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Confusion and clarification: Albert Einstein and Walther Nernst's Heat Theorem, 1911–1916

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Abstract

This paper discusses the early history of Walther Nernst's Heat Theorem and the first stages of its development into the Third Law of Thermodynamics. In addition to published papers, informal discussions were important in shaping the understanding of the meaning and validity of the Theorem. Special attention is given to the role of Albert Einstein in these discussions. As it turns out, Einstein played an important role in determining the limits of validity of the Heat Theorem.

Keywords: Heat Theorem; Third Law of Thermodynamics; Albert Einstein; Walther Nernst

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1. Introduction

Almost from the moment when Walther Nernst published the first formulation of his Heat Theorem in 1906 (Nernst, 1906), it has been surrounded by confusion and controversy. In spite of a series of publications in which Nernst presented what he claimed were proofs of the Theorem, many of his colleagues remained unconvinced and considered it an unproven or even unprovable hypothesis. What compounded the confusion was that the Theorem went through several successive reformulations and that it often remained unclear whether a new formulation was equivalent with the earlier one or whether a new element had in fact been introduced. Nernst himself contributed to this process, because of his habit of introducing hidden assumptions in his papers and making strong and sometimes unfounded pronouncements about the Theorem's meaning and its interpretation. It would take several decades before some degree of consensus was reached in the

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physics community and the Heat Theorem became the Third Law of Thermodynamics. Still, even now, most physicists will agree that the Third Law has a different, less fundamental status than the First or Second Laws.

The secondary literature on the history of the Third Law is scarce, and, as Erwin Hiebert has pointed out, a full history of the Third Law in all its aspects is long overdue.[1] An important contribution on the origins and the early history of the Heat Theorem is Diana Kormos Barkan's biography of Walther Nernst (Kormos Barkan, 1999), in which she puts Nernst's work in the broader context of his earlier research, rather than in the 19th-century tradition of thermochemistry.

What is still missing, however, is a full analysis of the way the Heat Theorem evolved after its inception, in particular, the various meanings and interpretations that it was given and its relation with classical thermodynamics and quantum theory. This paper is meant as a contribution to such a future analysis. It focuses on the contributions Albert Einstein made in the years 1911–1916 to the clarification of the meaning and the consequences of Nernst's Heat Theorem. I will in particular pay attention to discussions between Einstein and Nernst at the first two Solvay Congresses and to an exchange of letters between Einstein and Michael Polanyi.[2] I will show that Einstein played an important role in shaping his contemporaries' thoughts on the content and the implications of the Heat Theorem, and, perhaps more importantly, on its status within thermodynamics. In particular, Einstein's insistence on the impossibility to derive the Theorem from purely thermodynamical considerations was of great importance and has not been sufficiently noted in the historical literature. At the same time, this paper adds to the understanding of the history of the development of the Heat Theorem from a statement about the maximum work in chemical reactions to the now-familiar formulation in terms of the behavior of entropy at absolute zero.

To provide the necessary historical and physical context for the discussions of the Einstein–Nernst and Einstein–Polanyi controversies this paper starts with a section in which the physics of the Heat Theorem is introduced and its early history is sketched. The paper finishes with a brief overview of some major developments after 1916.

2. The Heat Theorem and its historical origin

2.1. Thermodynamics

From the second law of thermodynamics, it follows that the maximum external work that can be performed in a transformation at constant temperature (for instance, a chemical reaction) is given by the difference in the free energy $F = U - TS$ of the initial and final states. Consider a transformation from state 1 to state 2 at constant temperature and volume. If we use the thermodynamic relation

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{1}$$

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[1] See his review (Hiebert, 1960, p. 135). Other useful overviews are (Hiebert, 1978; Simon, 1956).

[2] There is also some correspondence between Einstein and Otto Stern from 1916 that touches on the Heat Theorem (see, Schulmann, Kox, Janssen, & Illy (Eds.), 1997, Docs. 191, 192, 198, 201, and 205). Since its main topic is the question whether mixed crystals can exist at absolute zero, however, I will not discuss these letters here.

the maximum work (or affinity) $A = F_1 - F_2$ takes the form

$$A = Q + T\left(\frac{\partial A}{\partial T}\right)_V, \tag{2}$$

where $Q = U_1 - U_2$ is the reaction heat. For transformations at constant pressure p, F has to be replaced by $G = U + pV - TS$ (the free enthalpy or thermodynamic potential), and Q by $U_1 - U_2 + p(V_1 - V_2)$, the enthalpy change. If we limit ourselves to condensed systems, so that both changes in volume and in pressure may be neglected, Eq. (2) can be written as

$$A = Q + T\frac{\mathrm{d}A}{\mathrm{d}T}, \tag{3}$$

which is known as the Gibbs–Helmholtz equation for the maximum work. In this equation the quantity Q can be determined from specific-heat measurements, because $\mathrm{d}Q/\mathrm{d}T$ is just the difference between the specific heats before and after the transformation. Thus, the equation would allow us in principle to calculate A and thus establish the direction in which a chemical reaction or any other transformation will proceed: the direction is always such that $A>0$.[3] In practice, there is a problem, however, which becomes clear if we integrate Eq. (3):

$$A = Q_0 - T\int_0^T \frac{Q - Q_0}{T^2}\,\mathrm{d}T + CT, \tag{4}$$

where C is a constant and the subscript zeroes refer to $T = 0$. Thus, A is only fixed by Q up to a term linear in T. This difficulty had been well-known to chemists from long before Nernst's days.[4]

Let us look somewhat closer at the properties of Eq. (3). If we want it to be well-behaved at absolute zero, $\mathrm{d}A/\mathrm{d}T$ has to remain finite. For $T = 0$, this gives

$$A_0 = Q_0. \tag{5}$$

It is also possible to find an explicit expression for C in terms of A: Eq. (4) implies

$$C = \lim_{T\to 0}\frac{A - Q}{T}, \tag{6}$$

which, together with (3) yields

$$C = \lim_{T\to 0}\frac{\mathrm{d}A}{\mathrm{d}T}. \tag{7}$$

Furthermore, Eq. (3) implies

$$\lim_{T\to 0}\frac{\mathrm{d}Q}{\mathrm{d}T} = 0, \tag{8}$$

or, in other words, at temperatures close to absolute zero the change in specific heats is constant for all transformations. In order to fix the integration constant, Nernst made

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[3] This condition takes the place of the older Berthelot principle $Q>0$, which implies that all chemical reactions are exothermic. As is shown below, Berthelot's principle is only valid at absolute zero.

[4] In his paper, Nernst does not use the above equation but simply points out that if $A = f(T)$ is a solution of (3), $A = f(T) + BT$ with B an arbitrary constant is a solution as well.

the following additional postulate:

$$\lim_{T\to 0}\frac{\mathrm{d}A}{\mathrm{d}T}=0, \tag{9}$$

or, in other words, he put the integration constant in Eq. (4) equal to zero. This is the Heat Theorem in its original formulation.

The theorem can be made plausible in the following way. At low temperatures A and Q approach each other as the temperature diminishes. Experimentally, it is found that Q tends to its limiting value in such a way that its derivative becomes smaller and smaller, so why would the same not hold for A as well?

At this point I briefly deviate from Nernst's paper to draw an important conclusion from the Heat Theorem, a conclusion that did not appear in the literature until much later.

Since

$$\frac{\mathrm{d}A}{\mathrm{d}T}=-\left(\frac{\partial\Delta F}{\partial T}\right)_V=\Delta S, \tag{10}$$

it follows that

$$\lim_{T\to 0}\Delta S=0. \tag{11}$$

Thus, at absolute zero all transformations are isentropic. Note that only entropy *changes* are considered and that the absolute value of the entropy is left unspecified. It is interesting that Nernst did not immediately notice this. A reason might be that it is experimentally very difficult to study chemical reactions close to absolute zero, and, as we will see below, Nernst had found a more accessible way to test his theorem experimentally.

2.2. *Implications*

The Heat Theorem in its original formulation has some important consequences in chemistry, as Nernst was quick to point out in (Nernst, 1906).[5] He considered a chemical reaction in the gaseous phase, symbolically written as

$$n_1A_1+n_2A_2+\cdots=n_1'A_1'+n_2'A_2'+\cdots\ . \tag{12}$$

(An example would be $2H_2+O_2=2H_2O$.) For an exothermic reaction the relation between the reaction heat Q and the reaction constant K is given by the Van 't Hoff equation for the reaction isochore:

$$Q=RT^2\,\mathrm{d}\log K/\mathrm{d}T. \tag{13}$$

It is known from experiments that the reaction heat does not depend very strongly on the temperature, so that it makes sense to write this quantity as a power series in T:

$$Q=Q_0+T\sum_i n_i\alpha_i+T^2\sum_i n_i\beta_i+\cdots\quad(i=1,\ldots). \tag{14}$$

(Note that for low temperatures, when higher powers of T can be neglected, the factor $\sum_i n_i\alpha_i$ is just the change in specific heats.) The Van 't Hoff equation can now

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[5] I am following here the slightly different approach Nernst took later in (Nernst, 1918).

be integrated:

$$\log K = -\frac{Q_0}{RT} + \frac{\sum_i n_i \alpha_i}{R} \log T + \frac{\sum_i n_i \beta_i}{R} T + \cdots + I. \tag{15}$$

Here α_i and β_i ($i = 1, \ldots$) are coefficients that are characteristic for the substances involved in the reaction and I is an undetermined integration constant.

The next step is to look at a system of saturated vapor in equilibrium with fluid. From the Clausius–Clapeyron equation for the vapor pressure curve, in combination with the ideal gas law, it follows that

$$\lambda = RT^2 \frac{\mathrm{d}\log p}{\mathrm{d}T}, \tag{16}$$

with λ the molar heat of evaporation. Like Q, this quantity can be written as a power series in T:

$$\lambda = \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3 + \cdots . \tag{17}$$

Combining (16) and (17), integrating and changing from p as variable to the molar density ξ (again using the ideal gas law) we find

$$\log \xi = -\frac{\lambda_0}{RT} + \left(\frac{\alpha_0}{R} - 1\right) \log T + \frac{\beta_0}{R} T + \cdots + c, \tag{18}$$

where the integration constant c is characteristic for the substance under consideration.

The final step is to make the connection with the maximum work and the Heat Theorem. It can be shown[6] that for the chemical reaction under consideration the maximum work becomes

$$A = RT\left(\sum_i n_i \log \xi_i - \log K\right). \tag{19}$$

If we replace $\log \xi_i$ by expression (18) and $\log K$ by expression (15), a power series in T results, in which the unknown constants c_i occur. By invoking the Heat Theorem in its form (9), however, these constants can be determined since according to the Theorem the power series for A should contain no terms linear in T. It is easily seen that this amounts to the relation

$$I = \sum_i n_i c_i. \tag{20}$$

As Nernst emphasizes, the importance of this result is that the unknown constant in Van ’t Hoff’s equation is now expressed as a sum of constants (dubbed the “chemical constants”) that are each characteristic for a specific substance and that can be experimentally determined, for instance from measurements of the vapor pressure curve of the substance in question. Thus, Eqs. (15), (18), and (19) together with condition (20), provide another method to calculate the affinity or the reaction rate of chemical reactions from experimental data such as vapor pressure curves and specific heats. In fact, in the remainder of the paper Nernst performs such a calculation for several different cases, the outcome of which is then compared with experimental data. It turns out that agreement is fair, which speaks in favor of the Heat Theorem.

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[6] See, for instance, (Nernst, 1898, Chap. IV.3).

So far, the emphasis in the discussion has been on the chemical aspects of the Heat Theorem, in accordance with Nernst's own approach. But, as Kormos Barkan has rightly pointed out, after the first papers the focus of Nernst's work quickly shifted to the more physical aspects of his Theorem. Indeed, one of the crucial thermodynamic quantities that Nernst focused on was the specific heat, in particular its behavior at low temperatures. From a long series of experiments carried out by Nernst and his collaborators, it appeared that specific heats tended to zero for low temperatures, instead of remaining at their high-temperature value, as classical theory predicted. For Nernst this provided important support for his Heat Theorem, as will be discussed below. It is outside the scope of this paper to elaborate further on Nernst's experiments and the related theoretical developments (see Kormos Barkan, 1999, for detailed discussions); let me just say that the anomalous behavior of the specific heats was an important factor in the development of quantum theory, especially after Einstein's 1907 theory of specific heats (Einstein, 1907) explained the vanishing of the specific heats as a quantum phenomenon.

3. Experimental and theoretical support

In the course of the years Nernst's presentation of his Heat Theorem went through several stages. Initially, as explained above, he used a plausibility argument to justify his hypothesis: it is very likely that not only A and U become equal, but that the same holds for their derivatives. Next, a mass of experimental evidence was presented that provided indirect support for the Theorem. Finally, Nernst reached the point where he claimed he could actually *prove* the theorem using thermodynamical arguments together with the assumption that at absolute zero the specific heats of all substances vanish.

A turning point in Nernst's approach is a discussion at the First Solvay Congress, which was held in Brussels in the fall of 1911. In a brief exchange after Nernst's lecture (Nernst, 1914), Albert Einstein questioned Nernst's claim that the theorem could be deduced from the vanishing of specific heats at $T = 0$.[7] Nernst's argument in his lecture runs as follows. From the vanishing of the specific heats it appears that from a certain temperature downward the concept of temperature loses its meaning. The consequence, according to Nernst, is that all physical properties become independent of the temperature. This rule seems to be followed by, for instance, the thermal expansion coefficient and the compressibility. To make this plausible, Nernst used the analogy of a dilute solution, the properties of which will roughly be proportional to the concentration of the solute. A similar conclusion can be drawn if quantum theory is applied to thermodynamic systems: for very low temperatures, there is very little thermal motion, i.e., few quanta of energy are distributed over many atoms. The system's properties are thus proportional to the number of atoms possessing a quantum of energy, and will in the end become essentially independent of the temperature. This holds a fortiori for the internal energy itself, so that we have $\mathrm{d}U/\mathrm{d}T = 0$. Because it is known from experience that the maximum work will not change much if small changes are made to a system, Nernst concluded that $\mathrm{d}A/\mathrm{d}T = 0$ will hold as well. Note the key role played in this argument by quantum theory. Nernst would stress the connection between his theorem and quantum theory time and again.

In the discussion following Nernst's lecture, Einstein objected to his argument, putting his finger on the weak spot: although the vanishing of specific heats makes the theorem

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[7] Einstein's discussion remarks are reprinted in (Klein, Kox, Renn, & Schulmann (Eds.), 1993a, pp. 510–514).

more plausible, it does not provide a proof. For that, he claimed, we would have to know whether close to absolute zero it is possible to perform an isothermal and reversible transformation from a state A into a state B *without adding heat*. Although in the discussion Einstein did not further elaborate on his statement, it is easy to reconstruct his line of thought. Let us look at the isothermal expansion of a gas. During this process heat has to be added, which is used to perform external work and to increase the internal energy. The amount of heat to be added is equal to $T\Delta S$. From the equation for the maximum work it follows for this case:

$$A - Q = T\Delta S. \tag{21}$$

If the transformation considered can be carried out without adding heat, the quantity ΔS will vanish, so that $(A - T)/T$ approaches zero as $T \to 0$, which is the Heat Theorem (cf. Eq. (6)).

Nernst had no response to Einstein's objection, but simply reiterated his earlier argument. A few months later, however, he published a paper in which he presented a new proof, based on thermodynamics and on the vanishing of the specific heat at absolute zero (Nernst, 1912).

This paper marks an important change in Nernst's thinking, because a completely new element is introduced in the argument, namely the postulated impossibility to reach absolute zero. This postulate, the validity of which was almost obvious in Nernst's eyes, became his starting point. What were his arguments? In the first place, Nernst pointed out that the unattainability of absolute zero had never been stressed before, because it was an obvious consequence of the classical result that specific heats remain finite at arbitrary low temperatures. This implies that even at low temperatures bodies would have a finite heat (or energy) content, and since according to the Second Law the amount of heat that can be removed from a body becomes smaller and smaller as T approaches zero, it would be impossible to reach absolute zero.

Nernst made his argument more explicit with the help of an interesting thought-experiment. He considered a Carnot cycle that runs between $T = \Delta T$ and 0. Because no heat is given off at $T = 0$, the heat absorbed at $T = \Delta T$ is completely transformed in work. Under the assumption that the specific heat does not approach zero, this amount of heat is finite, even if ΔT is extremely small. Thus, we have constructed a perpetuum mobile of the second kind. This is obviously unacceptable. The conclusion is that no finite processes exist that allow us to reach absolute zero.

Given this conclusion, what happens when quantum theory is taken into consideration, in particular its prediction that the specific heat vanishes at absolute zero? Nernst considered a number of possible processes and showed for each single one that the Heat Theorem in the form $\mathrm{d}A/\mathrm{d}T = 0$ is needed to keep absolute zero out of reach. A key assumption in his calculations is that quantities such as specific heats and compressibility can be written as simple power series in the temperature.

Despite his claim to the contrary, Nernst's argument does not constitute a proof of the heat theorem. He showed that the heat theorem implies that absolute zero is unattainable, not the inverse. It is a consistency argument, rather than a real proof. Still, it did provide a useful contribution to the discussion, inspiring several others, such as Lorentz (1913) and Michael Polanyi (see below), to proofs along similar lines.

4. Einstein's response and challenge

Almost immediately after Nernst's new proof had been published, Einstein wrote a reply, which he submitted to *Physikalische Zeitschrift*. As he wrote to his friend Heinrich Zangger, Einstein was convinced that Nernst had misapplied the second law. He had already pointed out the error in a letter to Nernst, to which the latter had replied in a fairly impertinent way ("ziemlich frech," as Einstein put it).[8]

The submitted paper was never published. Presumably, it was retracted, perhaps after Einstein's visit to Berlin in April 1912, during which he had a discussion with Nernst and settled the dispute "as far as possible" ("so weit wie möglich").[9] The discussion left Einstein with mixed feelings about Nernst, however. In the letter to Zangger cited above he describes him as "imperious and prickly" ("herrschsüchtig und empfindlich"), although not "dishonest" ("unehrlich"). To Ehrenfest he complains that Nernst is "not open to reason, because he is not enough of a logician" ("der Vernunft nich zugänglich (zu wenig Logiker))."[10]

In any case, the difference of opinion remained. It emerged again at the Second Solvay Congress in late October 1913. In the discussion following a lecture by Eduard Grüneisen, and in response to a remark by Nernst, Einstein made a lengthy intervention in which he sharply criticized Nernst's proof.[11]

Nernst started his remark by referring to the discussion in Brussels two years earlier, and pointed out that in the meantime much new experimental evidence in favor of the theorem had been assembled. As an example he mentioned work by Kamerlingh Onnes on the Peltier effect. But, he went on, the theoretical basis of the theorem had been strengthened as well. If one assumes the specific heat to go to zero, without at the same time admitting the validity of his theorem, one arrives at absurdities. For instance, if the quantity $\partial p/\partial T$ remains finite for very low temperatures, it is possible to reach absolute zero with a finite adiabatic expansion. To avoid this absurdity, we have to conclude that $\partial p/\partial T$ tends to zero, which, Nernst claims, constitutes the Heat Theorem. Strictly speaking, however, the heat theorem implies this relation, not the other way around.[12]

Einstein agreed with this point. But he went on to stress his doubts about Nernst's proof. His key point was that the cycle used by Nernst in his proof could not be realized. He claimed that, if one starts in point C (see Fig. 1) and compresses the system, it will follow the adiabatic to B and not the isotherm/adiabatic to D. The reason is that the compression can never be carried out in a fully reversible way, so that minute quantities of energy will be transformed into heat. This will force the system away from the isotherm $T = 0$. Still,

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[8] Einstein to Heinrich Zangger, before 29 February 1912 (Klein, Kox, & Schulmann (Eds.), 1993b, Doc. 366).

[9] Einstein to Heinrich Zangger, 20 May 1912 (Klein et al. (Eds.), 1993b, Doc. 398). In a letter to Paul Ehrenfest of 25 April 1912 (Klein et al. (Eds.), 1993b, Doc. 384) he even claims that Nernst had admitted that his proof was flawed.

[10] Einstein to Paul Ehrenfest, 25 April 1912 (Klein et al. (Eds.), 1993b, Doc. 384). In this letter he also makes the interesting remark that in Planck's view the unattainability of absolute zero is an axiom to which all else is subordinate.

[11] The text of Einstein's contribution is reprinted in its original, previously unpublished German version in (Klein, Kox, Renn, & Schulmann (Eds.), 1995, pp. 554–559); see (Solvay, 1921, pp. 290–301), for the published French version of the complete discussion.

[12] This follows from (Nernst, 1912).

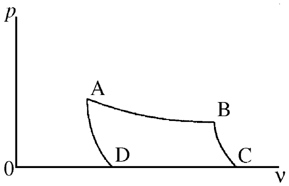

Fig. 1.

Einstein admits, even though the Nernst's particular example cannot be realized, the idea that adiabatics as *CD* might exist is disturbing.

An obvious way out would be to follow Nernst and elevate the impossibility of reaching absolute zero to a fundamental principle. But that too would have unwanted consequences. Einstein illustrated his point in the following way. For an adiabatic transformation of a system that is fully characterized by the parameters v and T (where v does not have to be the volume, but can be any thermodynamic parameter), we have

$$0 = \mathrm{d}Q = T\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\,\mathrm{d}T + \frac{\partial S}{\partial v}\,\mathrm{d}v\right) = C\mathrm{d}T + T\frac{\partial S}{\partial v}\,\mathrm{d}v, \tag{22}$$

with C the heat capacity. Thus,

$$\frac{\partial S}{\partial v} = -\frac{C}{T}\frac{\mathrm{d}T}{\mathrm{d}v}. \tag{23}$$

From experiments we know that C/T tends to zero; at the same time $\mathrm{d}T/\mathrm{d}v$ has to tend to zero, for otherwise absolute zero would be attainable with a finite expansion. Thus,

$$\lim_{T\to 0}\frac{\partial S}{\partial v} = 0. \tag{24}$$

Because v is an arbitrary parameter, we see that at $T = 0$ all states of the system have the same entropy. We have made no specific assumptions about the constitution of the system, so this holds for condensed systems as well as gases, for mixtures as well as homogeneous substances. But this creates an immediate problem. To understand it we have to look at the interpretation Planck gave to the heat theorem. In the 1911 edition of his textbook on thermodynamics (Planck, 1911) Planck had given a new formulation of the Heat Theorem, namely that not only at absolute zero all transitions are isentropic, but also that the value of the entropy itself is zero—a generalization that is permitted because the entropy is always determined up to an arbitrary constant.[13] There is one problem with this new formulation, however: for non-homogeneous substances, such as mixtures, the expression for the entropy contains one or more terms that depend on the concentrations, but not on the temperature. This term does not necessarily disappear at $T = 0$. According to Planck, this meant that the extended formulation of the heat theorem was only valid for homogeneous substances. This would be in contradiction with Einstein's conclusion.

The problem is made clear with the following example: consider a system in which a semipermeable membrane separates a dilute solution from pure solvent. The expression for

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[13] This generalization also implies the vanishing of the specific heats at absolute zero as a result of the relation $\mathrm{d}S = C\,\mathrm{d}T/T$.

the entropy contains a term in which the volume of the solution appears. Changing the volume of the solution at absolute zero by moving the membrane would change the entropy of the whole system, something Einstein has just shown to be impossible.

Again, Nernst did not admit defeat. He first (rightly) pointed out that Einstein's argument about the impossibility to actually realize reversible transformations would put into question numerous other thermodynamic theorems. But leaving this aside, he claimed that the fact in itself that the adiabatic BC cuts the $T = 0$ axis, and does not approach it asymptotically, is sufficient for the conclusion that the cycle considered by him is impossible to realize.

5. Berlin

Half a year after the Solvay Congress, Einstein returned to Nernst's theorem in a paper in the *Verhandlungen* of the *Deutsche Physikalische Gesellschaft* (Einstein, 1914). At the outset he stated his goal: to show how Nernst's theorem can be derived from thermodynamics in combination with quantum theory, and without the need to invoke Boltzmann's principle. To this he added the contention that any thermodynamical derivation using the vanishing of the specific heats as a starting point is bound to fail and offered to show this explicitly for any proof submitted to him.

From this point on, Einstein focused on the issue of the value of the entropy at absolute zero. One of the reasons he did this is that in the meantime, through the work of Sackur and Tetrode (see Sackur, 1912; Tetrode, 1912), it had become possible—with the help of molecular physics and quantum theory—to derive explicit expressions for the entropy of ideal gases in terms of fundamental constants and molecular parameters.[14] Einstein's derivation runs as follows: using the canonical ensemble, he calculated the mean energy for a system for which a discrete number of quantum states is possible and from this he derived a quantum version of Boltzmann's principle:

$$S = \frac{R}{N} \log Z, \tag{25}$$

with Z the number of microstates that correspond to the calculated mean energy. Note that the unspecified additional constant in the entropy is set equal to zero. Look at a system consisting of a two homogeneous components and let us suppose that the system is crystallized in some lattice. Furthermore, we assume that at absolute zero, the system is completely characterized if the positions of all individual molecules are specified. Because we can go from one microstate to another one by simply interchanging the positions of molecules of the same kind, Z has the form:

$$Z = n_1!n_2!, \tag{26}$$

so that the entropy has the same value for all states of the system. If, on the other hand, we deal with a mixture of two components, we can interchange all positions without any change in the thermodynamical properties of the system. That gives

$$Z = (n_1 + n_2)! \tag{27}$$

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[14] Since the chemical constants also occur in the molecular expression for the entropy, these quantities could be determined from the Sackur–Tetrode theory as well.

which for $n_1 = n_2 = N$ leads to an entropy difference between the mixed and unmixed states of

$$R \log 2. \tag{28}$$

Thus, quantum theory confirms Planck's restriction to homogeneous substances in his formulation of the heat theorem. A few months later, Einstein returned to this issue in an unpublished manuscript on the theory of Sackur and Tetrode.[15] He refined the earlier phase-space argument and succeeded in deriving an expression for the entropy of an ideal gas of particles with rotational as well as translational degrees of freedom. It turned out to be possible to make this result agree with earlier calculations by Tetrode (1915). Again, the conclusion was that the heat theorem in the Planck formulation is only valid for simple systems, not for mixtures.

6. Polanyi

One of the people who accepted Einstein's challenge to refute any thermodynamical proof of the heat theorem was Michael Polanyi.[16] In the spring of 1914 he had published a short paper (Polanyi, 1914) in which he presented a refinement of Nernst's earlier proof. Instead of considering processes at absolute zero—something he claimed was problematic—he reformulated the theorem in the following way: "There exists a range of temperatures close to absolute zero where a reversible isothermal change does not entail a change of entropy." In particular, he had in mind a body that can exist in two different modifications. Polanyi considered the following process: a succession of adiabatic expansions and isothermal compressions. This will lower the temperature. At some point the temperature is so low, that the next expansion will have no measurable effect on the temperature. The argument was that there would not be a change in entropy either. This conclusion followed from the vanishing of the specific heat at absolute zero and the following expression for the entropy:

$$S = \int_0^T \frac{c\,\mathrm{d}T}{T}. \tag{29}$$

Since $\lim_{T\to 0} c/T = 0$, this integral has a well-determined value, also for very low temperatures. Because each step in the succession of expansions and compressions corresponds with a finite decrease in entropy, however, at some point this decrease will become unmeasurable.

After Polanyi had asked Einstein to formulate his objections to this proof, Einstein pointed out that the argument was only valid if absolute zero would not be reached in a finite number of steps. The point is simple: if we start from an entropy value of S and the entropy after l steps is S_l, we can write:

$$S - S_l = (S - S_1) + (S_1 - S_2) + \cdots + (S_{l-1} - S_l). \tag{30}$$

On the assumption that $S - S_l$ is finite and that there are infinitely many terms on the right-hand side, we have $\lim S_{l-1} - S_l = 0$. But if absolute zero is reached after a finite number of steps, the proof fails, unless one can continue the process at the adiabatic/

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[15] The manuscript is published in Klein, & Schulmann (1996, Doc. 26).

[16] The discussion between Einstein and Polanyi took place in a series of letters from 1914 to 1915. (See, Schulmann et al., 1997, Docs. 41, 42, 55, 81, 89, and 93.)

isotherm at absolute zero. As in his discussion with Nernst, Einstein questioned that possibility, by pointing out that reversible changes at absolute zero cannot be realized in practice.

In addition to this argument, Einstein put forward a more detailed version of the thought experiment he had outlined at the second Solvay congress, which very strongly suggests that for mixtures Nernst's theorem is not valid. Consider a system with a semipermeable membrane separating a pure solvent from a dilute solution. The molecules of the solute are very similar to those of the solvent (for instance isotopes). Now consider the following cycle: at constant partial volumes raise the temperature from $T = 0$ to T_1, a temperature at which the law of osmotic pressure is valid, or, in other words, there is diffusion. This process corresponds with a certain increase in entropy. Now change the volume of the solution. This will change the entropy. Finally, lower the temperature back to zero. The change in entropy will be the same as the earlier change when we went from zero to T_1, because the specific heat will be independent of the volume. The net result is that we are back at absolute zero, with a different volume of the solvent, and thus a different value of the entropy, in clear contradiction with Polanyi's fundamental hypothesis.

As a result of the correspondence Polanyi published a new paper (Polanyi, 1915) in which he tried to modify his earlier proof, taking into account Einstein's objections. He focused on the case where absolute zero is reached in a finite number of step. His main point now is the question whether it is possible to realize reversible transformations at absolute zero. Such transformations are only possible if at absolute zero equilibrium between the system and its surroundings can exist. Polanyi admitted that for dilute systems, such as solutions and gases, this seemed unlikely: as the temperature goes to zero they will lose their capacity to reach equilibrium with their surroundings by changes in volume, because, as Einstein had argued, it is unlikely that diffusion can take place at absolute zero. This argument does not apply to condensed systems, however, so that for such systems reversible transformations are not excluded. The reason is, according to Polanyi, that transformations such as expansions of condensed systems can be reduced to the action of intermolecular forces. Thus, condensed systems can expand reversibly, even at absolute zero—as Einstein had admitted as well. Why then would, for instance, chemical reactions, or melting, in which molecular forces play a central role as well, be different, as Einstein had asserted?

In the end, we have to conclude that Einstein had successfully undermined the original proof: Polanyi had to retreat to a consideration of solids only, and could not produce more than a plausibility argument to support his claim that his proof worked for all condensed systems. It is interesting to note that he did not use Nernst's postulate that it is impossible to reach absolute zero.

7. Conclusion

The discussion between Einstein and Nernst and, to a lesser extent, the exchange between Einstein and Polanyi, make clear that the attempts to clarify the meaning of the Heat Theorem or provide proofs for it not always made things clearer. In particular, the fact that in the course of these discussions new formulations for the theorem were proposed sometimes led to confusion, because it was not clear whether these new formulations were equivalent to older ones or contained new elements. Also, the range of different examples proposed and systems discussed created grave doubts about the universal validity of the Heat Theorem, without, on the other had, providing proof for its falsity.

Let me conclude by summarizing some key points that emerged from the various controversies discussed in this paper:

- The shift from thermochemistry to physics in the evolution of the Heat Theorem. The original statement about the behavior of affinities evolved into claims about the low-temperature behavior of quantities such as specific heats and entropy and even led to the introduction of the new and fundamental principle of the unattainability of absolute zero.
- Einstein's emphasis that classical thermodynamics was simply not sufficient to formulate a proof of the Heat Theorem (or even understand it properly), which made the Theorem into a new element, added to the existing theory.
- The intimate connection between quantum theory and the heat theorem, as illustrated in the non-classical behavior of the specific heats and the successful calculation of the chemical constants from quantum theory by Sackur and Tetrode and later by Einstein.
- The failure to find a proof for the theorem that satisfied everyone. Each proof contained one or more elements, such as the unattainability of absolute zero, that were disputed by its critics.

Finally, a few words about later developments. In later years the confusion and uncertainty about its meaning and validity became so great, that in the thirties some physicists were even of the opinion that the Heat Theorem was "irrelevant and useless" and "though often true, sometimes false and failing in generality" (see Fowler and Sterne, 1932, p. 707). Nowadays it is the view of many that quantum theory provides a solid basis for the statement that at absolute zero all systems have zero entropy and that one can formulate the Third Law in this way. But others still confine themselves to the statement that one cannot reach absolute zero. In spite of these differences, however, there does seem to be a general consensus that the Third Law is of a different, less fundamental and more experimental character than the other laws of thermodynamics.

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