Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

W

1909: Wilhelm Ostwald

by J. Van Houten

Nobel Prize in Chemistry 1909
Wilhelm Ostwald (1852–1932)

in recognition of his work on catalysis and for his investigations into fundamental principles governing chemical equilibria and rates of reaction

This is the third in a series of thirteen essays appearing monthly that feature the work of 20th century Nobel Laureates in the field of chemical dynamics. The first two essays focused on the 1901 award to Jacobus van't Hoff (*1*) and the 1903 award to Svante Arrhenius (*2*).[W] It seems truly fitting that Wilhelm Ostwald should receive the Nobel Prize for his work in chemical dynamics shortly after the awards to van't Hoff and Arrhenius because both of them had studied with Ostwald—as what we would now call post-doctoral fellows. Another Nobel Laureate, Walther Nernst, winner of the 1920 chemistry Nobel Prize "for his work in thermochemistry" (*3*), also worked with Ostwald in Leipzig. Ostwald and van't Hoff are regarded together as the founders of the discipline of modern physical chemistry. Ostwald organized the Department of Physical Chemistry at Leipzig University; he founded the *Deutsche Elektrochemische Gesellschaft* (German Electrochemical Society) in 1894, which expanded to become the *Deutsche Bunsen-Gesellschaft für Angewandte Physikalische Chemie* (German Bunsen-Society for Applied Physical Chemistry) in 1902. Ostwald and van't Hoff together founded the first journal in physical chemistry, *Zeitschrift für Physikalische Chemie* in 1887; and Ostwald himself edited the first 100 volumes, until 1922 (*4*).

As was true for Arrhenius in 1903, Ostwald's 1909 Nobel presentation begins with a statement paying homage to Swedish chemist Jöns Berzelius (1779–1848): "As early as the first half of last century it had in certain cases been observed that chemical reactions could be induced by substances which did not appear to participate in the reaction themselves and which at all events were not altered in any way. This led Berzelius in his famous annual reports on the progress of chemistry for 1835 to make one of his not infrequent brilliant conclusions whereby scattered observations were collated in accordance with a common criterion and new concepts were introduced in science. He termed the phenomenon catalysis. However, the catalysis concept soon came up against opposition from another eminent quarter as allegedly unfruitful and gradually fell utterly into discredit" (*4*).

Ostwald's work, 50 years later, served to validate the catalytic theories of Berzelius as well as Berzelius's theories of acid and base dissociation. In particular, Ostwald observed that the rates of reactions with acids and bases could be related to the strengths of those acids and bases. Thus Ostwald laid the groundwork for systematic study of reaction kinetics and of catalysis. In addition, Ostwald utilized conductivity measurements to confirm Arrhenius's theories regarding ionic dissociation of acids and bases. In particular he showed that weak acids and bases were incompletely ionized in solution—the concept that we now associate with pK_a. By correlating his results from kinetic studies with his conductivity studies, Ostwald concluded that the effect of acids and bases in determining reaction rates was directly related to the hydrogen ion or hydroxide ion concentration, hence the strength, of the acid or base.

Wilhelm Ostwald and Svante Arrhenius

Photo: Aaron Ihde collection

As a result of his study of various catalytic processes, Ostwald developed the principle that a catalyst can modify the rate of a reaction without any net change in the catalytic material itself over the full course of the reaction. At the time Ostwald received the Nobel Prize in 1909, the importance of catalysts was just becoming widely recognized. Thus his Nobel presentation includes the statement: "The significance of this new idea is best revealed by the immensely important role—first pointed out by Ostwald—of catalytic processes in all sectors of chemistry. Catalytic processes are a commonplace occurrence, especially in organic synthesis. Key sections of industry…are based on the action of catalysts. A factor of perhaps even greater weight, however, is the growing realization that the enzymes, so-called, which are extremely important for the chemical processes within living organisms, act as catalysts and hence the theory of plant and animal metabolism falls essentially in the field of catalyst chemistry" (*4*). Ostwald first proved the catalytic action of enzymes in 1893.

The Nobel presentation for Ostwald contains a statement that seems to reflect the optimism of the first decade of the 20th century but which, with hindsight, is rather ironic. It reads: "The rate of a reaction is a measurable parameter and hence all parameters affecting it are measurable as well. Catalysis, which formerly appeared to be a hidden secret, has thus become what is known as a kinetic problem and accessible to exact scientific study. Ostwald's discovery

Nobel Centennial Essays

has been profusely exploited. Besides Ostwald himself a large number of eminent workers have recently taken up his field of study and the work is advancing with increasing enthusiasm. The results have been truly admirable" (*4*). That being said, it is, perhaps, surprising that the next Nobel Prize for work having to do with chemical dynamics was not awarded until 34 years later—the 1943 Nobel Prize to George de Hevesy for developing isotope tracer techniques (*5*), which will be the subject of the next article in this series.

In addition to his work on reaction dynamics, Ostwald is credited with helping to advance thermodynamics with his 1883 German translation of the work of Josiah Willard Gibbs (1839–1903) on the theory of chemical thermodynamics. Gibbs was on the faculty of physical mathematics at Yale University when he published a series of papers between 1873 and 1878 introducing the fundamental equations and relations to calculate multiphase equilibrium, the phase rule, and the free energy concept (*6*). The fact that Gibbs's work remained unknown has been attributed in part "largely to the fact that its mathematical form and rigorous deductive processes make it difficult reading for any one, and especially so for students of experimental chemistry whom it most concerns" (*6*). However, another factor may have been that Gibbs was an American and he published in English, which, unlike today, was not the principal scientific language of that era. Gibbs's thermodynamic models became much more accessible to the important scientists of his time with Ostwald's German translation in 1883, and later with Henri Le Châtelier's translation into French in 1899 (*7*, *8*).

Ostwald's 1909 Nobel citation made mention of the fact that important industrial processes of that time relied on catalysis, a statement that remains true today. Consider the fact that the 2001 Nobel Prize in chemistry was awarded for developing chirally catalyzed synthetic methods and that one of the recipients, William Knowles, was an industrial chemist. Although Ostwald's 1909 Nobel citation used sulfuric acid synthesis to exemplify an economically important industrial process, the so-called contact process for H_2SO_4 production using platinum (or, later, V_2O_5) as a catalyst in the oxidation of SO_2 to SO_3, that process was developed by Peregrine Phillips and patented in 1831 (*9*). Ostwald's own name, on the other hand, is inextricably linked with another catalytic industrial process—the one used to manufacture nitric acid from ammonia, which he patented in 1902. The Ostwald process uses a platinum catalyst in the oxidation of NH_3 by O_2 to form NO, which is further oxidized to NO_2. The NO_2 disproportionates in water to form HNO_3 and more NO, which is recycled. The Ostwald process accounts for virtually all the nitric acid produced today (about eight million tons per year in the U.S.) and it consumes about half the current supply of ammonia. It is featured in the descriptive chemistry section of many introductory textbooks.

The first three essays in this series have examined the life and times of the three Nobel Laureates in chemical dynamics in the first decade of the 20th century (*1*, *2*). It is clear that the Nobel committee chose wisely with the selections of van't Hoff, Arrhenius, and Ostwald, as their work has stood the test of time and remains important to us now a century later. Their names remain prominently featured in modern chemistry texts, both as historical figures and because of the equations and processes named for them. The important relationship between those three pioneers of chemical dynamics has long been recognized in the pages of this *Journal*. It was first discussed in 1930 by Benjamin Harrow in an article entitled, "The Meeting of Ostwald, Arrhenius, and van't Hoff" (*10*), and in 1934 C. W. Foulk wrote of "The Ostwald-van't Hoff Photograph and Other Memories of Ostwald's Laboratory" (*11*). In 1933 Ostwald was described as "a great protagonist and inspiring teacher" by Wilder Bancroft (*12*). More recently (April 1996) Deltete and Thorsell wrote an extensive discussion of Ostwald, focusing on his relationship to Gibbs (13). The 1996 article contains a quotation from Bancroft's 1933 article in which van't Hoff, Arrhenius, and Nernst are characterized as "men who discovered fundamental relations" and Ostwald is described as "absolutely at the head of [the group of]…men who do not make the great discovery but who see the importance and bearing of it…" and who then explain the important things to the rest of us.

The 1901, 1903, and 1909 awards can be viewed as constituting the first phase of Nobel Prizes in chemical dynamics. The second phase occurred during the middle decades of the 20th century—in 1943, 1956, and 1967 (*1*). The recipients of the mid-century awards may be less familiar to current students, although their work—isotope tracers, free radical reaction mechanisms, temperature jump, and pressure jump methods—is featured prominently in modern chemistry texts. The third phase includes three awards in the 1980s for work that forms the new foundation of modern chemistry—frontier orbital symmetry rules, mechanistic studies of transition metal complexes, molecular beams, and infrared chemiluminescence (*1*). Finally, in the 1990s, four awards represent the most recent (but probably not the final) phase of chemical dynamics—electron transfer theory, atmospheric chemistry, computational techniques, and femtochemistry (*1*). Although all but two of the Nobel Laureates from the first two phases are deceased, most of the Laureates from the last two phases remain very active today. Forthcoming essays will examine the remaining ten Nobel Prizes in chemical dynamics in turn, emphasizing the interrelationships between them.

W Supplemental Material

A list of all recipients of the Nobel Prize in Chemistry, their affiliations, and work for which the award was made is available in this issue of *JCE Online*.

Literature Cited

1. Van Houten, J. *J. Chem. Educ.* **2001**, *78*, 1570–1573.
2. Van Houten, J. *J. Chem. Educ.* **2002**, *79*, 21–22.
3. Nobel e-Museum—Nernst 1920 Chemistry Nobel Prize Presentation. *http://www.nobel.se/chemistry/laureates/1920/press.html* (accessed Nov 2001).
4. Nobel e-Museum—Ostwald 1909 (with links to Prize Presentation and Biography pages). *http://www.nobel.se/chemistry/lau-*

Nobel Centennial Essays

reates/1909/index.html (accessed Nov 2001).

5. Nobel e-Museum—de Hevesy 1943 Chemistry Nobel Prize Presentation. *http://www.nobel.se/chemistry/laureates/1943/press.html* (accessed Nov 2001).
6. School of Mathematics, Saint Andrews University, Scotland, MacTutor Mathematics, Biography of J. Willard Gibbs. *http://www-history.mcs.st-andrews.ac.uk/history/Mathematicians/Gibbs.html* (accessed Nov 2001)
7. Gibbs, J. W. *The Scientific Papers of J. Willard Gibbs;* Bumstead, H. A., Van Name, R. G., Eds.; Dover Publications: New York, 1961; pp xi-xxvi (cited in Ref. *6*).
8. Woodrow Wilson Leadership Program in Chemistry—History of Chemistry, Le Châtelier. *http://www.woodrow.org/teachers/chemistry/institutes/1992/LeChatelier.html* (accessed Nov 2001).
9. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Elmsford, NY, 1984; p 838.
10. Harrow, B. *J. Chem. Educ.* **1930,** *7*, 2697.
11. Foulk, C. W. *J. Chem. Educ.* **1934,** *11*, 355.
12. Bancroft, W. D. *J. Chem. Educ.* **1933,** *10*, 609.
13. Deltete, R. J.; Thorsell, D. L. *J. Chem. Educ.* **1996,** *73*, 289.

J. Van Houten is a member of the Department of Chemistry, Saint Michael's College, Colchester, VT 05439; jvanhouten@smcvt.edu.