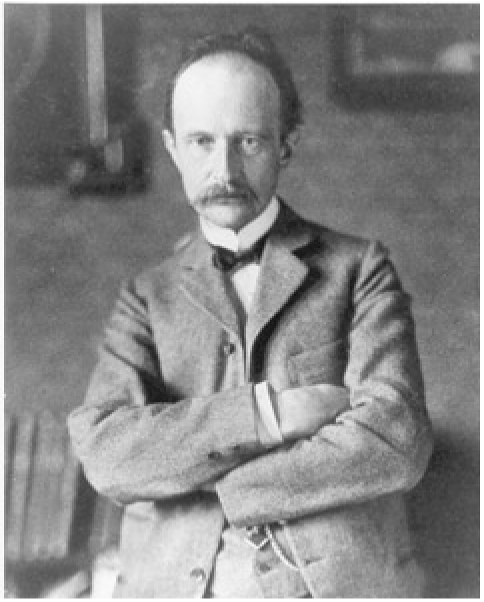
Walther Nernst, Max Planck, Albert Einstein, and the Third Law of Thermodynamics

Clayton A. Gearhart

St. John's University



Walther Nernst
1864 – 1941

- physical chemist
- studied with Boltzmann
- 1889: lecturer, then professor at Göttingen
- 1905: professor at Berlin

Nernst studied physics and chemistry as a student: “The system of study at a German university makes it impossible to decide whether Walther Nernst read physics or chemistry.” (Mendelssohn)

Nernst formulated his heat theorem (Third Law) in 1906, shortly after appointment as professor in Berlin

Nernst's Problem

Understand the "equilibrium constant" that governs chemical reactions.

If we consider the reaction

$$n_1 A_1 + n_2 A_2 + \ldots \rightleftarrows n_1' A_1' + n_2' A_2' + \ldots$$

where the *A*'s are chemical species, and the *n*'s are mole numbers or stochiometric coefficients. For example,

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

How can one understand the equilibrium point of such a reaction? This problem is of practical as well as theoretical interest (as the above example suggests!), and was investigated intensely by 19th century chemists and physical chemists.

Law of Mass Action

This law was first proposed by the Norwegian mathematicians Cato Maximilian Guldberg and Peter Waage in the mid-1860s. (It took some time for their work to become known, not least since much of it was written in Norwegian!)

As Nernst wrote it in his text *Theoretical Chemistry* (1st ed 1893), it stated:

$$\frac{c_1'^{\,n_1'} \cdot c_2'^{\,n_2'} \ldots}{c_1^{\,n_1} \cdot c_2^{\,n_2} \ldots} = K$$

where   Here the *c*'s are the "concentrations," or "the number of g.-mole of each of the substances … contained in 1 litre." *K* is the "equilibrium constant"-a function of temperature.

Nernst: **… we must regard the law of mass-action as an empirical law which is certainly proved, and therefore one which is independent of every theoretical molecular speculation.**

… How far the law of mass-action can be proved in a thermodynamic way, entirely independently of every molecular hypothesis, will be discussed in the last book.

Nernst and thermodynamics

Nernst: **The sum of the heat produced in the reaction, and of the external work performed, … we will call the "heat of reaction" in question: of course, this can be either positive or negative.… The heat of reaction represents therefore the change in total energy of the system.** (Theoretical Chemistry, Book IV)

Let U be the *heat of reaction* and A the *maximum available work* of an isothermal, reversible process. (The two are of course related through the First Law: $U = A - Q$). Nernst summarized both the First the Second Laws in the equation

$$A - U = T\frac{dA}{dT}$$ Gibbs-Helmholtz equation

This equation tells us a good deal about how Nernst approached thermodynamics.

Nernst and thermodynamics

$$A - U = T\frac{dA}{dT}$$

Today, we would write this equation as

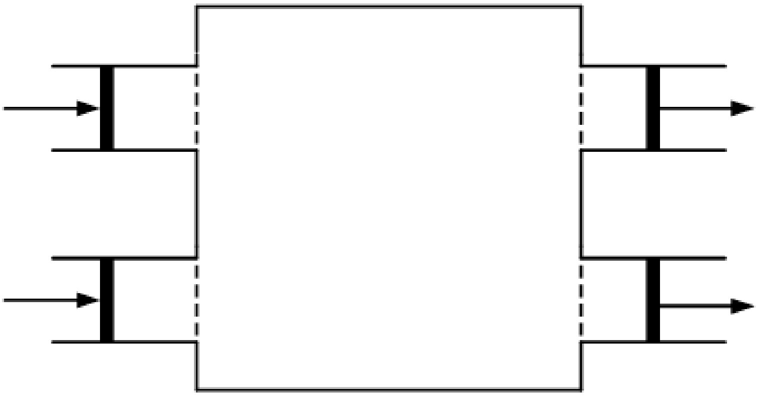
$$\Delta F - \Delta U = T\left(\frac{\partial \Delta F}{\partial T}\right)_V$$

where F is the Helmholtz free energy, and U the internal energy.

Thus, we would be inclined to think of A as the difference in the Helmholtz free energy. Nernst preferred to think of it as available work. He disliked thermodynamic potentials, and, for example, never used entropies! Early in his *Theoretical Chemistry* Nernst introduced the entropy, only to say

> **We shall henceforth always work with the intelligible notion of the maximal work (free energy) and not with its negative temperature coefficient (entropy) …**

Equilibrium Box



Thus, Nernst calculated *A* by considering an isothermal, reversible reaction in which reactants and products entered and left an “equilibrium box” or “van’t Hoff box” mediated by pistons and semi-permeable membranes--again, preferring these sorts of arguments to the more general ones of Gibbs and Planck:

> **A cursory examination of the literature of thermodyamics will afford evidence that in every case where a definite solution has resulted, recourse has been had to … a suitable cyclic process.**

Aside: Planck and entropy

Planck, by contrast, was a firm defender of entropy and thermodynamic potentials generally, and criticized

In spite of the convenience that these general methods offer, one very often finds … physicists and chemists, who, in the deriviation of new consequences of the second law, do not rely on these assumptions but use certain special thermodynamic cycles, devised for the particular purpose at hand, to which they apply the *primitive* [my emphasis] **law that heat cannot be transformed into work without compensation.** (Planck 1891)

Finding the equilibrium constant *K*

Nernst proceeds (following the work of others, especially van’t Hoff)

$$A - U = T\frac{dA}{dT}$$

Second law

For an isothermal chemical reaction in an “equilibrium box” show that

$$A = RT\ln K$$

Combine these two equations to show

$$U = -RT^2\frac{d}{dT}\ln K$$

and assuming that the heat of reaction U is reasonably constant,

$$\frac{d}{dT}\ln K = -\frac{U}{RT^2}$$

$$\ln K = \frac{U}{RT} + \textbf{constant}$$

Note the constant of integration

$$\ln K = \frac{U}{RT} + \textbf{constant}$$

If we could find the constant of integration, we could determine the equilibrium constant K, and the maximum available work A from thermal data (heat of reaction U).

Aside: This approach was problematic throughout the late 19th century. Prominent chemists, especially Julius Thomsen and Marcellin Berthelot, thought that the heat of reaction determined the course of a chemical reaction. Only slowly did the work of physical chemists such as Ostwald, van’t Hoff, Arrhenius, and Nernst make it clear that the free energy was the appropriate measure of “chemical affinity”.

Nernst's Heat theorem

Nernst postulated that $\frac{dA}{dT} \longrightarrow 0 \quad \text{as} \quad \mathrm{T} \longrightarrow 0$

Which, together with $A - U = T\frac{dA}{dT}$ implies $A = U \quad \text{at} \quad T = 0$

$$\frac{dU}{dT} \longrightarrow 0 \quad \text{as} \quad \mathrm{T} \longrightarrow 0$$

This postulate leads to the determination of the constant of integration:

We integrate $A - U = T\frac{dA}{dT}$

to obtain $A = -T\int \frac{U}{T^2}dT + \text{constant} \times T$

$$\Rightarrow \text{constant} = 0 \quad \text{if} \quad \frac{dA}{dT} \longrightarrow 0 \quad \text{as} \quad \mathrm{T} \longrightarrow 0$$

So that A may be determined from the heat of reaction data U

Summary and implications

$$A - U = T\frac{dA}{dT}$$ Second Law

$$\frac{dA}{dT} \to 0 \quad \text{as} \quad \mathrm{T} \to 0$$ Nernst’s hypothesis

Implications: $A = U \quad \text{at} \quad T = 0$

$$\frac{dU}{dT} \to 0 \quad \text{as} \quad \mathrm{T} \to 0$$

Note that this last equation means $\frac{d\Delta U}{dT} \to 0 \quad \text{as} \quad T \to 0$

and hence for any chemical reaction, or any phase transformation involving liquids or solids,

$\Delta c \to 0$ where c is the specific heat

Specific Heats at low temperatures

Measurements at low temperatures were becoming possible in the late 19th and early 20th centuries, but even by 1905, there was not a large body of specific heat data available.

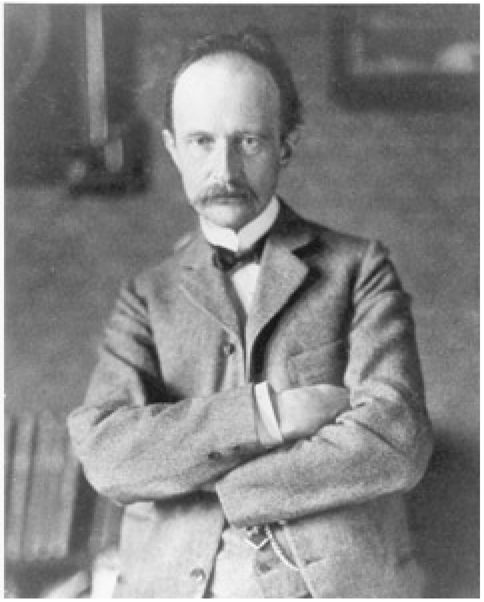
> **For the specific heats of liquids or solids at the absolute zero, our hypothesis requires that every atom shall have a definite value for the atomic heat, independent of the form, crystallized or liquid …, and of whether it is in chemical combination with other atoms.** (Nernst 1906)

Nernst and his students spent considerable time and effort in the years after 1905 investigating specific heats and other properties of matter at low temperatures. Not until 1910 did he begin to report results (down to liquid hydrogen temperatures).

> **"… one gets the impression that the specific heats are converging to zero as required by Einstein's theory."** (Nernst 1910)

Note that this statement permits a stronger statement of Nernst's heat theorem.

And now the physics



Max Planck had spent the early years of his career, up to about 1895, contemplating the second law of thermodynamics and its application to chemistry. He was therefore intrigued by Nernst's discovery, and added a section on the Nernst heat theorem to the 3rd (1910) edition to his thermodynamics text.

Planck, of course, had no objection to entropy! His form of the third law stated that the entropy itself approached zero as T approached zero.

$$\frac{dA}{dT} \to 0 \Leftrightarrow \frac{d\Delta F}{dT} \to 0 \quad \text{or} \quad \Delta S \to 0 \text{ as } T \to 0$$

Planck suggested the stronger form, $S \to 0$ as $T \to 0$

and by 1911, was suggesting that his new quantum hypothesis held the key to a deeper understanding of Nernst's heat theorem.

Enter Einstein

To see what Planck might have meant, recall that in 1907, Einstein published a paper arguing that if one treated a solid as a collection of quantized harmonic oscillators, the specific heat should go to zero as $T \to 0$.

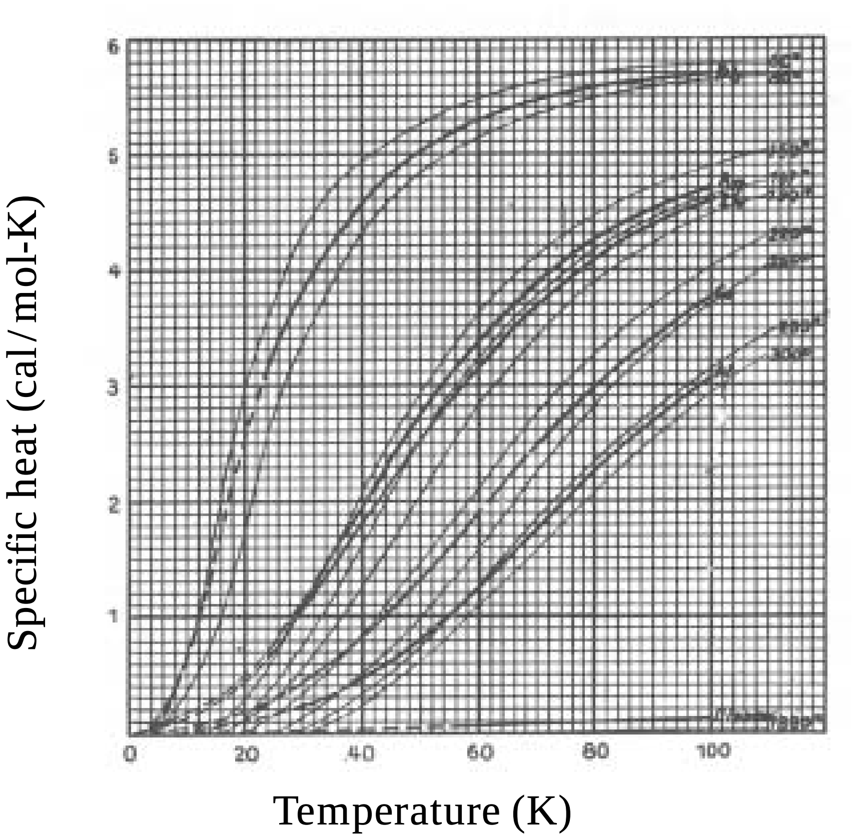
Note the connection to Nernst, whose reaction was to seek out Einstein in Zürich!

On my trip here I visited Prof. Einstein in Zürich. It was for me an extremely stimulating and interesting meeting. I believe that, as regards the development of physics, we can by very happy to have such an original young thinker, a "Boltzmann redivivus"; the same certainty and speed of thought; great boldness in theory, which however cannot harm, since the most intimate contact with experiment is preserved. Einstein's "quantum hypothesis" is probably among the most remarkable … ever.

Nernst to Arthur Schuster, March 1910

First Solvay Conference (1911)

Both Einstein’s and Nernst’s papers dealt with specific heats. Nernst gave pages of data for such materials as copper, aluminum, lead, lead cloride, silver iodide, and others. Einstein’s paper contained the graph.



… Nernst, who rescued all the results pertaining to this question from their theoretical limbo…

Einstein (1911)

And thereafter

- Sakur-Tetrode Equation (entropy constant for ideal gas) (1912)

$$S = Nk \ln \left\{ \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{5/2} \right\}$$

- rotational spectra and quantization of rotational energy in gases (1912)
- Einstein called to Berlin (1914)
- specific heat of hydrogen and suggestion of degenerate gases (1914)

Resources

Resources:

Walther Nernst, *Theoretical Chemistry* (1893 and thereafter)

Walther Nernst, *Thermodynamics and Chemistry* (1906)

Walther Nernst, *The New Heat Theorem* (1917)

Martin J. Klein, “Einstein, Specific Heats, and the Early Quantum Theory,” Science **148** (1965) 173--180.

Erwin Hiebert, “Nernst,” *Dictionary of Scientific Biography*

Kurt Mendolsohn, *The World of Walther Nernst*

Diana Barkan, *Walther Nernst and the Transition to Modern Physical Science*