Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

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1901: Jacobus van't Hoff

by J. Van Houten

Introduction

December 2001 marks the centennial of the Nobel Prize. The Nobel Prize was instituted in the last will and testament of the Swedish industrialist Alfred Nobel (1833–1896) who invented dynamite in 1866. The first Nobel Prizes were awarded on December 10, 1901, the fifth anniversary of Nobel's death. With the Nobel Prize centenary in mind, this is the first in a series of thirteen essays that will appear in this *Journal* in the coming months reviewing the Nobel Prizes in chemical dynamics.

Obviously, it would be impossible in the space available to review all the chemistry Nobel Prizes awarded during the Twentieth Century.[W] The topic chemical dynamics was chosen for this series because the very first chemistry Nobel Prize was awarded to Jacobus van't Hoff in 1901 "for his pioneering work on chemical dynamics and osmotic pressure in solutions" and because during the ensuing century the chemistry Nobel Prize has been awarded 13 times to 22 individuals for work related to chemical dynamics (*1*). That work includes formulating underlying principles for studying and understanding reaction rates and mechanisms, developing new techniques for measuring reaction rates, and for following the course of reactions, developing new theories and computational methods for addressing problems relating to chemical dynamics, and, of course, directly studying reaction dynamics experimentally. In some cases those categories overlap; for example, experimentalists who develop new techniques often go on to use those techniques themselves to study aspects of chemical dynamics that had been previously inaccessible. Other Nobel Laureates in addition to those chosen for this series of essays have made important contributions to the study of chemical reactions. However, in the author's opinion, the work for which these Nobel Prizes was awarded was not as directly related to chemical dynamics as that of the 13 selected for these essays.

The 13 awards that will be discussed in the forthcoming series were listed earlier (*2*). This series of essays will examine those 13 awards in chronological order, and interrelationships between the research recognized in those prizes will be noted. In the process, the essays will examine how the field of chemical dynamics (as well as all of chemistry) has evolved during the Twentieth Century. For example, van't Hoff received the first Nobel Prize in 1901 for chemical dynamics, *per se,* and for studying osmotic pressure of solutions, which led to a much better understanding about the nature of molecules in solution. The theory of electrolytic dissociation proposed by Arrhenius (Nobel 1903) extended van't Hoff's ideas about the nature of molecules in solution into the realm of acids, bases, and salts. Although it was not mentioned specifically in his Nobel presentation, the Arrhenius equation is fundamental to all subsequent studies of reaction energetics and catalysis. The studies of catalysis by Ostwald (1909) were guided by the work of van't Hoff and Arrhenius, both of whom had studied with Ostwald. Isotope tracer methods developed by de Hevesy (1943) have been invaluable to chemists studying the courses of reactions of all types. Hinshelwood and Semenov (1956) unraveled the mysteries of free-radical chain reactions, and Crutzen, Rowland, and Molina (1995) showed the importance of free radicals in the destruction of stratospheric ozone. Eigen, Norrish, and Porter (1967) developed methods that extended our ability to study reactions into the submillisecond regime for the first time, and Taube (1983) used those methods to study electron-transfer reactions of metal complexes, while being guided by the theories of Marcus (1995). Molecular beam and infrared chemiluminescence methods developed by Herschbach, Lee, and Polanyi (1986) were an important part of Crutzen, Rowland, and Molina's work, and molecular beams are central to the femtochemistry studies of Zewail (1999). Furthermore, Zewail's femtosecond lasers can be viewed as direct descendents of Norrish and Porter's flash lamps. Finally, the orbital symmetry theories of Fukui and Hoffmann (1981), and the computational methods of Kohn and Pople (1998) have been invaluable to several recent Nobel Laureates, including some whose work will not be discussed in this series.

Today the Nobel Prize is universally recognized as the highest honor a person can receive in his or her field. It is truly remarkable how much of the work of Nobel Laureates has made its way into the teaching of chemistry at all levels. In one sense this is to be expected, but it is astonishing nevertheless to note how much work that was once considered to be the pinnacle of the science of its time has now become common textbook material. Tracing the history of the 13 Nobel Prizes covered in this series of essays provides interesting and informative insights into developments in the field as well as our attitude toward the science of chemistry.

Much of the material in the descriptions that follow is taken directly from material prepared by the Nobel Foundation at the time the prizes were awarded. Those annual announcements include succinct descriptions of the work being honored and the text of those announcements forms the basis of much of this essay. This provides a historical perspective as it examines the attitude of the scientific community at the time of each award. Quotations from Nobel presentations used in this series of essays are taken from the Nobel Foundation "e-Museum" web site at *www.nobel.se*, which contains considerably more information about the prizes and the prizewinners than could be included here.

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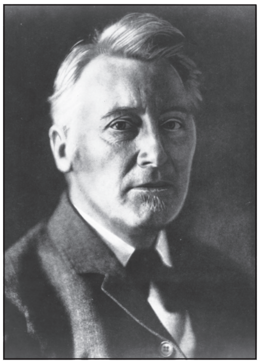
Nobel Prize in Chemistry 1901
Jacobus Henricus van't Hoff (1852–1911)

for his pioneering work on chemical dynamics and osmotic pressure in solutions

"Your Royal Highnesses, Ladies and Gentlemen.

The [Royal Swedish] Academy has awarded the Nobel Prize for Chemistry to Jacobus Henricus van't Hoff, Professor in the University of Berlin, for his pioneering work on chemical dynamics and osmotic pressure in solutions. As a result of his investigations in the fields of atomic and molecular theory van't Hoff has made the most important discoveries in theoretical chemistry since Dalton's time." (*3*)



Jacobus van't Hoff

Thus began the very first chemistry Nobel Prize presentation speech at a ceremony in Stockholm, Sweden a century ago. Although van't Hoff was officially cited "for his work on chemical dynamics and osmotic pressure in solution," the full text of the presentation speech in 1901 also recognizes some of van't Hoff's other contributions and places them in context. The relationship between osmotic pressure and chemical reaction dynamics is under-appreciated today, although the so-called "van't Hoff equation" for osmotic pressure, $\Pi = (n/V)RT$ appears in all modern physical chemistry books and in most current general chemistry texts. van't Hoff himself recognized that this equation is really just another form of the ideal gas law, $PV = nRT$. During the 19th Century most of the research regarding chemical reaction dynamics had been conducted in the gas phase; solution phase chemistry was poorly understood. Of course, the modern spectroscopic and electrochemical techniques that we now consider routine for solution phase work were not developed until much later.

van't Hoff showed that the behavior of molecules in dilute solution and the behavior of molecules in a gas both followed the same principles. van't Hoff also showed that Avogadro's principle, stating that the number of particles in a given volume is the same for all gases at a given temperature and pressure, could also be applied to dilute solutions by replacing the gas pressure with the osmotic pressure; hence the molar concentration term, n/V, in the van't Hoff equation. This led to the conclusion that molecules (particularly of non-electrolytes) existed in solution as well as in the gas phase—a concept that we now take for granted, but which was undreamed of at the time. That conclusion allowed researchers to begin to apply the principles of chemical dynamics, which had been developed for gas phase molecules, to the study of reactions in solution, where we commonly study them now. Subsequent work by Arrhenius, which will be covered in the next essay in this series, produced refinements taking ionic dissociation into account and led to what is now called the "van't Hoff *i factor*."

Although it was not, technically, work for which he was awarded the Nobel Prize, the Royal Swedish Academy also made note of van't Hoff's contribution to our understanding of molecular structure, stating: "With regard to atomic theory van't Hoff, following an idea put forward by Pasteur, advanced the hypothesis that the elementary atoms have attachment points geometrically oriented in space—a hypothesis which insofar as carbon compounds are concerned led to the theory of the asymmetry of carbon atoms and to the founding of stereochemistry" (*3*). van't Hoff first published those ideas (in Dutch) a few months before his doctoral dissertation in 1874 in a small pamphlet (*4*). That pamphlet put forward the concept of the asymmetrical carbon atom, which provided an explanation of the occurrence of numerous isomers of organic compounds that could not be explained by the two-dimensional models of the time. van't Hoff also pointed out the relationship between optical activity and the presence of an asymmetrical carbon atom, while acknowledging that Joseph-Achille Le Bel had simultaneously and independently arrived at the same ideas, though in a more abstract form. Given van't Hoff's contribution to our understanding of the relationship between optical activity and asymmetrical carbon atoms, it is interesting to note that now, a century later, the 2001 Nobel prize went to chemists who developed methods for synthesizing optical isomers using chirally-catalyzed reactions.

van't Hoff was clearly ahead of his time with regard to his theories of atomic and molecular structure. It is worth bearing in mind that when van't Hoff received his Nobel Prize in 1901, the concepts of atomic and molecular structure were nothing like what they are today. J. J. Thomson performed his now-famous experiments on cathode rays and measured the mass/charge ratio of the electron just four years earlier, in 1897. Robert Millikan's famous "oil drop" experiment to measure the fundamental unit of electrical charge did not occur until 1910, and the Bohr theory of the atom was not published until 1913 (Niels Bohr was only 16 years old in 1901 when van't Hoff received the Nobel Prize). Thomson, Bohr, and Millikan received the physics Nobel Prize in 1906, 1922, and 1923, respectively. van't Hoff's proposal that carbon is tetrahedrally coordinated became widely accepted after Linus Pauling's orbital hybridization theory was published in 1928. Pauling received the chemistry Nobel Prize in 1954.

van't Hoff also studied the relationship between thermochemistry and equilibrium. In his 1884 book *Études de Dynamique Chimique* (Studies in Dynamic Chemistry) he discussed the principles of chemical kinetics, methods for determining the order of a reaction, and the effect of temperature on reaction equilibria. The same year, Henri Louis Le Chatelier (*5*) extended that last principle to include effects of volume and pressure changes on gaseous equilibria. The principle, now generally associated with Le Chatelier alone, was originally known as the van't Hoff–Le Chatelier principle. In 1887 van't Hoff founded the first journal in physical chemistry, *Zeitschrift für Physikalische Chemie* together with Wilhelm Ostwald (*6*). Ostwald's 1909 Nobel Prize in chemistry "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction" will be discussed in the third essay in this series.

The 1901 Nobel presentation speech for van't Hoff concludes: "By applying these simple principles, which were originally borrowed from mechanics and thermodynamics, van't Hoff became one of the founders of chemical dynamics. His researches have been a substantial factor in bringing about the magnificent advances in physical chemistry, in which field his discoveries match the great contributions which other investigators, including those in our country [Sweden], have made in the field of electrochemistry and in the theory of chemical reaction. This has opened up great prospects for scientific research. On the other hand, the investigations on the state of substances in solutions have had and will continue to have the greatest practical consequences—consequences whose benefit to mankind can best be appreciated if we remember that chemical reactions occur predominantly in solutions and that the vital functions of living organisms are maintained by metabolic processes which take place in solutions." (*3*) Future essays in this series examining Nobel Prizes throughout the 20th Century will demonstrate just how prophetic those words were.

[W]Supplemental Material

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

Literature Cited

1. Nobel e-Museum—Chemistry. *http://www.nobel.se/chemistry/laureates/index.html* (accessed June 2001).
2. Van Houten, J. *J. Chem. Educ.* **2001,** *78*, 860.
3. Nobel e-Museum—van't Hoff (with links to Prize Presentation and Biography pages). *http://www.nobel.se/chemistry/laureates/1901/index.html* (accessed June 2001).
4. *Voorstel tot Uitbreiding der Tegenwoordige in de Scheikunde Gebruikte Structuurformules in de Ruimte* (Proposal for the Development of Three-Dimensional Chemical Structural Formulas)
5. Le Chatelier, Henri Louis. in *Comptes rendus* **1884,** *99*, 786
6. Nobel e-Museum—Ostwald (with links to the Prize Presentation and Biography pages). *http://www.nobel.se/chemistry/laureates/1909/index.html* (accessed June 2001).

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Reading List

In addition to the literature cited, supplementary information can be found in several published sources.

Feldman, B. *The Nobel Prize: A History of Genius, Controversy, and Prestige*; Arcade Pub.: New York, 2000.

James, L. K., Ed., *Nobel Laureates in Chemistry*; American Chemical Society & Chemical Heritage Foundation: Washington, 1993.

Magill, F. N., Ed. *The Nobel Prize Winners. Chemistry*; Salem Press: Pasadena, 1990.

The official Nobel Lectures, delivered by the Laureates on the occasion of the Nobel Prize ceremonies held each December in Stockholm, have appeared in the Nobel Foundation's annual publication, *Les Prix Nobel*, in the language in which they were presented, along with the presentation addresses to the Prizewinners and their biographies. These were later published in English by the Elsevier Publishing Company, Amsterdam until 1970. In 1991 the Nobel Foundation gave World Scientific Publishing Co. in Singapore the right to bring the series up to date from 1971 in the fields of Physics, Chemistry, Physiology or Medicine, and Peace, and from 1968 in Literature.