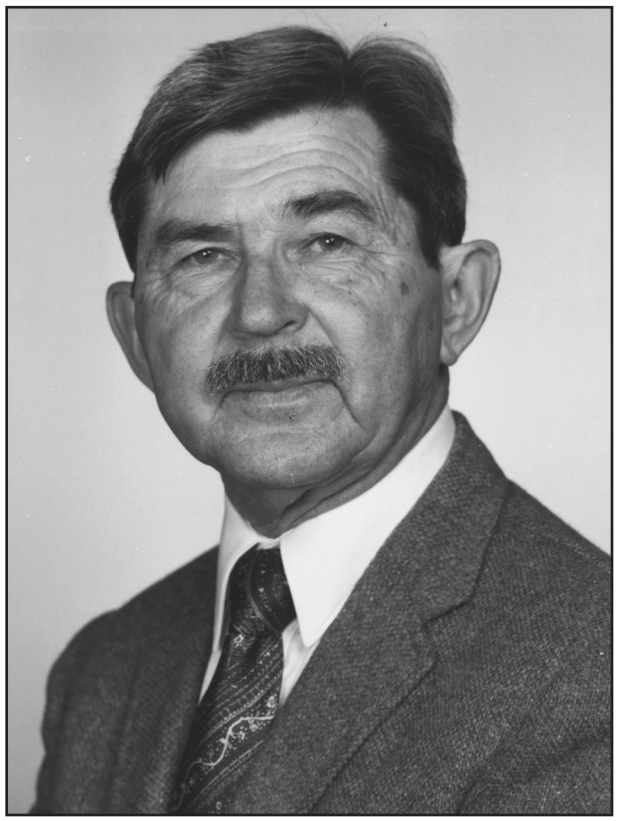
HENRY TAUBE



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HENRY TAUBE received 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 held academic appointments at Cornell (1941–1946), Chicago (1946–1961), and Stanford (from 1962) and was the Marguerite Blake Wilbur Professor of Chemistry at Stanford.

Taube revolutionized the way scholars 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 understanding 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 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, many 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 1950s 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 transduction 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 classic 1954 paper with Howard Myers, that the reduction of $Co(NH_3)_5Cl^{2+}$ by 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, $Ru(NH_3)_5$(pyrazine) $Ru(NH_3)_5^{5+}$, now known commonly as the *Creutz-Taube ion*. In such substances two like metals in different formal oxidation states are 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 was an important theme of Taube's work.

Work on electron transfer and atom transfer reactions continued unabated in Taube's laboratory for years after he received the Nobel Prize. His study of the formation and stability of oxo ions (the "yl" ions) as a function of the electronic structure of the transition metal gave a real boost to attempts to understand the wide range of rates that are found for oxygen atom transfer reactions. The relevance of this work to the development of mechanistic models for biological hydroxylating systems such as the cytochrome P-450 family was soon recognized.

Taube also was 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 $Ru(NH_3)_5H_2O^{2+}$ 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, $Ru(NH_3)_5N_2Ru(NH_3)_5^{4+}$; and 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 was extremely important because it contributed to 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 π bonding (often called π *backbonding*) in Werner-type coordination complexes. (This involves mainly the study of M N π interactions, in contrast to the more familiar M C π backbonding that is the province of organometallic chemists.) His work conclusively demonstrated that dramatic changes in Brönsted acid-base equilibria, redox potentials, and other physical and chemical properties can be brought about by π 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 became an important area of chemistry. Technetium complexes are used in the field of medicinal radiochemistry, especially in the diagnosis of diseased internal organs.

Henry Taube was a rare figure among internationally acclaimed scientists. He did little or no horn-tooting. Instead, he spent a great deal of time encouraging others, especially young people, to pursue research. (We admit that at certain of these times, we watched 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. In this tribute, we acknowledge the tremendous influence he 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 advances in the understanding of electrode processes and biochemical redox phenomena continues to be recognized far and wide.

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