

## The 1983 Nobel Prize in Chemistry

Henry Taube has been selected to receive the 1983 Nobel Prize in Chemistry for his pioneering work on the mechanisms of inorganic oxidation-reduction (redox) reactions. Taube was born in Neudorf, Saskatchewan, on 30 November 1915, and he received B.S. (1935) and M.S. (1937) degrees at the University in Saskatoon. He moved to Berkeley to do his doctoral research (Ph.D., 1940) with W. C. Bray, and he became a U.S. citizen in 1941. He has held academic appointments at Cornell (1941 to 1946), Chicago (1946 to 1961), and Stanford (since 1962) and is now the Marguerite Blake Wilbur Professor of Chemistry at Stanford.

Taube has revolutionized the way we think about inorganic redox reactions, and the impact of his work has been felt throughout chemistry and biology. In

retrospect, it is not clear that Taube planned the course of his work from its inception, but it would seem so. The experimental base that supports our current understandings of rates and reaction paths of redox processes required the development of new experimental methodologies. In several instances these were first introduced by Taube, who needed them to investigate particular questions. Taube also recognized the importance of understanding the relationship between the electronic structures of metal complexes and the rates of redox processes and of ligand substitution reactions. His beautiful elucidation of these electronic structure-reactivity relationships has had a profound effect on chemistry.

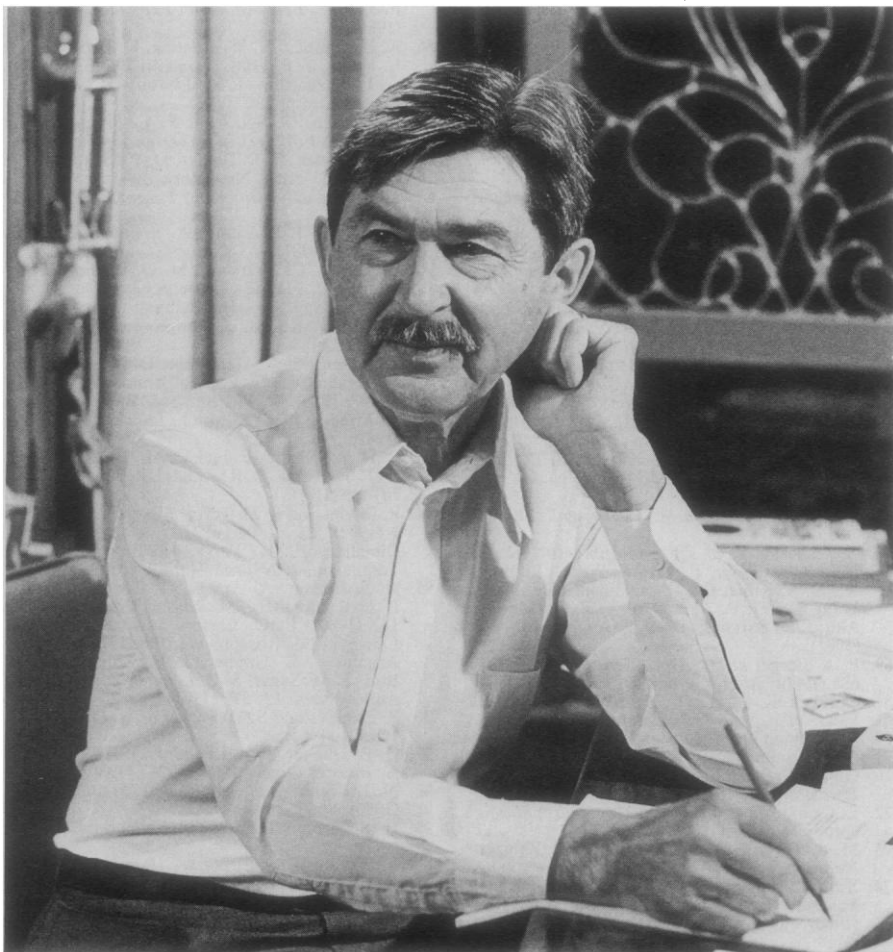
Early on, Taube pointed out the connection between hydration numbers of

metal cations in solution and rates of exchange between water molecules in the first coordination sphere and the aqueous environment. In a 1952 paper, published in *Chemical Reviews*, he was able to show a sweeping correlation between ligand substitution rates and electronic configuration for coordination compounds of the transition metals. (Now, 30 years later, this correlation still dominates the way we think about the reaction chemistry of coordination compounds, and the paper is one of the true classics in inorganic chemistry.) It also was in the 1950's that Taube laid the experimental foundation for mechanistic studies of substitution reactions involving transition metal complexes. Examination of selected examples of his work from this period illustrates the far-reaching nature of his contributions to the development of these fundamental methodologies. In particular, his use of isotopes to study a wide variety of inorganic reactions clearly demonstrated the power of the technique in mechanistic deduction.

Taube is best known for his pioneering work on the mechanisms of redox reactions, especially those involving transition metal ions. Largely as a result of his work, the words "outer sphere" and "inner sphere" are part of the redox mechanistic vocabulary of every inorganic chemist. Both outer-sphere (electron transfer) and inner-sphere (atom transfer) reactions are known to be involved in critical energy transfer processes throughout biology.

In a key paper with Joseph Halperin in 1952, Taube established, by employing oxygen-18 as a tracer, that the reaction between chlorate and sulfite in solution proceeds by oxygen atom transfer. He then demonstrated, in his now classic 1954 paper with Howard Myers, that the reduction of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  by  $\text{Cr}^{2+}$  in aqueous solution occurs by transfer of a chlorine atom from cobalt to chromium through an inner-sphere activated complex containing a Co-Cl-Cr bridging group. Twelve years later, he and F. R. Nordmeyer provided the first examples of redox mechanisms that involve remote attack of the reductant on a conjugated ligand of the oxidant.

The desire to develop well-defined systems to study electron transfer through bridging ligands led Taube and Carol Creutz in 1969 to prepare and characterize a mixed valence cation,  $\text{Ru}(\text{NH}_3)_5(\text{pyrazine})\text{Ru}(\text{NH}_3)_5^{5+}$ , now known commonly as the "Creutz-Taube ion." In such substances two like metals in different formal oxidation states are



Henry Taube [Stanford University]

linked by a conjugated ligand. Electron transfer between two metals connected by a bridging ligand can occur at rates that range from very slow to so fast that a fully delocalized electronic description is appropriate. Understanding the structural features that control these intramolecular electron transfer rates has been an important theme in Taube's work.

Work on electron transfer and atom transfer reactions continues unabated in Taube's laboratory. For example, he and D. Geselowitz in 1980 demonstrated an unambiguous case of stereoselectivity in an outer-sphere redox reaction. Further, his recent study of the formation and stability of oxo ions (the "yl" ions) as a function of the electronic structure of the transition metal has given a real boost to attempts to understand the wide range of rates that are found for oxygen atom transfer reactions. The relevance of this new work to the development of mechanistic models for biological hydroxylating systems such as the cytochrome P-450 family is beginning to be recognized.

In relatively recent time Taube has been a leader in developing the chemistry of ruthenium and osmium complexes. He and D. E. Harrison demonstrated in 1967 that molecular nitrogen will displace water in  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$  to form the stable complex that A. D. Allen and C. V. Senoff had prepared by an indirect route in 1965. Shortly thereafter, he, Harrison, and E. Weissberg prepared

the first bridging dinitrogen complex,  $\text{Ru}(\text{NH}_3)_5\text{N}_2\text{Ru}(\text{NH}_3)_5^{4+}$ ; and, more recently, he and John D. Buhr demonstrated the oxidative coupling of ammonia ligands to form dinitrogen-bridged complexes. The finding that coordinated ammonias can be oxidized to dinitrogen is extremely important because it is the development of a useful model for the biological path.

Taube's work on dinitrogen complexes of ruthenium and osmium led him to explore metal-to-ligand  $\pi$  bonding (often called  $\pi$  backbonding) in Werner-type coordination complexes. (This involves mainly the study of  $\text{M} \rightarrow \text{N}$   $\pi$  interactions, in contrast to the more familiar  $\text{M} \rightarrow \text{C}$   $\pi$  backbonding that is the province of organometallic chemists.) His work has shown conclusively that dramatic changes in Brønsted acid-base equilibria, redox potentials, and other physical and chemical properties can be brought about by  $\pi$  backbonding interactions that are linked to changes in the oxidation state of certain central metals. It is a good bet that Taube's interest in backbonding stimulated him and R. A. Armstrong in 1976 to prepare a low-valent ammine complex of technetium, which in turn provided a strong stimulus to what has become an important area of chemistry. Technetium complexes are being increasingly used in the field of medicinal radiochemistry, especially in the diagnosis of diseased internal organs. Edward A. Deutsch of the University of

Cincinnati, who in one of Taube's former students, and Alan Davidson of the Massachusetts Institute of Technology are among the leaders in this rapidly growing field of research.

Henry Taube is a rare figure among internationally acclaimed scientists. He does little or no horn-tooting. Instead, he spends a great deal of time encouraging others, especially young people, to pursue research. (We admit that at certain of these times we have seen him savor a bit of sour-mash whiskey while listening to one of his wonderful old Maria Inogün phonograph records.) For these reasons, and more, he has been a real hero of ours for many years. It is truly delightful to have this opportunity to acknowledge the tremendous influence he has had on our lives and our work. And it is extremely heartening that the connection between Taube's brilliant elucidation of the fundamentals of inorganic solution redox chemistry and recent impressive advances in the understanding of electrode processes and biochemical redox phenomena is beginning to be recognized far and wide.—HARRY B. GRAY AND JAMES P. COLLMAN

*Harry B. Gray is a professor in the Division of Chemistry and Chemical Engineering at the California Institute of Technology, Pasadena 91125. James P. Collman is a professor in the Department of Chemistry, Stanford University, Stanford, California 94305.*

## The 1983 Nobel Prize in Economics

Gerard Debreu, the 21st scholar to receive the Nobel Prize in Economics since the award was established in 1969, is a mathematical economist's mathematical economist. Formed in the crack *École supérieure normale* of France, Debreu came to this country as a postdoctoral scholar, enriching the environment at the Cowles Foundation for Economic Research in its University of Chicago and Yale incarnations. For almost two decades he has graced the economics and mathematics departments at the University of California, Berkeley, serving as a magnet there for scholars from

all over the country and indeed the world.

I emphasize Debreu's French origins because of the deplorable headlines that stress the clean American sweep of the 1983 prizes. Credit always adds up to more than 100 percent: if you moved to Harvard 1 day before you got the prize, Harvard would bask in your reflected glory; and so would the kindergarten back in good old Champaign. Back in Paris, when Debreu was coming of age, Professor Maurice Allais, an engineer turned economist, had largely worked out on his own during the Occupation of

Paris the fundamentals of advanced economics. Himself of Nobel caliber, Allais gathered around himself after World War II a brilliant cadre of graduates from the engineering faculties which trace back to Napoleon. Marcel Boiteux, then a brilliant young mathematical economist and now the head of the state-owned electricity system in France, was one of them. And so was Debreu.

America did give Debreu's native genius and fine mathematical training the scope for its full development. Jacob Marschak and Tjalling Koopmans, themselves new Americans who gave and received here, recognized Debreu's talents. The names of the scholars Debreu worked with, or whose work he paralleled and built upon, tells much of his quality and opportunities: John von Neumann, Abraham Wald, Kenneth Arrow, Leo Hurwicz, John Nash, Samuel Karlin, Herbert Scarf, Robert Aumann, Roy Radner, Karl Vind, Werner Hilden-