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HYLE Book Reviews

Elisabeth Crawford, Arrhenius: From Ionic Theory to the Greenhouse Effect, Science History Publications, Canton, 1996 (Uppsala Studies in History of Science, Volume 23), -xiii, 320 pp. (ISBN: 0-88135-166-0)

Diana Barkan, *Walther Nernst and the Transition to Modern Physical Science*, Cambridge University Press, Cambridge, 1999, -xii, 288 pp. (ISBN: 0-521-44456-x)

by Peter J. Ramberg*

Svante August Arrhenius and Walther Nernst were two of the founders of the new physical chemistry. Arrhenius was one of the original triumvirate with Wilhelm Ostwald and Jacobus Henricus van't Hoff, Nernst one of a second generation of physical chemists, although only five years younger than Arrhenius. Importantly, Nernst was the first German chemist to become a disciple of the new physical chemistry. In 1886-7, Nernst and Arrhenius became close friends as colleagues in Friedrich Kohlrausch's Würzburg physics institute, and both spent an additional year together in Graz in Ludwig Boltzmann's institute. They later would become estranged, and Arrhenius would play a large part in preventing Nernst from receiving the Nobel Prize until 1921. These two recent biographies of Arrhenius and Nernst, relying heavily on extensive archival research, provide intriguing insights into the deteriorating relationship between Nernst and Arrhenius, but more significantly, the different factors involved in the emergence of the 'new' physical chemistry of the 1880s and 1890s. This biographical approach provides a convenient method for understanding the unique confluence of theoretical traditions in chemistry and physics – chemical affinity, electrochemistry, thermochemistry, conductivity, quantum physics – that occurred during the late nineteenth century. Were Nernst and Arrhenius chemists or physicists? As it becomes clear on reading both volumes, it is difficult to tell where one discipline ends and the other begins.

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Arrhenius' life can be conveniently divided into three major portions, corresponding to the three major sections in Crawford's biography: his education and work in solution theory (for which he is most famous), his study of cosmic physics, and his work in immunochemistry (Arrhenius invented the term). His childhood and early education in Uppsala involved training in physics under Robert Thalén, chemistry under P.T. Cleve and the *Dozent* Otto Petterson, who would later be one of Arrhenius' strongest supporters at the Stockholm *Högskola*. Arrhenius studied physics under Erik Edlund at the Stockholm *Högskola*, where he attempted to apply the concepts of physics to problems in chemistry, in particular the conductivity of solutions, already an established research area.

Arrhenius' own study of conductivity began in the fall of 1882 with an attempt to determine molecular weights by measuring conductivity. His now famous dissertation was written between March and June 1883, and divided into an experimental and theoretical part. The experimental part treated the conductivity of electrolytes at dilute solution to test Friedrich Kohlrausch's hypothesis that molecular conductivities become constant at high dilution. In the theoretical part, Arrhenius explained the results of the first, by introducing the concept of *active* (conducting) and *inactive* (non-conducting) molecules, and the *activity coefficient*, which elaborated on the Clausius-Williamson hypothesis that assumed the molecules were dissociated *before* the current was applied, and that all ions had the same amount of electricity. He applied Berthollet's law of mass action using Guldberg and Waage's notion of

'active mass' as dependent on concentration. Arrhenius also derived this mass law from another direction, as an equilibrium between active and inactive molecules, measured by conductivity – the activity coefficient was related directly to the 'active mass' in solution. Arrhenius' famous four-hour defense of his thesis has become the stuff of legend, and Crawford provides an excellent analysis of the reasons for why Arrhenius' defense was only partially successful (he passed, but without the grade necessary for permission to teach), in particular the roles played by various faculties at the University, and the form as well as the content of the dissertation.

Crawford argues that physics, not chemistry, was uppermost in Arrhenius' mind during his dissertation work. His ideas concentrated on the physics of corpuscles, and the physical processes of constants, laws, and effects, not on chemical transformations. When he established that the ions were charged, but did not explain anything about the nature of the ions themselves, Arrhenius answered questions from physics, not chemistry. Chemists focussed on the nature of electrolytes, and the prevailing solution theory in chemistry, advocated by Armstrong, Mendeleev, and Raoult, supposed chemical reactions, the formation of hydrates, between solute and solvent. This theory influenced Arrhenius, but he would eventually replace it with a more physical theory.

During the 1890s, Arrhenius moved into the area of cosmic physics, or geophysics, which had originally been institutionalized in Austria before it took root and flourished in Sweden in the 1890s (primarily at the Swedish Physical Society). While in Graz, Arrhenius had already become interested in atmospheric chemistry, looking at the influence of ultraviolet light in conductivity of air, but during the 1890s, he took up the problem of the influence of carbon dioxide on the earth's climate, building on Arvid Högbom's extensive study of the carbon dioxide cycles in the atmosphere. In 1896, Arrhenius would link the levels of carbon dioxide specifically to climate. Developing his model required the complex calculation of the influence of CO_2 levels at various latitudes on the earth, determining the various heat absorption coefficients of CO_2 , the processes that contribute to the equilibrium between the earth's surface temperature and that of the atmosphere, and average local humidities. The result was a detailed chart of the expected change in temperature with CO_2 content, according to latitude, that clearly showed a rise in temperature with increasing CO_2 content. Arrhenius would later attempt to summarize the field of cosmic physics by writing the thousand page *Lehrbuch der kosmischen Physik* (1903), and a shorter best-selling version for a popular audience, *Världarna utveckling* (*Worlds in the Making*, 1906).

At the end of the 1890s, Arrhenius' interest in immunochemistry was piqued by the arrival of the Dane Thorvald Madsen, a specialist in bacteriology and serology, at his laboratory. Madsen had been involved in the current debate in immunology between the cellular (or biological) and humoral (or chemical) theories of immune response, and had favored the cellular theory. Arguing against Paul Ehrlich's theory of immune response, Arrhenius and Madsen attempted to show that the toxin-antitoxin reaction followed the physico-chemical laws of equilibrium and mass action, and, with less success, that the neutralization of toxins with antitoxins followed a curve resembling the neutralization of a weak acid by a weak base.

Armed with these results, Arrhenius became convinced of the physico-chemical nature of the immunological response, and set the stage for the conflict with Paul Ehrlich. Crawford provides an excellent summary of sources of the conflict between Ehrlich and Arrhenius. Ehrlich saw the practical uses of serum therapy, whereas Arrhenius was interested in the purely intellectual scientific questions of immune response. Ehrlich's approach was based on the principles of organic chemistry and especially physiology, where systems and functions of individual cells are given primary importance. Arrhenius emphasized the simplicity of solutions (a carryover from his view of simple ions in solution) and kinetics, with a minimum of hypotheses. As a result, Ehrlich considered interaction between cell and pathogen irreversible, involving new, undissociable chemical bonds. Arrhenius, on the other hand, considered the process to be equilibrium-governed.

As rich as it is in the details of Arrhenius' scientific work, Crawford's biography is also important for our understanding of the institutional history of Swedish science. Among other topics, she treats the tension between the Högskola and the University of Uppsala, the role of science in the growing Swedish nationalism, and the formation and administration of the Nobel Prizes, in which Arrhenius became extensively involved.

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In her biography of Nernst, Barkan recasts his career in order to integrate what previously appeared to be separate unrelated strands of his scientific interests, and thereby present an alternative view of the formation of Nernst's most famous contribution to physics and chemistry: the heat theorem. One of her main theses is to portray the emergence of the heat theorem from within a constellation of issues in both physics and chemistry –solution theory, quantum theory, and the relationship between specific heats and extreme temperatures. In doing so, she casts doubt on the traditional demarcation of scientists into specific disciplines. Rather, she portrays Nernst as following his own unique path, independent of disciplinary boundaries, and her version of Nernst's research path is

continuous, from his research in Wilhelm Ostwald's laboratory to the organization of the first Solvay Congress of physics in 1911.

Barkan divides her treatment of Nernst into three parts. In the first part, she discusses his education and training at Würzburg (under Friedrich Kohlrausch) and Graz (under Ludwig Boltzmann) during the 1880s, where he became involved in the traditional problems in physics and electrochemistry. In 1887, he moved to Leipzig, where he became acquainted with the methods and techniques of the new physical chemistry under Wilhelm Ostwald, where he focussed on understanding, in a physical sense, the nature and causes of electromotive force in galvanic cells. Called to Göttingen as an assistant by Eduard Riecke, Nernst continued independent research on the theory of solutions and kinetics of electrolytic processes, in which he tied his interpretation closely to thermodynamic principles.

The second part of Barkan's biography focuses on Nernst's invention of the electrolytic lamp, placing it in the context of the emerging technology of, and market for, electrical lighting in Wilhelmine Germany. Barkan addresses the set of technical and theoretical questions Nernst's invention raised in order to show how it led to the formulation of the heat theorem in 1907. The theoretical problem of light emission from a high temperature filament, and the problem of producing a constant illumination required Nernst to thoroughly understand the behavior of materials and the variation of physical constants such as specific heats and molecular weights at high temperature. Upon his move to Berlin in 1905, Nernst shifted to the measurement of specific heats at low temperatures, when he realized that a consequence of the difference between the heat and work of a chemical reaction should asymptotically reach zero at low temperatures. This built on the previous conceptions of thermochemistry by Berthelot, Julius Thomsen, and van't Hoff, in which it became clear that the heat of a reaction and the work generated by the reaction were not the same thing. Nernst then developed new technology with the sensitivity required for measuring specific heats of materials at supercooled temperatures. The heat theorem was, Barkan argues, the natural outcome of Nernst's interests that combined electrolytic theory, thermochemistry, and thermodynamics.

In the third part, of less interest to the philosophy of chemistry, Barkan analyzes the incorporation of the heat theorem within the chemical and physical communities, culminating in the Nobel Prize of 1921. The last chapter reveals larger historical claims indicated in the title of the book, and Barkan argues that the roots of modern physical science lay as much in chemistry as in physics, and the role of chemistry has been overshadowed by the physicists' version of the development of modern physical science.

Overall, Barkan provides an excellent overview of Nernst's training in physics, and of Ostwald's view of the place of physical chemistry at the time of his move to Leipzig. Barkan's argument that Nernst's work should be seen as a comprehensive whole rather than a series of fragmented projects, is well thought out and largely convincing, although it is difficult to follow in places for those unfamiliar with previous interpretations of Nernst's work. The principal weakness in her continuity argument is the lack of a clear connection between the invention of the electrolytic lamp and Nernst's *earlier* work in solution theory. A slightly more detailed discussion of how the lamp worked and how it related to his initial study of conductivity, would have helped enormously.

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Although Barkan and Crawford do not directly attack philosophical issues, both of their books contain grist for the mill of philosophy of chemistry. Most obvious is the constantly shifting border between physics and chemistry and the identifying characteristics of both sciences. Both Arrhenius and Nernst were trained as physicists, yet ultimately both received Nobel Prizes in *chemistry*. How are we to identify their work as uniquely chemical or physical? In this sense, Barkan is correct – it is difficult to demarcate 'chemistry' from 'physics' in the domain of physical chemistry, and as the twentieth century progressed, the remaining disciplinary boundaries became less distinct. But moving from chemistry to *biology*, there seem to be greater differences between explanations deriving from different disciplines. As Crawford makes clear, the dispute between Arrhenius and Ehrlich over immunochemistry is particularly relevant for understanding how methodology and theory are shaped by disciplinary constraints. The case studies in these two useful biographies then can help philosophers of chemistry identify what makes an explanation 'chemical', 'physical', or 'biological', or even if such a demarcation is possible.

Peter J. Ramberg: Max-Planck-Institute for the History of Science, Wilhelmstr. 44, 10117 Berlin, Germany; <u>ramberg@mpiwg-berlin.mpg.de</u>

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