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978-0-521-44456-9 - Walther Nernst and the Transition to Modern Physical Science

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*Nernst, the Historiography  
of His Science, and Its Context*

This is physical chemistry, formerly a colony, now a great, free land.

J. H. van't Hoff

This book is about a set of scientific and technical concerns that emerged toward the end of the nineteenth century at the intersection of physics, chemistry, and technology, and about the role that Walther Nernst (1864–1941) and some of his colleagues and collaborators played in the formulation of novel, even revolutionary, scientific theories and experimental techniques.

Nernst, who won the 1920 Nobel Prize in chemistry, was a key figure in the transition to a modern, quantum theoretical physical science that occurred over forty years or so at the end of the nineteenth and the beginning of the twentieth centuries. He was scientifically and personally engaged with many of the major figures of the period, including Planck, Einstein, van't Hoff, Ostwald, and Arrhenius. His foremost contributions to science include the study of electrolytic solutions, chemical thermodynamics, the theory of chemical equilibria, quantum chemistry, low-temperature phenomena, photochemistry, and his celebrated heat theorem, known also as the Third Law of Thermodynamics. Nernst's career exemplified the increasing connection between German technical industry and German academic science, inasmuch as he himself invented and patented a new type of electric lamp and other devices. Hence, his life and work provide entry into most of the significant and powerful developments in physical science that would profoundly affect the world in the twentieth century.

Nernst's professional career, which spanned the period from Wilhelminian Germany through the First World War and the Weimar Republic to the Third Reich, and from experimental electrical studies through physical chemistry and quantum theory to modern astrophysics, instantiates the connections between theory and experiment, concepts and practice, academia and industry. One of the more prominent representatives of German science, Nernst has been described as the first "modern" physical

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chemist, as the originator of solid-state physics, and as an able entrepreneur. Yet, little attention has been given to the relationship among the different strands of his scientific life. Therefore, this account examines the interconnections between physics and chemistry, the fluidity of disciplinary allegiances and identities, and the importance of concrete, manageable, and task-directed work in the larger picture of scientific research.

Because of their work on the properties of matter, Nernst and his colleagues in Berlin played an important role in the reception of Einstein's quantum theory of solids and, more generally, in the development of quantum theory and its relevance to chemical properties and reactions. The events surrounding Nernst's organization of the first Solvay conference in 1911 illustrate aspects of the precarious role of quantum theory at the time. The shifts in fundamental conceptions about the nature of matter and radiation, and their correlation to his heat theorem, account, at least in part, for the tortuous path toward Nernst's Nobel Prize.

The centerpiece of Nernst's scientific work was his postulation of the heat theorem, now called the Third Law of Thermodynamics. Trying to solve the problem of predicting chemical equilibria, Nernst postulated at the end of 1905 that at low temperatures, the internal and free energy of the reactants of a chemical transformation become equal in magnitude. This assumption allowed for the elimination of a troublesome integration constant that had previously hampered the ability to predict whether a chemical reaction was feasible. It simplified the problem by allowing the calculation of the equilibrium constant of the reactions from measurements of the specific heats of the reactants at low temperatures.

In its current formulation, the Third Law of Thermodynamics states that it is impossible to reach absolute zero temperature in any finite number of steps, and that the entropy change between states of a system that can be connected by a reversible process vanishes at absolute zero. Accordingly, near the absolute zero of temperature, matter attains a perfectly ordered state. Nernst's observation about the peculiar behavior of matter in the vicinity of absolute zero is considered a milestone in the history of physical chemistry because it furnished an algorithm that enabled researchers to predict the feasibility of chemical reactions from experimentally available thermal data on chemical substances.

After its publication in early 1906, Nernst's heat theorem received several refinements and reformulations. Albert Einstein's paper on the quantum theory of solids, published in 1907, provided proof for Nernst's prediction that specific heats tend to zero at absolute zero temperature. Confirming Nernst's singular intuition that low temperatures in the solid phase are ideal loci of experimentation on peculiar quantum phenomena that do not take place at ordinary temperatures, Nernst's paper and that

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of Einstein became the basis for the development of an entirely new field of theoretical and experimental studies, later called solid-state physics. A decade later, it became evident that molecular and atomic entropies were critical elements for the understanding of the behavior of matter, leading to quantum statistical treatments of a variety of physical and chemical properties.

**The Problems**

One important historical puzzle concerns the original formulation and conceptual and experimental sources of the heat theorem. How and why did Nernst arrive at the heat theorem?

An early account, which persists to this day, was presented in the 40th Guthrie Lecture delivered before the Physical Society of England in March 1956 by one of Nernst's best-known students, Sir Francis (Franz) Simon. Having worked on low-temperature experiments in Germany before emigrating to England after the Nazi seizure of power, Simon located the origins of this heat theorem in Nernst's "intense interest in gas reactions, partly because of the relative simplicity of the problem involved . . . and partly because of the economic possibilities" which its solution might bring to the industrial synthesis of ammonia. "Thus there was every incentive for physical chemists to develop the theory of gas reactions systematically." Simon wrote that, "*starting from vague and rather inconclusive beginnings*, [the heat theorem] was at first mainly regarded as a useful rule for calculating chemical equilibria" (emphasis added). This initial work by Nernst was followed by a "period when the quantum theoretical foundations of the theorem were recognized and physicists became interested in it, particularly when quantum statistics made possible a direct calculation of the entropy constants of gases. Later on, further quantum statistical considerations led to a discussion of the general validity of the law when applied to solid phases."

Simon's account is open to question on a number of grounds. The published evidence that Nernst had been substantially interested in predicting chemical equilibria prior to 1906 is at best only indirect. His main line of work between 1895 and 1905 was the improvement of the new electric lamp. An analysis of Nernst's own chronology of events, as well as the record of his own and others' publications, shows that Nernst's research on the heat theorem proceeded simultaneously with other work into electrical conductivity, Maxwellian electromagnetism, heat and light radiation, and the needs of the electro-technological and illumination industries of the day.

According to Simon, after postulating the heat theorem, Nernst left “aside the gas reactions” and “switched to the condensed phases” and the investigation of solids at low temperatures. Nernst then switched back to gas reactions, “for after all these started the whole problem. Moreover nearly all the equilibrium data which were available at that time concerned gas reactions.” Later, the obtained specific heat data were applied “to predict a number of chemical equilibria, particularly in galvanic cells and crystallographic transitions.”<sup>1</sup> While it is correct that the heat theorem could fundamentally be confirmed only through the study of solids, difficulties arise when one attempts to reconcile Nernst’s work until 1905 with this alleged overriding preoccupation with the “calculation of chemical equilibrium constants from thermal measurements.”<sup>2</sup> The standard view, as indicated in Simon’s account of the origins of Nernst’s heat theorem, is misguided. Simon may have been misled by the title of Nernst’s first paper on the topic and by the rather rapid publication of two important monographs on the application of the heat theorem to chemical transformations between 1910 and 1920.

The heat theorem’s roots lay not only in a “pure” concern with chemical equilibria *per se* but also in the nexus of theoretical as well as practical or, more broadly, technological issues in which Nernst was absorbed at the time. The theorem originated in a thorough blending of electrochemical, electrical, and chemical researches with studies on the constitution of matter that preoccupied the Nernst laboratory, and many others, in the years 1891 to 1909. Accordingly, we shall examine in great detail the precise path of Nernst’s researches and the context of the formulation of the heat theorem.

An equally significant historical puzzle concerns Nernst’s move, after 1906, to low-temperature investigations. This experimental work has been seen to flow directly from the postulation of the heat theorem. Because it is generally presumed that in physical-chemical research the locus of major interest to chemists at the time was the prediction of equilibria, Nernst’s awareness of the importance of low temperatures is viewed as an outcome of his examination of the free energy curves and the internal energy curves of physical and chemical transformations: Nernst assumed, correctly, that in the vicinity of absolute zero these curves coincide asymptotically and become tangent to each other. However, Nernst’s perceptive insights and his low-temperature investigations actually emerged

1. F. Simon, “The Third Law of Thermodynamics. An Historical Survey,” 40th Guthrie Lecture, *Year Book of the Physical Society* (1956):1–6.

2. Keith J. Laidler, *The World of Physical Chemistry* (Oxford: Oxford University Press, 1993), p. 127, is the latest history of the field to continue this line of explanation.

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from a deeper and different understanding of his own previous electrical conductivity researches and their relation to similar work carried out elsewhere. He was “looking at” low temperatures before he “saw” the special feature of the energy curves that helped him formulate the heat theorem. The mind had been prepared in advance.

In sum, a good case can be made for a more textured reading of Nernst’s work, both during his apprenticeship in Graz, Würzburg, and Leipzig and later in his laboratories in Göttingen and Berlin. Detailed examination of the work not only of Nernst but also of myriad collaborators and colleagues in various fields and laboratories triggers a departure from previous historical reconstructions. They have read back into its origins the “chemical” benefits that flowed from Nernst’s postulation of the heat theorem, and they have taken low-temperature physics as its natural outgrowth. In fact, the low-temperature investigations that followed were not a major shift but rather constituted a program of correlating existing data and eliciting new data for atomic heats, electrical conductivity, and melting points. All this information was useful for both chemical and physical investigations.

In general, histories of the field tend to include a statement on the rather sudden “insight” about the energy balance at low temperatures that occurred to Nernst in late 1905, and describe how this “Eureka” experience – alleged to have taken place during a regular university lecture – consequently led him to an unexpectedly swift transition to the field of low-temperature research. The central point of these accounts, however, has remained the concern about the predictability of chemical equilibria.

I dispute this account. The conventional chronology seems to be a teleological, retrospective narrative, culminating in Simon’s own scientific field of expertise, and constructed almost half a century after the postulation of the heat theorem. It is an account of the origins of solid-state, low-temperature work carried out by some of Nernst’s former students in the 1930s and afterward at the Clarendon Laboratories in Oxford.

I will show that what ultimately came to be regarded as an important insight, innovation, or solution did not stem from any purposeful attempt to answer precisely the problem eventually solved. Simon and historians following him overlooked some essential features of the heat theorem’s etiology. For although Nernst was indeed interested in gas reactions, they were not only those of the industrially desirable ammonia formation, as Simon suggests. And although Nernst did indeed engage briefly in exploring the synthesis of ammonia from elements, the study of the behavior of gases was a major research topic of physicists and chemists concerned with radiation phenomena – with the dissociation of matter at elevated temperatures.

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Nernst's ongoing electrolytical and electrochemical research into conduction processes constituted the core of his experimental investigations. For example, he did not merely "apply" the data gained from the application of the heat theorem to the galvanic cells (batteries), as might be concluded from cursory readings of his papers and of Simon's account. Instead, the production of mechanical work by galvanic cells was a long-standing project, which he had begun during his student years.

Nernst's work from 1886 to 1914, his most productive years between the ages of 22 and 48, was embedded in the theoretical and experimental culture of the period, was to a large extent influenced by the particular laboratory and its environment, and was characterized by the slow, often piecemeal practice of electrical and thermodynamic studies carried out at the time. My account, thus, accords with the stress that recent scholars have placed on the heterogeneity and cultural specificity of both scientific theory and practice. In particular, scholars have been concerned with explaining the nature of "negotiated" knowledge, how consensus is reached, and how theories and skills are stabilized, replicated, and multiplied in the academic, industrial, and larger milieus.<sup>3</sup> Many of these studies address the alternation of consensual intervals in the growth of science, focusing on Kuhnian incommensurability and the disruptions that punctuate placid normal science.<sup>4</sup> Their aim is to understand and to explain how successful theoretical and experimental candidates survive a presumed chasm of mutual incomprehensibility; in this effort, studies of general change alternate with microstudies of power.<sup>5</sup>

It has become clear, however, that our categories of theory, observation, and experiment have a history of their own, and that the armamentarium of concepts and criteria that we have so far employed might not be adequate for a description of recent science. In his most recent work, Peter Galison has insisted that different cultures of theoreticians, instrument builders, experimentalists, and engineers live in distinct milieus, and that

3. On negotiation and scientific controversies, see in particular Bruno Latour and Steve Woolgar, *Laboratory Life: The Construction of Scientific Facts* (Princeton: Princeton University Press, 1986). On construction and stabilization of the objects of experimental work, see M. Norton Wise, "Mediating Machines," *Science in Context* 2 (1): 77–114 (1988); David Gooding, Trevor Pinch, and Simon Schaffer, eds., *The Uses of Experiment*, (Cambridge: Cambridge University Press, 1989). Specifically, for Nernst, Haber, and chemical industry, see Timothy Lenoir, "Practical Reason and the Construction of Knowledge: The Life World of Haber-Bosch," (MSS).

4. Thomas S. Kuhn, *The Structure of Scientific Revolutions*.

5. For example, by moving from the quantum or relativistic to the larger probabilistic revolution, in Lorenz Krüger et al., eds. *The Probabilistic Revolution*, vol. 1. *Ideas in History* (Cambridge, Mass.: MIT Press, 1987).

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the traditions, skills, goals, and vocabularies of these differing segments of the very large community of physicists operate under varying constraints in their mode of argumentation, in their understanding of a problem and of the paths taken toward its solution. In Galison's view, these subcultures coexist but are not diachronically accessible to us across the board. Developments and transformation in one "tradition" do not necessarily reverberate synchronically in all others. Thus, change in "theory" and change in "experiment" do not have simultaneous life histories.<sup>6</sup> One aspect of what follows may serve as further illustration of Galison's important argument for the existence of an inner and an outer life of the experiment: We shall see that in the case of Nernst and his contemporaries, it was still possible to entertain a lively dialogue between the laboratory and the outside, between academia and industry, and that certain instruments circulated, albeit haltingly at times, between the two. Moreover, our description of this circulation of devices between inside and outside will illustrate Galison's argument that theory and experiment cannot be followed along a single, linear story.

The experimental and theoretical network of interactions that figure in Nernst's life may be a test for recent treatments of discursive formations, of local reconfigurations, coexistence, and grouping of statements.<sup>7</sup> However, the particular concepts of disciplinary coherence and regularity do not figure prominently in my account. The search for uniformities and constraints regulating "discipline formation," or research programs, seems to belong to the perennial quest for ordering and systematizing. The accounts of discipline formation and disciplines as a "Ding an sich" are often taken as a given entity in many science studies, rather than as a conclusion.<sup>8</sup>

Recent scholarship has also focused on the question of whether there has ever developed a peculiarly "chemical" as opposed to "physical" view of nature and, as a corollary, whether chemical laboratory practices have ever acquired a life of their own, distinct from other kinds of practices.<sup>9</sup> Many arguments have been advanced in support of a consolidation of disciplines during the twentieth century, and for the consequent stabilization

6. Peter Galison, *Image & Logic. A Material Culture of Microphysics* (Chicago: University of Chicago Press, 1997).

7. Timothy Lenoir, "The Discipline of Nature and the Nature of Disciplines," pp. 70–102, in Ellen Messer-Davidow, David Sylvan, and David Schumway, eds., *Knowledges: Historical and Critical Studies in Disciplinarity* (Charlottesville: University of Virginia Press, 1993), p. 5.

8. For a recent discussion, see Mi Gyung Kim, "Labor and Mirage: Writing the History of Chemistry," *Studies in History and Philosophy of Science* 26 (1995): 155–66.

9. Mary Jo Nye, *From Chemical Theory to Theoretical Chemistry*, 1994.

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of distinct “cultures” of scientific practitioners.<sup>10</sup> These views draw on studies of professional identity and stress differences between cultures over cross-cultural similarities. Indeed, the enduring quest for national styles of scientific research, styles of reasoning, epistemic styles, and many of their variants derives from similar preoccupations.<sup>11</sup>

Inevitably, however, once a particular tool (theoretical, such as the quantum hypothesis; mathematical, such as the calculus; or instrumental, such as the liquefier) becomes available, it cannot help but permeate scientific practice in many related fields. Therefore, alongside the increasing specialization that characterized all sciences at the turn of the century, one must also take note of the pragmatic appropriations that promoted, rather than inhibited, cross-disciplinary discourse. Physical chemistry, for instance, employed and was modulated by a variety of tools from physics, ranging from electricity and thermodynamics to instrumentation, error calculus, graphs, and other methods. Conversely, various advances in chemistry introduced new goals, practices, and perspectives into the emerging fields of biochemistry and solid-state physics.

The picture that emerges from my study is the ongoing practice of appropriation across disciplinary boundaries, always in tension with the demands of intradisciplinary coherence. Furthermore, disciplines, research programs, and institutions never act in isolation. Scientific activity takes place in a number of intersecting arenas, and each scientist inevitably partakes of multiple spheres of scientific communication.

The work of Nernst, as well as that of Max Planck, Albert Einstein, Heike Kamerlingh Onnes, and many others, was in constant and multidimensional flux. Picking data out of a certain context and applying them in another, or taking theoretical formalisms and expanding them, or looking anew at older data in a fresh light are all processes that negate a simple story of the development of new disciplines. Nor can “new disciplines” straightforwardly be credited with the production of new ideas or new practices. The ability continually to make “the world anew by bringing us back to familiarity with it, by paying attention to what we are doing,”<sup>12</sup> was a pertinent feature of much fin-de-siècle science, as well as art and culture. Thus, innovation occurred not by breaking the shackles or shaking the foundations of an old edifice but by reconfiguring what was meant by force, matter, field, and heat in a variety of specific problems.

10. Peter Galison, *How Experiments End*.

11. For a recent discussion, see Marga Vicedo, “Scientific Styles: Toward Some Common Ground in the History, Philosophy, and Sociology of Science,” *Perspectives on Science* 3 (1995): 231–54.

12. Kirk Varnedoe, *A Fine Disregard: What Makes Modern Art Modern* (New York: Harry N. Abrams, 1990), p. 277.



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**Nernst and Physical Chemistry**

The usefulness of the notion of a discipline as an analytic tool for the history and sociology of scientific practice – an issue that has recently attracted the attention of many historians – is exemplified by Nernst and his “school” of physical chemistry. Nernst is considered one of the more successful descendants of the original “triumvirate” of Ostwald, van’t Hoff, and Arrhenius and the institutions, journals, and networks they created. But at least in the case of Nernst, the category of physical chemistry is convenient only as a taxonomic shorthand. It often appears that a preoccupation with disciplines is a result of the ethos of specialization and professionalization, which has dominated the histories of the last century, but this focus loses its persuasiveness when placed in the context of the highly “interdisciplinary” practice of the natural and exact sciences within academic as well as industrial settings in both the recent past and the present.<sup>13</sup>

Physical chemistry has become something of an archetype for the new sciences born from the turmoil of a nonphysical, nonmathematical, somewhat premodern chemistry at the opening of the twentieth century. In many ways physical chemistry has afforded scientists and historians a unique opportunity to study modern science in the making. After all, chemistry, physics, and medicine had all been around for centuries. But here was, or so it seemed, a self-conscious effort on the part of the more enlightened, physicalist chemists to rejuvenate a science that was gradually becoming submerged in a surfeit of new chemical elements and substances, with a lack of systematic nomenclature, a profusion of explanatory models, and a wealth of reactions and applications. Did atoms truly exist? Did they react with each other, and if so, how? Did mechanical, electrical, magnetic, or gravitational forces play a role in chemical reactions? What was affinity, and how could it be measured? Was wet chemistry different from dry chemistry? Was inorganic matter different from organic substances in any fundamental way?

Physical chemistry emerged in the mid-1880s as part of modern physical science. By the early decades of this century, physical chemistry was considered to have grown into a lively, well-populated, and well-organized scientific discipline, primarily through the determined efforts of Wilhelm Ostwald, Jacobus Henricus van’t Hoff, and Svante Arrhenius.<sup>14</sup> It grew

13. Lenoir, 1993, suggests, for instance, that disciplinary programs “adapted locally to the political economy” are more useful categories than monolithic “disciplines.”

14. This historiography of physical chemistry has also been criticized because it has purportedly relied too heavily on the self-image of turn-of-the-century Continental physical chemists, who saw themselves as distinctive specialists. R. G. A. Dolby, “Thermochemistry

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out of a new understanding of the nature of solutions and the constitution of matter therein. One prominent feature of the historiographical background is the examination of the self-representation and intellectual hagiography of a small number of well-known physical chemists. The theme of disciplinary demarcations is a recurring one, if for no other reason than that it plays a paramount role in the transmission of historical narratives, and has significantly influenced recent histories of physics and chemistry, as well as a number of biographical studies. These problematic self-locations show that later scientific research and controversies – in addition to the subsequent historical analyses of these events – relied on certain retrospective “disciplinary” accounts, which lacked contextual references, and thereby promoted a misleading “single perspective” on the development of low-temperature physics, quantum chemistry, and chemical thermodynamics.

In the mid-nineteenth century, Claude Louis Berthollet called attention to the special role of solutions in chemistry. He had unsuccessfully tried to define chemical affinity by linking it to the masses of reactants in a solution, postulating the existence of forces akin to Newtonian gravitational attraction.<sup>15</sup> In the mid-1880s, Arrhenius and van't Hoff further probed the nature of the processes in liquid solutions. They demonstrated not only that solutions are composed of matter that exists in a state of dissociation but also that different kinds of solute coexist in solutions.

It was assumed, for example, that in the solid state, crystals of table salt are constituted of molecular entities of sodium chloride, in which the atoms of sodium and chlorine are physically bound, or connected. It was assumed that the chemical molecule as a whole continues to exist in solution, as it did in the gaseous phase. But by 1887, in an elaboration of his rather bold and quite speculative dissertation of 1884, Arrhenius developed his ionic dissociation theory of electrolytic solutions: A solution of table salt in water is not composed of molecules of salt distributed in water but of separate ions of sodium and chlorine, in addition to undissociated molecules of sodium chloride. Whereas Arrhenius had argued in his dissertation of 1884 that such ions were present when an electric current was passed through a solution, by 1887 he postulated the existence of “free ions,” regardless of the presence of such a current. Furthermore, Ostwald, Arrhenius, van't Hoff, and Nernst showed in the late 1880s that many physical and chemical properties of solutions could be explained

versus Thermodynamics: The Nineteenth Century Controversy,” *Hist. Sci.* 22 (1984): 379–80.

15. John W. Servos, *Physical Chemistry from Ostwald to Pauling: The Making of a Science in America* (Princeton: Princeton University Press, 1990), p. 14.