

Department of Chemistry Kolthoff Lectureship in Chemistry

April 13-15, 2015 **Professor James Mayer** Department of Chemistry at Yale University

Website: http://www.chem.yale.edu/faculty/mayer.html Faculty Host: William Tolman



Professor James "Jim" Mayer was born and raised in Manhatten, New York. He attended the United Nations International School, which fostered his passion for science. He started doing research in inorganic chemistry just after high school at Hunter College. with Professor Edwin H. Abbott. He was an undergraduate at Harvard University from 1975-78. He received his doctorate in 1982

from the California Institute of Technology, working with Professor John E. Bercaw on organometallic chemistry of tantalum hydride complexes. He then spent two years as a visiting scientist in the Central Research Department of the DuPont Company. In 1984, he was appointed to the faculty at the University of Washington, where he rose through the academic ranks. He became a professor of chemistry at Yale University in 2014. He has served as chair of the American Chemical Society Division of Inorganic Chemistry and currently serves as an associate editor of the journal Inorganic Chemistry.

Professor Mayer's research interests span coordination chemistry, catalysis and electrocatalysis, bioinorganic chemistry, organometallic chemistry, physical organic chemistry, electron transfer, and reactions of nanoscale materials. His focus is on discovering and understanding new reaction chemistry, particularly the involvement of protons in all sorts of redox reactions that make or break chemical bonds. Chemical reactions of this type are involved in many biological, industrial, energy, and environmental processes.

Lecture 2: Coupling Proton and Electron Transfers: A Deeper Look and Extensions to Electrocatalysis

9:45 a.m. Tuesday, April 14, 331 Smith Hall

The coupling of electron and proton transfers can be considered on many levels, and harnessed for many purposes. In the first part of this presentation, we will look deeper into this coupling and its implications. The concept of the thermodynamic coupling of will be discussed, and its possible correlation with the distance between the two particles. Then we will discuss the ability of separated reagents to have an effective bond dissociation free energy to donate or accept a hydrogen atom, and the utility of this concept. The case of phenol-base compounds, with well defined OH...N hydrogen bonds, will be discussed using Professor Sharon Hammes-Schiffer's theory of PCET. This section will conclude with recent studies of photoinduced unimolecular PCET in an anthracenyl-phenol-pyridine triad (shown at right).



The second portion of the presentation will describe our attempts to apply these ideas to electrocatalysis of the oxygen reduction



reaction (ORR), $O_2 + 4e^- + 4H^+ \rightarrow 2 H_2O$. Efficient electrocatalysis of this reaction is a key challenge in energy technologies such as fuel cells. We have explored iron porphyrin ORR electrocatalysis that incorporate proton relays in the second coordination sphere, such as the tetrakis(2-carboxyphenyl) derivative shown at left. Many such compounds are active and selective catalysts, both electrochemically and with chemical reductants. Comparisons will be presented between different catalysts, and of the same catalyst in different media, or under different conditions. These studies give a more complex view of how proton transfer affects PCET electrocatalysis, and show the challenges of using PCET ideas to design better catalysts.

Izaak Maurits Kolthoff was born on February 11, 1894, in Almelo, Holland. He died on March 4, 1993, in St. Paul, Minnesota. In 1911, he entered the University of Utrecht, Holland. He published his first paper on acid titrations in 1915. On the basis of his world-renowned reputation, he was invited to join the faculty of the University of Minnesota's Department of Chemistry in 1927. By the time of his retirement from the University in 1962, he had published approximately 800 papers. He continued to publish approximately 150 more papers until his health failed. His research, covering approximately a dozen areas of chemistry, was recognized by many medals and memberships in learned societies throughout the world, including the National Academy of Sciences and the Nichols Medal of the American Chemical Society. Best known to the general public is his work on synthetic rubber. During World War II, the government established a comprehensive research program at major industrial companies and several universities, including Minnesota. Kolthoff quickly assembled a large research group and made major contributions to the program. Many of Kolthoff's graduate students went on to successful careers in industry and academic life and, in turn, trained many more. In 1982, it was estimated that approximately 1,100 Ph.D. holders could trace their scientific roots to Kolthoff. When the American Chemical Society inaugurated an award for excellence in 1983, he was the first recipient.

