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Photo by Constance W. Miller

Tribute to James A. Miller

Nature and Scope of Jim Miller's Achievements

Jim Miller is one of the most influential combustion modelers in the world; it is difficult to overestimate the impact that Jim Miller's work has had on the combustion community. But because of the rigor and detail of his chemistry contributions, his remarkable influence spreads beyond the sphere of combustion to the heart of fundamental gas-phase chemical reaction theory. In the late 1970s Jim was among the first researchers to systematically establish chemical kinetic models for gas-phase combustion processes. Following his graduation from Cornell in 1974, Jim joined Sandia National Laboratories in Livermore, CA. This was during the time that the United States was facing its first "energy crisis", and Sandia was rethinking its mission and seeking to contribute to solving energy problems. Jim played an important role in recognizing that combustion research was an area where Sandia could contribute. By 1980 Sandia's Combustion Research Facility (CRF) was established by the United States Department of Energy.

With his formal education in both chemistry and engineering, Jim brought an extraordinarily strong and multidisciplinary perspective to combustion research. He recognized that developing and coupling detailed models of chemical kinetics, molecular transport, and fluid mechanics was necessary to understand the complexities of flame structure. Jim was able to articulate his vision about how combustion modeling should proceed and what it could accomplish in the following decades. His work over the last 25 years has contributed tremendously to our understanding of combustion chemistry. It includes high-level theoretical work on elementary reactions, the systematic development and validation of detailed reaction mechanisms, the modeling and analysis of a range of laboratory experiments (low-pressure flame data, shock-tube data, jet-stirred reactor data, and flow reactor data), the outlining of implications for practical systems, the reviewing of combustion research from both scientific and popular perspectives, and the development of novel theoretical methods and software.

Mechanism Development

Jim was among the pioneers in the development of detailed reaction mechanisms for combustion. By the late 1970s only a handful of researchers worldwide were capable of modeling the

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details of even relatively simple hydrogen−air flames using elementary chemistry. It was clear to Jim that new software tools would be needed to extend such research to hydrocarbon fuels and consider pollutant emissions. This was the motivation to begin developing the capabilities that eventually resulted in CHEMKIN. Especially in its formative stages, Jim was the central figure in setting the theoretical foundation on which CHEMKIN was built.

His mechanisms for the oxidation of light hydrocarbons such as acetylene and methane were important progenitors to the now widely used GRI-MECH. However, the majority of Jim's mechanistic work in the 1980s dealt with nitrogen chemistry. On the basis of his important work on the oxidation of ammonia and hydrogen cyanide, and on the chemistry of Thermal DeNO_x, Jim was, in the mid-1980s, the first scientist to establish a fundamental reaction mechanism for the interaction between hydrocarbon and nitrogen chemistry in combustion. Together with Tom Bowman he then wrote the famous paper reviewing nitrogen chemistry in combustion.[1] This article, which is largely the culmination of a series of papers, both theoretical and experimental, that Jim wrote with a number of co-authors in the 1980s, continues to be the backbone of our understanding of nitrogen chemistry. It was much more than a review paper, using theoretical and modeling tools, together with a careful selection of experimental results from literature, to develop a truly comprehensive mechanism for high-temperature nitrogen chemistry. His insight into such phenomena and processes as prompt NO, NO_x from fuel-bound nitrogen, Thermal De-NO_x, RAPRENO_x, reburning, and staged combustion comes through in this review. Even though later work has improved our understanding of details in this chemistry, the major reactions and oxidation pathways proposed by Miller and Bowman are still considered to be valid.

Jim is rightfully proud that this "review" paper has garnered over a thousand citations and is the most highly cited paper in the history of the journal *Progress in Energy and Combustion Science*, and indeed the most highly cited paper in any combustion journal. Jim is also proud of having 10 papers with more than 100 citations. Half of these papers involved studies of nitrogen chemistry.[2−5]

Kinetics Tools

In 1977 Jim published a paper in the *Journal of Physical Chemistry* on "Chemical Nonequilibrium Effects in Hydrogen−Air Laminar Jet Diffusion Flames".[6] Effectively using the computers of those days required very careful attention to judicious approximations in the fluid mechanics that would enable the incorporation of complex chemistry and transport. This early work predated CHEMKIN but was already starting to establish some of the required capabilities. The boundary-layer model developed for this paper was extended in several directions, including into microelectronics processing. These code developments also resulted in two highly cited publications related to the treatment of chemical vapor deposition.[7,8] The 1984 paper with Mike Coltrin and Bob Kee became one of the 25 most-cited papers in the history of the *Journal of the Electrochemical Society*.

As the CRF grew, there were increasing numbers of visiting researchers from around the world. Many noticed the growing capabilities in the CHEMKIN tools and requested copies of the software. Over time Chemkin became very widely used, as it still is today. For several years Jim tried to keep track of CHEMKIN citations. For many years running every volume of the major combustion journals had at least one paper using CHEMKIN. It is reasonable to argue that the availability of this widely used software has substantially and beneficially altered the course of combustion research over the last twenty-five years. During the same time period, (i.e., the 1980s) Jim was also playing an important role in the physical and mathematical formulation of the problems and solutions, and in the testing and application of the code and the related application codes such as PREMIX, PSR, SENKIN, OPPDIF, and CRESLAF. CHEMKIN, with its derivative software, has become the gold standard in the field for chemical kinetic modeling in combustion. Nowadays, reaction mechanisms are exchanged simply by exchanging CHEMKIN files.

Molecular Weight Growth and Soot Formation

Jim has been greatly motivated by important environmental concerns in combustion processes, as evidenced by his body of work on nitrogen chemistry. About 15 years ago, Jim began to also focus his efforts on understanding the formation of aromatic compounds in fuel-rich hydrocarbon flames. He was among the first to propose that the recombination of resonantly stabilized radicals could be a major source of ring formation, a hypothesis which has been confirmed in subsequent work by him and others. These ideas now pervade the field of PAH growth and soot formation in combustion.

His landmark paper with Carl Melius[9] identified the recombination of propargyl radicals (C_3H_3) as the most likely cyclization step in rich, low-pressure acetylene flames, providing a potential energy surface to justify the conclusion, and is the most cited paper in the history of *Combustion and Flame*. Subsequent modeling studies in various groups together with further theoretical studies of Jim's have clearly demonstrated the dominant importance of the propargyl + propargyl recombination reaction in the formation of the first aromatic ring compound. Jim has continued to refine and improve the $C_3H_3 + C_3H_3$ potential computed by Jim and Carl, to the point where he was able to make the first truly quantitative prediction of the rate coefficient and product distribution of this pivotal reaction. This latter work is probably the most sophisticated analysis of an elementary combustion reaction ever performed.

Theoretical Methods and Fundamental Computational Kinetics

Jim recognized, from the earliest stages of his career, the important synergy between the capability to model complex chemically reacting flow and the need to understand and extend the underlying chemistry fundamentals. As his career progressed, Jim's scientific interest and energy grew increasingly in the direction of fundamental chemistry. A hallmark of Jim's mechanisms has always been their foundation on firm theoretical kinetic principles. Indeed, much of his work has involved the development and application of novel and useful methods for theoretically estimating and representing elementary rate coefficients. His collaborative work with Carl Melius, in addition to providing valuable estimates of important rate coefficients for combustion models, also provided some of the earliest indications of the value of a priori theoretical kinetic estimates. Indeed, their numerous collaborations can be viewed as the progenitor to the now standard practice of coupling ab initio quantum chemistry with transition state theory in order to obtain accurate rate estimates for key combustion reactions. Jim continues these a priori kinetics studies focusing on reactions relevant to the formation of the first aromatic ring.

Jim's classical trajectory studies of the HO_2 reaction system were also groundbreaking. He was the first to identify non-RRKM behavior in the $H + O_2 \leftrightarrow OH + O$ reaction, thus richly enhancing our understanding of the most important reaction in combustion. Furthermore, in studying collisions of highly excited HO_2 molecules with helium, he was the first to suggest the biexponential form for the energy transfer function, something that is now commonly accepted. This paper[10] is another of his highly cited papers.

More recently, Jim has worked at establishing improved theoretical methods for analyzing complex elementary reactions over a potential energy surface with multiple potential wells and/or multiple bimolecular products. His paper[11] that delineates procedures for extracting rate coefficients from master equation simulations will no doubt prove to be another of his classic works. It was his application of this approach to the $C_3H_3 + C_3H_3$ reaction that provided the first quantitative predictions for the kinetics of this single most important reaction in soot formation. His earlier related studies of the $C_2H_5 + O_2$ and $C_3H_7 + O_2$ reactions are taking on a similarly seminal role for radical oxidation reactions.

Closing Tribute

We would like to point to a particularly rare and significant aspect of Jim's contribution: his ability to form a bridge between fundamental research and practical applications. In our opinion, it is amazing that a researcher, on the basis of deep insights into physical chemistry, can have such a great impact on such a practically oriented group as the combustion community. The scope and depth of Jim's knowledge of combustion chemistry is formidable. Jim has kindly shared this formidable understanding with the rest of the scientific community via his numerous well written reviews.[12−17]

Part of the reason for Jim's influence is his strong demand for thoroughness and rigor in all his work. At presentations, many have seen Jim answer audience questions about whether he has considered alternative mechanisms or other reactions with a curt "Doesn't happen." This two-word reply generally hides extensive exploration of those alternatives and rigorous reasons that they are unimportant. Fortunately, his scientific scrupulousness is combined with a willingness to instruct and an approachable manner. Most of his collaborators will recall numerous initially casual conversations, generally beginning on a topic like baseball or his children's achievements, that somehow smoothly shift into chemistry and often end with some new scientific insight.

Jim's work, ranging from high-level theoretical studies of elementary reactions to analysis of practical methods for pollution control, has had a large impact not only on the academic society, but also on the ability of industry to understand and model practical processes. It is our pleasure to present this tribute to Jim Miller, our friend, respected and valued colleague, and exemplary scientist.

Robert J. Kee
Peter Glarborg
Stephen J. Klippenstein
Craig A. Taatjes

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