \implies \exists \sigma^{-1}(\Lambda) : Q' \geqslant \Lambda \times \sigma^{-1}(\Lambda) = Q'_{\min}. \tag{8}$$

This most efficient engine is depicted in figure 2 by the cycle 1–2–3–4–1, which consists of two isotherm and two processes that differ in a shift of entropy; exchanges of energy and

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[3] This question inspects the behaviour of W, or Q', once the hot reservoir and the absorbed heat are fixed. It is also customary to inspect the behaviour of W once the hot and cold reservoirs are fixed. This problem is related to the concept of irreversibility [10] and lies out of the scope of the following discussion.
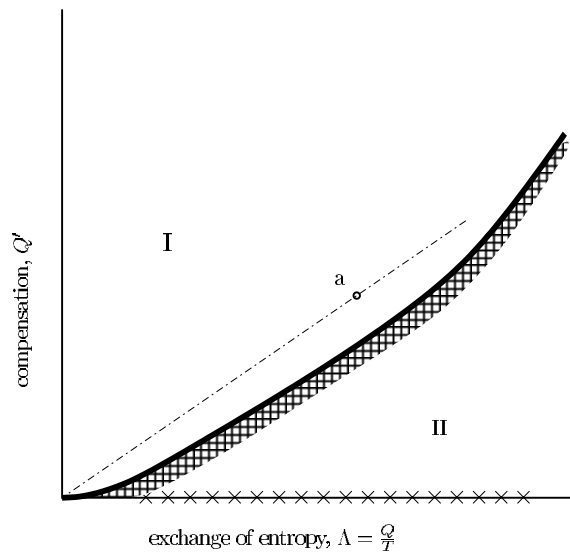
Figure 3. Plot of $\Lambda - Q'$ for a given working fluid. A point of region I, say a, represents a set of engines each having the same Q' and Λ and the same temperature of the cold reservoir (the slope of the straight line). The thick line, which depends on the working fluid, represents equation (8) and comes to $\{0, 0\}$ with zero slope. For the working fluid under consideration, it is impossible to build an engine that enters in region II. The symbol $\times$ represents the restriction posed by the classical reading of the Kelvin–Planck statement.

entropy in 2–3 cancel with those of 4–1 so the reservoirs needed for these two processes play no role in the problem[4]. The performance of work equals $W_{max} = \Lambda \times [T - \sigma^{-1}(\Lambda)]$.

It is very noticeable that the value of Q'_{min} is now a function of the parameters of the problem: Q, T and the working fluid which enters through σ^{-1}. Moreover, the minimal compensation is a function of the exchange of entropy Λ.

Although the particular value of Q'_{min} depends on the thermophysical properties of the working fluid, it is a fact worth noting that, as a general rule, Q'_{min} is never arbitrarily close to zero for a given Λ since, according to the Nernst theorem, σ^{-1} is not arbitrarily close to zero either (see figure 2).

The universal resemblance of equation (8) allows us to outline the plot $\Lambda - Q'$ (see figure 3). Note that, in the context of the classical reading of the Kelvin–Planck statement, this plot would have no restriction other than the exclusion of the points of the type $\{\Lambda \neq 0, Q' = 0\}$; these points are shown in the figure by the symbol $\times$. Now, if we take into account the Nernst theorem it is clear that points of the type $\{\Lambda, Q' < Q'_{min}(\Lambda)\}$ should also be excluded. The points define a region whose boundary is given by equation (8); the analogy between regions I and II, and the boundary of figure 2 and those of figure 3 is immediate. From the Nernst theorem it is easily proven that Q'_{min} goes to zero with zero slope as Λ goes to zero. Summarizing the meaning of figure 3 it should be stressed that the Nernst theorem excludes a region around those points actually excluded by the classical reading of

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[4] It would be possible to decrease Q' by considering the cycle 1–2–3–5–4–1 (see figure 2) because entropy will be deposited to colder reservoirs, but the condition of two reservoirs is broken. However, in that case, the compensation is equally expressed by $\sigma''\Lambda$ where σ'' is an unknown temperature ranging between T_5 and $T_4 = \sigma^{-1}(Q/T)$. The essential of the following discussion also applies to this compensation.

the Kelvin–Planck statement. This is in agreement with Carathéodory's argument posed in section 3.

The limit $\Lambda \to 0^+$ is the unique possibility to obtain $Q'_{\min} \to 0^+$. In this case, taking T as a bounded, constant parameter, it is clear that Q will also vanish and, as an ultimate consequence, W will also vanish. Hence

$$Q' \to 0^+ \Longrightarrow W \to 0^+. \tag{9}$$

This proposition contains the essence of the Nernst theorem. Its dramatic meaning is best viewed noticing that $Q' \to 0^+$ and $\eta \to 1^-$ are equivalent. This then means that *as the most efficient engine is achieved, the delivery of work is decreasing to zero.*

It should be pointed out once again that, in the preceding discussion, x plays no role and it is in this sense that the restrictions figure 3 and equation (9) are *universal*. This feature comes from the property of uniformity. On the contrary, if the Nernst theorem is just considered as a limit, without the requirement of uniformity, then equation (9) and figure 3 would be just valid for transitions between two given values of x; see [9, figure 23.9] and [23]. Therefore, equation (1) does not lead to any proper restriction, as the boundary of figure 3 will come arbitrarily close to the restriction posed by the classical reading of the Kelvin–Planck statement provided that we consider the appropriate values for x_1 and x_2. Hence, the improvement of an engine would be a matter of practical limitations if equation (1) were valid[5].

5. The Nernst theorem and the statement of the second law

Section 4 clearly shows that the Nernst theorem is restricting the conversion of heat into work in a way which is independent from the mechanical configuration of the system. It should be desirable to link it to the Kelvin–Planck statement of the second law.

One of the most important results of section 4 is the leading role played by Q', the compensation, in the problem of the conversion of heat into work. This importance comes from the fact that its minimum value is universally expressed by equation (8).

From a historical point of view, the role of the cold reservoir was the key of the second law. The first known statement of the law, due to Kelvin [2], stated that it is impossible to build an engine that both produces work and cools the coldest of the available reservoirs, no matter what happens to hotter reservoirs (see figure 4).

Planck simplified the statement by noticing that it is impossible to build an engine that performs work by cooling just one reservoir [1]. In that sense, a cold reservoir is to be heated (compensation) in some amount (see figure 4). Yet he said nothing about the 'size' of the compensation so that we hope it might be negligible; this is the 'classical' reading of the statement that has prevailed from the beginning of the statement.

Furthermore, if the Nernst theorem is taken into account through hypothesis I, we obtain the ultimate restriction. A minimal compensation is given by the properties of the working fluid and the exchange of entropy (see equation (8) and figure 4): *if you wish to transform a finite amount of heat into work, you must* certainly *pay a tax (a compensation), namely the tax does not become finiteless at your willing.* The emphasized proposition is an informal statement for equation (9).

The reader should notice that, in fact, equation (9) is something more than the bare statement of the Nernst theorem since it also recalls the Kelvin–Planck statement. This is the dome that crowns the leitmotif of the principles of thermodynamics by putting forward the ultimate restriction on Q'. In fact, if the relation were clothed in a negative way, the reader

[5] If the working fluid behaves like equation (2), the engine could always be improved by obtaining arbitrarily large values of x.
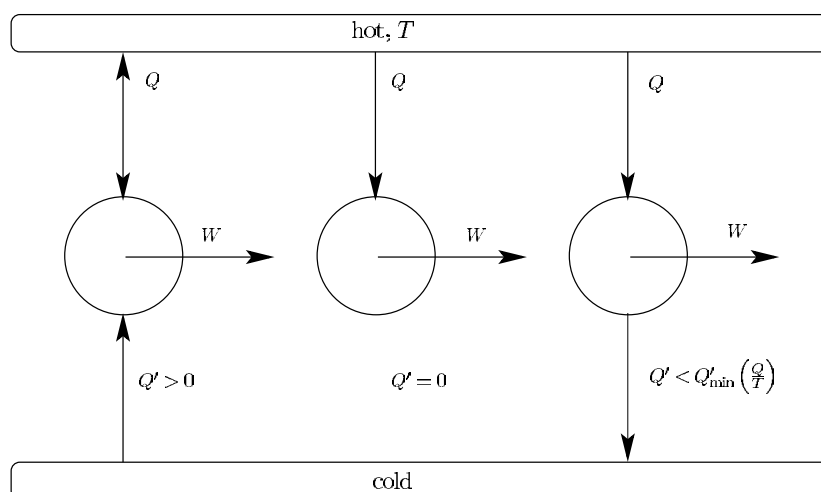
Figure 4. The staircase of the statements of the second law. The reader should notice the restrictions on the compensation that arises from the violations of the statements. From left to right, we have a violation of the Kelvin statement, of the classical reading of the Kelvin–Planck statement, and of a 'comprehensive' reading of the Kelvin–Planck statement. In this last case, Q'_{min} is given by equation (8).

would have found a statement very much like any of the second law: *it precludes delivering a* finite *work without a* finite *compensation*.

6. From the Kelvin–Planck statement to the Nernst theorem

The preceding sections analysed the Nernst theorem through hypothesis I, putting forward its close relation to the problem of the conversion of heat into work. Here we want to do the reverse: starting at the Kelvin–Planck statement, upon which assumption hypothesis I is derived.

In our opinion, the classical reading of the Kelvin–Planck statement could be said to be 'crude' in the sense that the cause (heat absorbed from the hot reservoir) and the unavoidable effect (the minimal compensation) has been taken as uncoupled since the early stage of thermodynamics. A more comprehensive reading of the statement of the second law would have led to some coupling between W_{max} or Q'_{min} and Q since a finiteless absorbed heat is necessary to obtain a finiteless compensation; see equation (8) and figure 2. We now put forward the fact that this hypothesis, called *hypothesis II*, suffices for the Nernst theorem:

> *the compensation of a Carnot engine approaches indefinitely zero* only if *the heat absorbed from the reservoir is vanishing*.

The significance of the hypothesis would be revealed by the conclusions that it draws, however the reader should not conclude that hypothesis II is additional to the Kelvin–Planck statement since it is embedded in its words. The point is the meaning of the word 'effect' that appears in the statement. We can explicitly obtain hypothesis II by changing 'effect' into 'finite effect' in the statement so that any 'finite' absorbed heat necessarily leads to a 'finite' compensation. But, in fact, any effect is actually finite so that the modification would be a pleonasm.

The fact that the hypothesis leads to the Nernst theorem is surprisingly straightforward. Notice that the compensation of an engine equals $Q' = T' \times \Lambda$ where T' is the temperature of the cold reservoir and Λ is the exchange of entropy. The magnitude becomes zero (1) if T' goes to zero regardless Λ or (2) if Λ goes to zero regardless T'. The hypothesis excludes option (1), i.e. it excludes any alteration of entropy in the neighbourhood of absolute zero. Hence, the Nernst theorem as stated in section 1 and as analysed in section 3 comes of necessity.

It is then concluded that hypotheses I and II are equivalent propositions so that the Nernst theorem ultimately follows from a comprehensive reading of the Kelvin–Planck statement through hypothesis II[6]. This proposition is valid as far as systems suitable to be working fluids of engines are considered.

7. Discussion and conclusion

In 1909, Carathéodory [4], following a suggestion by Born, successfully translated the classical statements of the second law, which deal with the problem of production of work, into a statement which refers to physical properties of an isolated system. This work introduces the reverse trip for the Nernst theorem. The theorem has been supposed to deal with the properties of systems in the neighbourhood of $T \to 0$; the study here presented (see section 4, especially equations (8) and (9)) relates the theorem back to the problem of production of work. The theorem expresses a universal property of the continuous production of work.

The reader may ask which assumptions make the Nernst theorem independent from the Kelvin–Planck and which do not. The goal of the second law of thermodynamics is to restrict the continuous production of work putting forward the existence of a fundamental asymmetry: work is dissipated into heat but the reverse is not true. The goal enters by a statement which expresses, in words, a restriction. We have shown in this paper that the degree of restriction matters and has an influence on the properties of systems. The classical reading of the Kelvin–Planck statement assumes just that the compensation is non-zero. Upon this assumption the general properties of systems in the neighbourhood of $T = 0$ need to be summarized as an independent law. Yet, a comprehensive reading of the statement through the cautious hypothesis II presented in section 6 leads to some of these general properties: the unattainability statement and the vanishing of the expansion coefficients. We should again recall that the formulation presented here is insensitive to whether or not specific heats come to zero as the temperature comes to zero.

The new reading of the statement overcomes the embarrassing fact that W must differ from Q (to what extent?) by stating that they must do so in a measurable quantity which also depends on the working fluid which does play a role in the problem. The words of Carathéodory quoted in section 3 again make sense in this discussion: if the condition $W = Q$ is excluded, $W = Q^-$ should have been excluded as well[7].

Any exception to the hypotheses would result in a failure of the consequences quoted in sections 3.3 and 3.4: (a) an experiment that would allow $1/T$ to increase indefinitely; (b) an

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[6] Thus, the second law ensures that the entropy goes to a value which does not depend on x at the absolute zero. Its precise value, or whether this value is finite or infinite (Planck's formulation) is alien to this description since the second law just concerns variations of entropy.

[7] We present an analogy between the words of Carathéodory and the results of this work. It is not our wish to state that the former derives from the latter or conversely. It is a coincidence of sorts that both problems speak about the same law of nature.

experiment that would allow entropy to decrease indefinitely; or (c) a substance that would have non-zero thermal expansion coefficients[8].

It is out of the scope of this paper to describe the microscopic relevance of the hypothesis, i.e. to determine which kind of Hamiltonians (interactions) would lead to uniformly vanishing ΔS as well as their symmetry properties. Well-known models, especially ideal gases, do not satisfy the hypotheses presented here. However, the reader should not consider them as an 'exception' to the hypotheses since the hypotheses are grounded on experimental macroscopic basis and not on the analysis of microscopic models.

The relation between interactionless models and the Nernst theorem has been recently suggested [14, 17] and it seems that the role of interactions cannot be neglected in real systems at sufficiently low temperatures. The suggestion comes from the analysis of the independent spin system. The model does not satisfy the Nernst theorem since the ground state is degenerate. Yet, independent spin systems do not occur in nature since *real* solids always exhibit magnetic correlation and ordering at sufficiently low temperatures. The resulting ordering, usually a macroscopic new phase, either ferromagnetic or antiferromagnetic, would satisfy the Nernst theorem.

Quite the same analysis can be made on free particle systems. The reader should notice that the classical ideal gas allows us to envision a process of types (a) and (b); moreover it satisfies (c) in contradiction with the Nernst theorem. On their own, quantum ideal gases [10] obtain vanishing thermal expansion coefficients and preclude experiments of type (b) since entropy is necessarily a low bounded function. Yet, the quantum model still allows us to envision type (a) experiments which do not occur in nature and which do preclude the meaning of the Nernst theorem. Of course, in real systems 'ordering' does always occur and the settlement of condensed phases seems unavoidable.

It is then likely that interactionless models, either kinetic, magnetic or whichever, do not accurately describe the properties of *real* systems at sufficiently low temperatures since interactions cannot be neglected.

Acknowledgments

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[8] The reader should notice that the unattainability of the zero isotherm does not guarantee the Nernst theorem. The model $S(T, x) = \chi \log T \times (x + a)/(x + b)$ with $\chi, a \neq b > 0, x \in \mathbb{R}^+$ provides a mathematical example of system which precludes experiments (a) and (b) but fails to obey the Nernst theorem.

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