

A Pioneer of Direct Measurements to Advance Modern Gas-Phase Chemical Kinetics

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Born October 2, 1935 in South Whitley, Indiana, United States, Joe V. Michael received his bachelor's degree in Chemistry from Wabash College in 1957 and his Ph. D. in Chemistry from the University of Rochester in 1963, working with W. A. Noyes, Jr. He had two postdoctoral stints, one at Harvard University in George Kistiakowsky's group between 1962-1964 and the second at Brookhaven National Laboratory with Ralph Weston Jr. in 1965 before accepting a tenure-track faculty position at Carnegie Institute of Technology (now Carnegie-Mellon University).

Personal Notes from the First Few Years (JRB)

In 1965, when Joe Michael accepted a position as Assistant Professor of Chemistry at Carnegie Tech, he was assigned office and laboratory space in the Coal Research Building, which was adjacent to the Bureau of Mines building on Forbes Avenue (now the Heinz College of Information Systems and Public Policy building at Carnegie-Mellon). Joe was given limited start-up funds and he began to assemble his laboratory by fabricating a glass vacuum line and a fast flow tube kinetics apparatus, which was equipped with an atomic hydrogen resonance lamp and ionization detector for monitoring Lyman- α absorbance.

Electronic equipment, vacuum stopcocks, and materials, such as mercury (for manometers and diffusion pumps), were very expensive. To save some money, Joe was given a 100 lb canister of mercury that remained from the defunct Coal Research Laboratory. But the mercury, covered in a layer of oil, had to be purified before it could be used for high vacuum work. This Joe accomplished by decanting and then vacuum-distilling the mercury. He had to buy glass tubing and other items, but quite a number of stopcocks and ground glass joints could also be found by scrounging in the waste bins behind the Bureau of Mines. He did all of the glass-blowing himself, while training his new graduate students in an art that is now unknown to current students.

Joe was a very good glass blower, dating from his days as a graduate student with W. A. Noyes, Jr. He liked to tell stories about his student days with Noyes. He also told older stories, which he heard from Noyes and from George Kistiakowsky, with whom he had been a post doc. Noyes had been a student with Le Chatelier at the Sorbonne and Kistiakowsky had been a student with Bodenstein in Berlin. In one story, probably from Kistiakowsky, Bodenstein always insisted that each of his students must fabricate his own vacuum line. When he learned that one student had instead employed a professional glass-blower, Bodenstein used one sweep of his walking cane to destroy the vacuum line, including all of the mercury manometers and mercury-filled Toepler pumps. A dramatic way to teach a student!

Joe's use of atomic resonance absorption for kinetics experiments evolved from his post-doc research with Ralph Weston, Jr. at Brookhaven National Laboratory. Joe prided himself in fabricating atomic

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resonance lamps. These required metal-to-glass seals and ring joints, which were especially challenging. After hand-blowing the glass lamps, he placed them in a muffle furnace for annealing, where they sometimes softened too much and sagged if the furnace was too warm.

After a little more than a year, Joe had the lab up and working, and kinetics experiments began. It was a lot of fun. Every day, Joe would arrive, smoking his favorite, very pungent Balkan Sobranie pipe tobacco. For lunch, the group would often walk a few hundred meters down the hill to a small bar on Forbes Avenue, drink a beer or two, and play a few games of pin-ball.

Computing power at Carnegie Tech was outstanding in its day, but the electro-mechanical Marchant calculator was more reliable and more convenient for day to day data analysis. From the very beginning, Joe was always interested in comparing his experimental data to the latest theoretical calculations. He was proud to be an experimentalist, but he always took care to understand the latest theoretical concepts. Joe always took great delight in explaining his experimental data by using simple models, especially when the simple models performed better than the latest theories. His durable interest in comparing experiments with theory was a motivating force throughout his scientific career.

50 Years of Direct Measurements to Advance Modern Gas-phase Chemical Kinetics

Joe Michael had a long-standing career in experimental gas-phase kinetics, particularly high-temperature shock-tube kinetics from its infancy in the 1960's. As part of his post-doc work at Harvard with Prof. George Kistiakowsky, Joe demonstrated for the first time the utility of a time-of-flight mass spectrometer experiment for probing high-temperature kinetics behind shock-waves. He utilized this apparatus to study initiation in acetylene pyrolysis and to characterize the nature of chemi-ions. His second postdoctoral stint was at Brookhaven National Labs with Ralph Weston, Jr. Here, Joe developed a microwave discharge flow system to measure absolute concentrations of H-atoms using Lyman- α photometry and he used this apparatus to probe the kinetics of vinyl and ethyl radicals. This was an era in chemical kinetics when most rate constants were measured using relative rate techniques and absolute measurements were quite rare. Joe pioneered the development and application of photometric (absorption and fluorescence) and mass-spectrometric techniques that have stood the test of time for measuring absolute rate constants.

In his subsequent academic career on the faculty in the Chemistry Department at Carnegie Institute of Technology, Joe mentored ten graduate students (nine Ph.D. and one M.S. student) who have gone on to distinguished careers in academia and industry. The experimental studies that Joe performed with his students at Pittsburgh during that time were some of the first direct studies that probed the role of the pressure dependence in chemically activated molecules. These experiments lent support to RRKM theory which is now accepted as the norm, but at that time was the subject of rigorous debate. During this period, Joe performed numerous experimental studies on bimolecular reactions of relevance to atmospheric and combustion chemistry. In the late 70's, Joe subsequently moved on to a research position at the NASA-Goddard Space Flight Center (Greenbelt, MD) and on the faculty at Catholic University (Washington, DC). His research emphasis during this period involved the measurement of rate constants for reactions of halogenated species and hydrocarbons relevant to ozone destruction, a societal problem that had gained visibility not only among scientists but also among the general public. His direct measurements helped lay the foundation for accurately modeling ozone destruction in the stratosphere.

In the early 80's, Joe transitioned to a staff position in the Applied Science department at Brookhaven. Joe re-initiated his studies on elementary kinetics at high temperatures with the development of the

Flash Photolysis-Shock Tube (FP-ST) technique using resonance absorption (ARAS) diagnostics. A few years later, it was quite fitting that Joe would be the first experimental hire into the Theoretical Chemistry group at Argonne to provide strong experimental support to help validate the theoretical kinetics methods developed there. Joe has left an indelible mark on the kinetics of reactions in the all-important $\text{H}_2\text{-O}_2$ system. With the FP-ST and ST-ARAS technique, Joe made direct measurements for the kinetics both in the forward and reverse directions for many elementary reactions in the hydrogen oxidation mechanism and thereby greatly reduced the uncertainties in modeling combustion systems. Along the way, Joe also made important contributions to other areas, including the kinetics of soot-precursors and chlorinated/fluorinated hydrocarbons.

An analysis of the NIST chemical kinetics database¹ reveals more than 125 absolute kinetics measurements attributed to Joe, which ranks among the top five in the now mature field of gas-phase chemical kinetics. Perhaps more remarkable is that Joe is probably the only kineticist to have made sustained contributions to direct kinetics measurements for a variety of unimolecular and bimolecular reactions at conditions relevant to both atmospheric chemistry and high temperature combustion. Joe is an AAAS fellow (elected 2008) and a Combustion Institute fellow (elected 2019), and his contributions to thermal kinetics were honored in a J. Phys. Chem. A Festschrift in 2015.² Joe participated in the 1995 conference held at Heidelberg to commemorate 100 years of chemical kinetics since Max Bodenstein's first studies in 1895. Not surprisingly, of the innumerable "chemical descendants" of Max Bodenstein, Joe is one of only 35 to figure in the Max Bodenstein chemical family tree depicted on the front of conference proceedings, which were published by Springer.³ It should be noted that the names listed in the tree reads like a who's who in the field of chemistry and includes at least three Chemistry Nobel Prize winners and numerous other distinguished researchers.

Personal Notes from the Last Few Years (RS)

My first introduction to Joe Michael was at the 2003 American Institute of Chemical Engineering (AIChE) annual meeting at Indianapolis, where my graduate advisor Ken Brezinsky (University of Illinois-Chicago) remarked that I should make it a point to talk to one of the pioneers of shock tube chemical kinetics. Joe had an informal standing invitation to speak from his former postdoc (S. S. Kumaran), who was a chair and organizer of the Combustion and Pyrolysis session. I had heard of Joe's name and had read a few of his research papers, but now I could put a face to that name. In his conversations with me I was immediately struck by his genial nature and his genuine warmth towards students. He had not yet started using PowerPoint to give talks, but with his printed slides and a ruler in hand, he gave a simple and elegant talk on the recombination kinetics of $\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$ in multiple bath gases. To date, his investigation of this important elementary reaction remains the only direct experimental study with numerous combustion-relevant colliders.

A few months before my PhD defense one of my advisors at UIC, Rob Tranter, took a Chemist position at Argonne and Nanda Srinivasan, my grad school buddy who had graduated from John Kiefer's group (UIC-Chemical Engineering) also left to take a postdoc position with Joe. Being in Chicagoland afforded me the opportunity to continue my interactions with Rob and Nanda, and Joe was always kind enough to act as the host at Argonne the few times I visited there. The bonus was of course the chance to also learn and interact with Joe. When Nanda's postdoc tenure came to an end, Joe was looking for a new postdoc and asked me if I would be interested. I jumped at the opportunity! Joe's hands-on approach to research continued into his final years as an experimentalist. Joe's shock tube had a unique (for modern shock tubes) setup, which included a manually operated knife edge to rupture aluminum diaphragms and thus initiate shockwaves. As most shockwave researchers know, a clean and rapid diaphragm rupture is essential to generate strong shockwaves at required Mach

numbers and all of Joe's former postdocs and students were well aware of his remarkable success at this. As an added bonus, Joe often treated his postdocs to a humming/whistling performance during changeovers between shocks, particularly if he knew that the experiment was a success (Joe was an active member of the Naperville Men's Glee Club).

With the availability of a professional glass blower a few doors away from his lab, Joe did not indulge in glass blowing at Argonne, but his affinity for glassware persisted into his last few years. He was especially proud of his all-glass mixing rig for preparing gas mixtures for shockwave experiments. It consisted of multiple 22 l glass bulbs and numerous smaller bulbs to allow bulb to bulb distillations and dilutions. He often commented on the integrity of his dilute gas phase mixtures, which were safely stored for months in his "inert" glass bulbs and re-used for experimental studies when required. Another quality that persisted over his research career was his penchant for rarely ever discarding an experimental measurement, unless there was an obvious reason for doing so. Having pioneered the development of very sensitive absorption techniques, Joe relied on the mantra "dilution is the solution" for chemical isolation of an elementary reaction of interest. Because of the low concentrations, his experiments were very "clean" and could be analyzed using only a few coupled chemical reactions. His approach reduced experimental uncertainties and thereby facilitated direct thermal kinetics measurements for novel dynamical phenomena like "roaming", which was a hot topic in his last few years. Throughout his entire research career, Joe's experimental studies were performed to support/advance theory and this goal is reflected even in his last published paper, which provided the basis for theoretical and modeling studies on prompt dissociations of free radicals.

Joe enjoyed attending and presenting his work at numerous national and international conferences, particularly the International Symposia of the Combustion Institute,⁴ the International Symposia on Gas Kinetics,⁵ and the annual Basic Energy Sciences Gas-Phase Chemical Physics Contractors' Meetings⁶ (U.S. Department of Energy). Scientific, political, and general discussions at these conferences continued quite late into the night over several beers with friends and colleagues and Joe often regaled us with old stories and interesting tidbits that occurred at past meetings. During his nearly 30-year stint as a senior scientist at Argonne, he mentored nine postdoctoral scientists. Joe was actively involved in his experiments right up to his retirement at the age of 80 in 2015. Joe subsequently became an Argonne Emeritus Scientist, a status accorded only to a select few lab scientist retirees. He continued to come to the lab regularly and contributed post-retirement, until he was forbidden to drive his car. Even in my limited visits to his home after he was bedridden, he enjoyed hearing about happenings at the lab and about research work published by our group and by the kinetics research community in general. He even managed to proofread his last publication before submitting it to the Proceedings of the Combustion Institute.

Joe was an outstanding example to us all, not just because of his pioneering research career, but also because of his exceptional humanity. While Joe's scientific contributions have and will continue to stand the test of time, this genial kineticist, mentor, and advisor will be missed by his numerous colleagues, friends, and students in the combustion and atmospheric chemistry communities.

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