

## Nobel Centennial Essays

## A Century of Chemical Dynamics Traced through the Nobel Prizes

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1983: Henry Taube

by J. Van Houten

Nobel Prize in Chemistry 1983  
Henry Taube (1915– )*for his work on the mechanisms of electron transfer reactions, especially in metal complexes*

This is the eighth in a series of essays (1) written in commemoration of the centennial of the Nobel Prize, examining the history of chemical dynamics in the 20th century.<sup>W</sup> As his Nobel citation (2) states, Henry Taube studied electron transfer reactions of transition metal complexes. The Nobel Prize to Taube came exactly seventy years after it was awarded to Alfred Werner (3) for developing the structural chemistry of inorganic transition metal complexes. During the entire 20th century, Taube and Werner are the only inorganic transition metal chemists to win a Nobel Prize.<sup>1</sup> In fact, many of the complexes that Taube studied were first prepared or characterized by Werner.

Taube's citation (2) concludes with the statement: "There is no doubt that Henry Taube is one of the most creative research workers of our age in the field of coordination chemistry throughout its extent. He has for thirty years been at the leading edge of research in several fields and has had a decisive influence on developments." The citation also asserts that the field of mechanistic transition metal inorganic chemistry "was dominated both experimentally and theoretically by Taube, who according to one of the nominations has in eighteen listed instances been first with major discoveries in the entire field of chemistry."

The years between the end of Werner's scientific career and the beginning of Taube's showed little progress in the mechanistic chemistry of transition metal complexes. Taube began his scientific life as a main-group physical inorganic chemist. His master's and doctoral work focused on the photodecomposition of chlorine dioxide in solution and on redox reactions of ozone and hydrogen peroxide in solution, respectively. At Cornell University, where for the first three years he worked without assistance, the main theme of his research was to learn whether in the encounter of two redox reagents, the initial act involves a one-electron or two-electron change. His studies of redox reactions continued at the University of Chicago, where from the outset coworkers participated and where he began to apply isotopic tracers to the study of reaction mechanisms (4, 5). Some of Taube's earliest work with transition metal complexes involved determining the coordination number of aqua-ions in solution using <sup>18</sup>O NMR relaxation techniques (4): this at a time when NMR was in its infancy.

Taube's research was intimately related to the contributions of several other Nobel Laureates in addition

Henry Taube, shown on the cover of *C&E News*. Reprinted with permission from *Chemical & Engineering News*, May 21, 1984. © Copyright 1984 American Chemical Society.

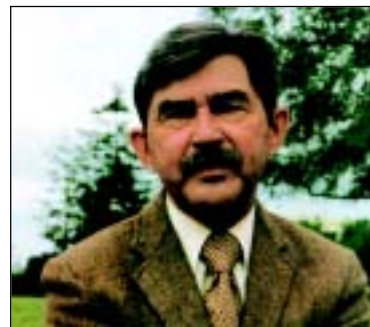


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to Werner's. His early mechanistic studies relied heavily on isotope tracer techniques developed by George de Hevesy, the 1943 Nobel Laureate (1d). The second of the 100 references in Taube's Nobel lecture (6) is to a 1920 paper where de Hevesy used naturally occurring lead isotopes to follow the exchange reaction between Pb<sup>2+</sup> and Pb<sup>4+</sup> (7). Taube's first major award was the ACS Award for Nuclear Applications in Chemistry in 1955 (2). He utilized the rapid kinetic techniques developed by Manfred Eigen (1f), the 1967 Nobel Laureate, to study reactions of labile metal complexes. Taube has frequently acknowledged that his electron transfer studies were guided by the theories developed by Rudy Marcus (8, 9), the 1992 Nobel Laureate.

Wilhelm Ostwald's 1909 Nobel citation (1c, 10) recalled Jöns Berzelius's "not infrequent but brilliant conclusions whereby scattered observations were collated in accordance with a common criterion and new concepts were introduced in science." That same statement could just as well be applied to Taube's work. Beginning around 1950, Taube began to amass data on reactions of transition metal complexes based on results from his own as well as other labs. He used that information to develop the principles describing the lability of metal complexes and the mechanisms of electron transfer that are now universally accepted.

Taube published "The Exchange of Water between Aqueous Chromic Ion and Solvent" (11) in 1950. He was the first to recognize the correlation between the rate of ligand substitution and the *d*-electron configuration of the metal, which he described in detail in 1952 in the long review, "Rates and Mechanisms of Substitution in Inorganic Complexes in Solution" (12). The following year he published a third seminal paper, "Observations on the Mechanism of Electron Exchange in Solution" (13). That was the first of many papers in which Taube and his co-workers defined the concepts of inner-sphere and outer-sphere electron transfer mechanism of transition metal complexes.

In his Nobel lecture (6) and in an interview published a month later in *Chemical and Engineering News* (14), Taube revealed that his interest in coordination chemistry began three years after teaching an advanced course in what might be described as physical inorganic chemistry. Dissatisfied with the dearth of descriptive content he turned to the chemistry of coordination complexes (5). Instead of using a textbook he decided to use a descriptive approach based on the Gmelin references on the chemistry of the cobaltamines. Taube has observed that teaching enhances research in words reminiscent of Roald Hoffmann's (19): "I became interested in why some of these compounds undergo substitution so slowly. I was very interested in substitution on carbon and it became obvious to me that the same issues were relevant to the whole field of inorganic chemistry, which had not really been looked at systematically...I began to wonder why certain metal centers undergo substitution slowly and others more rapidly" (14). Many more details of the genesis of his research on these reactions were discussed in his Nobel lecture (6).

In his January 1984 *C&E News* interview (14) he went on to point out that the "primary flaw" in his correlation between ligand substitution rates and the electronic configuration of the metal ion was that it was developed in 1952 (12), before crystal field theory and ligand field theory had become well established and, hence, was couched in terms of valence bond theory. In that interview and in his Nobel lecture (6) Taube revealed that he had difficulty getting graduate students interested in working on electron transfer reactions because "no one foresaw what it might lead to, and also because it seemed less exciting than other work in progress in my laboratory, much of it concerned with isotopic tracer and kinetic effects. The bulk of the [first] work...was done with my own hands." He went on to say "They were test tube experiments to begin with, which is something I still find interesting" (14). The first experiment to demonstrate the "capture" property of  $\text{Cr}^{2+}$  in reducing a substrate involved  $\text{I}_2$  as oxidant and made use of an aqueous solution of  $\text{Cr}^{2+}$  (5).

In 1967 Taube summarized much of his early groundbreaking work on transition metal redox reactions in a series of lectures at Brooklyn Polytechnic Institute (8). In addition to his early work referenced above, there are a number of reviews of his work.<sup>2</sup> Taube's contributions to the field of mechanistic inorganic chemistry are prominently featured in all current textbooks on that subject. His impact on the field is truly remarkable, and the list of his students and co-workers reads like a "Who's Who" of inorganic chemistry for the second half of the 20th century—many of whom are mentioned by name in his Nobel lecture (6).

For someone who has played such an important role in his branch of chemistry, Henry Taube is a very unassuming individual. One of his former post-doctoral researchers told me that when Taube learned he had won the Nobel Prize, he expressed with chagrin that now he would be "famous"

(15). He began his Nobel lecture (6) by saying that it would be a "historical perspective" of the field of electron transfer reactions, which, "may have some human interest and may even have some scientific interest of a kind which cannot be gathered from scientific journals...[where] the course of discovery as it actually took place may be rewritten to invest it with a logic that it did not fully acquire until after the event." His Nobel lecture provides an excellent account of the way science is "done" and the excitement that accompanies being on its cutting edge.

A year after receiving the Nobel Prize, Taube was awarded the Priestley Medal, the highest award of the American Chemical Society. On the occasion of its presentation his Stanford colleague, John I. Brauman, said that Taube "almost single-handedly invented the field of mechanistic inorganic chemistry. We are only now learning enough to fully understand what he has been telling us." (16) Nevertheless Taube didn't talk about his own accomplishments in his Priestley address, but about the work of his Ph.D. mentor, William C. Bray, who had died some forty years earlier. Taube said that Bray taught his students "to slow down and observe carefully; to make capital not only out of what happens [in a chemical system], but what doesn't happen" (16).

Taube's humility could be a reflection of his background (2, 4). He was born in the tiny agricultural community of Neudorf, Saskatchewan. As he said: "Certainly there is nothing about my first 21 years in Saskatchewan, taken in the context of those times, that I would wish to be changed. The advantages I enjoyed include: the marvelous experience of growing up on a farm, which taught me an appreciation of nature, and taught me also to discipline myself to get necessary jobs done; that of receiving my elementary education in a one room school; of receiving my high school education at Luther College—and of continuing through the M.Sc. degree at the University of Saskatchewan" (17).

Although he became a naturalized citizen of the U.S. in 1942, Taube is the first Canadian-born chemist to receive the Nobel Prize. He received his B.S. and M.Sc. from the University of Saskatchewan in 1935 and 1937, respectively. During his final years in Saskatoon, he studied with another Canadian who would win the Nobel Prize, Gerhard Herzberg, who had just immigrated to Canada as a refugee from Germany (18). Taube reported (17) that as a teacher Herzberg "had a truly exceptional capacity to make important matters, no matter how difficult, seem at least reasonable and, usually, fully understandable to students in his classes." In October 1997, on its 90th anniversary, the University of Saskatchewan dedicated a Nobel Laureate Plaza in honor of Henry Taube and Gerhard Herzberg (17, 18).<sup>3</sup>

Henry Taube moved to the United States in 1937 to begin studies for his Ph.D. at the University of California in Berkeley. He completed his Ph.D. in 1940, and remained in Berkeley for a year as an instructor. He had a strong desire to return to his native Canada, but was unsuccessful in

## Nobel Centennial Essays

finding a faculty position there. Gilbert N. Lewis (perhaps the greatest 20th century chemist *not* to win the Nobel Prize), was dean of the college of chemistry at Berkeley. Lewis recommended Taube to the head of the department at Cornell University, where he was hired as an instructor at a salary of \$1,800 (17). He remained at Cornell for five years and was promoted to assistant professor. In 1946 he moved to the University of Chicago, where Herzberg was then working. At Chicago, Taube rose through the academic ranks to professor and department chair. In 1961 he moved to Stanford University, where he has remained, and is now Professor Emeritus.

Taube's research career is best summarized by a simple statement from his Nobel Prize nomination papers (4): "Henry Taube founded the modern study of inorganic reaction mechanisms."

### Supplemental Material

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

### Notes

1. Recall that E. O. Fischer and G. Wilkinson shared the 1973 Nobel Prize for their work on "sandwich" organometallic compounds. However, Taube and Werner worked on what most inorganic chemists consider to be strictly inorganic complexes. Although some of Werner's and Taube's complexes have organic ligands, they have no metal-carbon bonds and are thus classified as inorganic; their chemistry is different from that of organometallics.

2. See for example: a. Lippard, S. J., Ed.; *Prog. Inorg. Chem.* **1983**, *30*, "An Appreciation of Henry Taube," which is a compilation of papers honoring Taube that was presented in 1982 at the ACS national meeting, the year before he received the Nobel Prize. b. See references 6, 8, 9, 11–14, and 16.

3. Herzberg came to Canada with the assistance of Taube's thesis advisor, J. W. T. Spinks, who had himself worked with Herzberg in Darmstadt earlier. He left Saskatchewan in 1945 to become professor of spectroscopy at Yerkes Observatory of the University of Chicago. He returned to Canada in 1948 as Director, Division of Physics at the National Research Council in Ottawa, where he spent most of his professional career, and became a recognized world authority on molecular spectroscopy. In 1971 Herzberg became the first Canadian chemist (albeit not Canadian-born) to receive the Nobel Prize. The first Canadian scientists to receive a Nobel Prize in any field were Frederick Banting and John Macleod of Toronto, who received the Prize in medicine and physiology in 1923 for their discovery of insulin.

### Literature Cited

1. a. Van Houten, J. *J. Chem. Educ.* **2001**, *78*, 1572–1573; b. *ibid.* **2002**, *79*, 21–22; c. *ibid.* **2002**, *79*, 146–148; d. *ibid.* **2002**, *79*, 301–304; e. *ibid.* **2002**, *79*, 414–416; f. *ibid.* **2002**, *79*, 548–550; g. *ibid.* **2002**, *79*, 667–669.
2. Nobel e-Museum—Chemistry 1983 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1983/index.html> (accessed April 2002).
3. Nobel e-Museum—Chemistry 1913 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1913/index.html> (accessed April 2002).
4. Walsh, J. in James, L. K., Ed.; *Nobel Laureates in Chemistry 1901–1992*; American Chemical Society and Chemical Heritage Foundation: Washington, 1993; pp 660–666.
5. Taube, H. personal communication.
6. Taube's Nobel Prize acceptance speech, entitled "Electron Transfer between Metal Complexes: Retrospective", is reprinted in *Science* **1984**, *226*, 1028–1036 and in *Angew. Chemie Int. Engl. Ed.* **1984**, *23*, 329–339.
7. von Hevesy, G.; Zechmeister, L. *Ber. Deutsches Chem. Ges.* **1920**, *53*, 410 (cited by Taube in Ref. 6 of this essay using the Germanic variant of de Hevesy's last name)
8. Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970.
9. Taube, H. *J. Chem. Educ.* **1967**, *45*, 452–461.
10. Nobel e-Museum—Chemistry 1909 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1909/index.html> (accessed April 2002).
11. Hunt, J. P.; Taube, H. *J. Chem. Phys.* **1950**, *18*, 757–758.
12. Taube, H. *Chem. Rev.* **1952**, *50*, 69–126.
13. Myers, H.; Rich, R.; Taube, H. *J. Am. Chem. Soc.* **1953**, *74*, 4118–4119.
14. Baum, R. M. *Chem. & Eng. News* **Jan. 9, 1984**, 43–44.
15. Ford, P. C., personal communication.
16. Baum, R. M. *Chem. & Eng. News* **May 21, 1984**, 31–32.
17. Remarks on behalf of Henry Taube delivered by his sister-in-law at the dedication of the Nobel Laureate Plaza of the University of Saskatchewan on October 24, 1997. [http://www.usask.ca/pubrel/events/90/plaza/plaza\\_opening/taube.html](http://www.usask.ca/pubrel/events/90/plaza/plaza_opening/taube.html) (accessed April 2002).
18. Remarks on behalf of Gerhard Herzberg delivered by his daughter at the ground-breaking ceremony of the Nobel Laureate Plaza of the University of Saskatchewan on April 3, 1997. [http://www.usask.ca/pubrel/events/90/plaza/plaza\\_breaking/herzberg.html](http://www.usask.ca/pubrel/events/90/plaza/plaza_breaking/herzberg.html) (accessed April 2002).

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