

BIOGRAPHICAL MEMOIRS

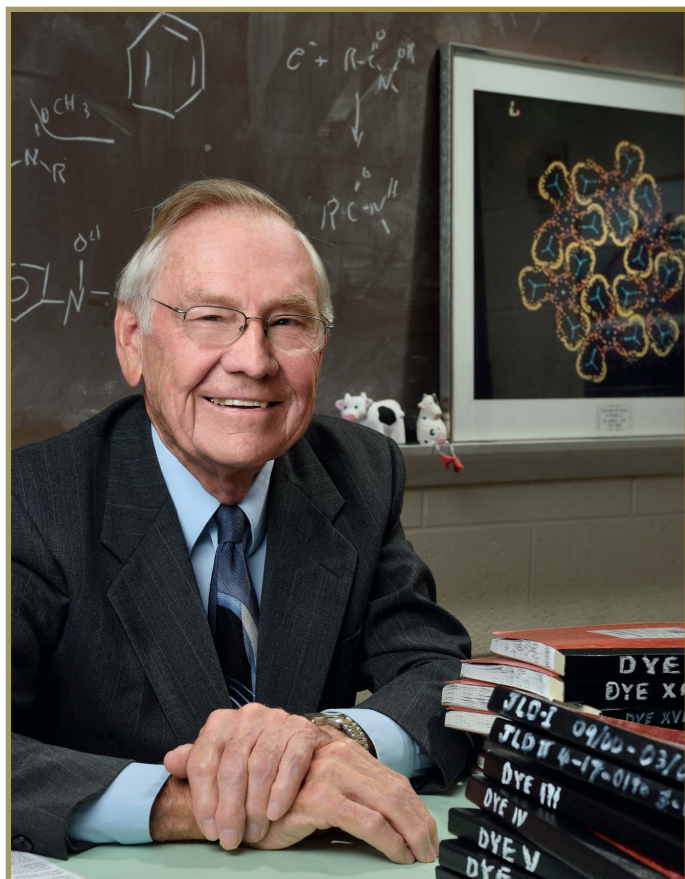
JAMES L. DYE

July 18, 1927–October 8, 2021
Elected to the NAS, 1989

*A Biographical Memoir by
Michael James Wagner*

JAMES LOUIS DYE, University Distinguished Professor of Chemistry Emeritus at Michigan State University (MSU), was the pioneer of the study of two entirely new classes of compounds, alkalides, and electrides, which showed that alkali metals and, even more remarkably, electrons can act as anions in salts.

Jim was born on July 18, 1927, in Soudan, Minnesota, to Ray and Hildur Dye. He was raised with modest means, his father supporting the family as an underground iron ore miner. His first home was a tent, his parents being caretakers of a park at the time, and they moved into a house to survive his first Minnesota winter. The leisure activities of his youth were focused on the outdoors, particularly camping and



fishing, with the latter becoming a lifelong passion. In 1942, his family purchased a 40-acre farm with a log cabin for \$300, and he spent his years at Virginia High School in Virginia, Minnesota, living without the conveniences of electricity or plumbed water. He once recounted a story of converting a truck into a tractor during his youth. It is easy to imagine that his upbringing gave him his infectious drive and “can-do” attitude, the confidence and courage to build the complex apparatus and instruments and take on the difficult problems that characterize his career.

Jim served in the United States Army for thirteen months after being drafted in 1945, too late in the war for



Jim with siblings and cousins with their family's 1928 Hupmobile.





Jim during army service.

deployment overseas. He rose to the rank of corporal but, as he put it, he “really didn’t do anything” for the Army, but “they were good” to him, because the GI Bill provided money for him to attend Gustavus Adolphus College after discharge. Graduating with a bachelor’s degree in chemistry and math in 1949, he chose to further his education under the guidance of Frank H. Spedding at Iowa State University, earning his Ph.D. in chemistry and joining the chemistry department faculty at Michigan State College, renamed to MSU soon after his arrival in 1953.

At MSU, Jim drew inspiration from three outstanding researchers: Harold Hart, Max Rogers, and Carl Brubaker. His initial research included the extension of his Ph.D. research in theoretical and experimental work on ion mobility, which he referred to as his “tenure insurance” and studies of metal-ammonia solutions. Jim had become intrigued with these unusual solutions after attending a seminar on the subject presented by a graduate student during his first term at MSU. He later referred to his decision to study the mobilities, activity coefficients, and optical spectra of metal-ammonia

solutions as a “near-fatal mistake from the standpoint of tenure,” discovering that it required the design and realization of an intricate apparatus that included a thermal bath with temperature control to within 0.01°C . It would then take six years to finally publish a paper on the subject. In 1959, he was awarded tenure but remained an assistant professor, a rare case of tenure without a promotion. He would later go on to serve as the chair of the MSU chemistry department for four years (1986–1990).

The choice to take on such challenging problems had nearly ended his academic career, but it instead led directly to the very studies that defined it. He continued his studies of metal-ammonia solutions, spending his first sabbatical leave as a National Science Foundation (NSF) Science Faculty Fellow (1961–1962) with future Nobel laureate Manfred Eigen in Göttingen, Germany. In that role, he conducted stopped-flow studies of the reaction of solvated electrons with water and the spectra of alkali metals in ethylenediamine. His fascination with metal-amine solutions led to his studies of the species M , $e\text{-solv}$ and $M\text{-}$ species by EPR, optical spectroscopy, and pulse radiolysis. In 1963, through correlating optical and EPR spectra, his group was the first to identify the solvated monomeric metal atomic species, M , in alkali metal-amine solutions. During this time, he built the first stopped-flow apparatus featuring a rapid scanning monochromator, thus allowing the acquisition of large spectral regions for study of moderately fast reactions. He used this unique instrument to study metal ammonia and amine solutions, greatly contributing to the fundamental understanding of the reactivity and species present. He delved deeper during his second sabbatical leave with Leon Dorfman at the Ohio State University, conducting pulse radiolysis studies of the optical spectra of $e\text{-}$ in ethylenediamine-water and ammonia-water mixtures.

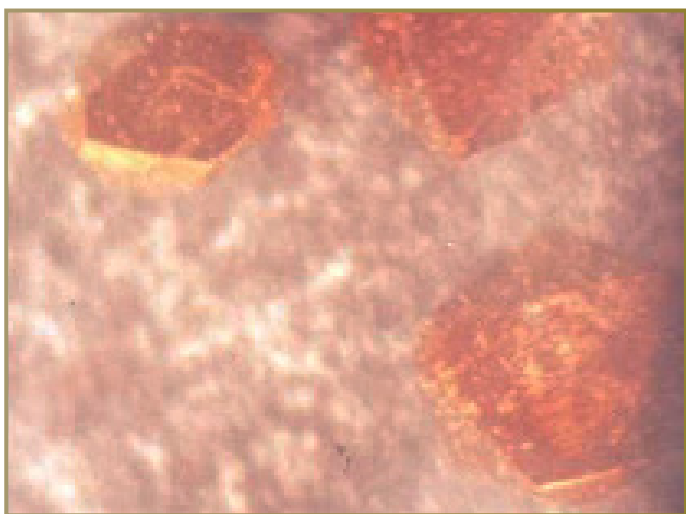
The low concentrations of alkali metals solutions greatly restricted their study and usefulness. This challenge was



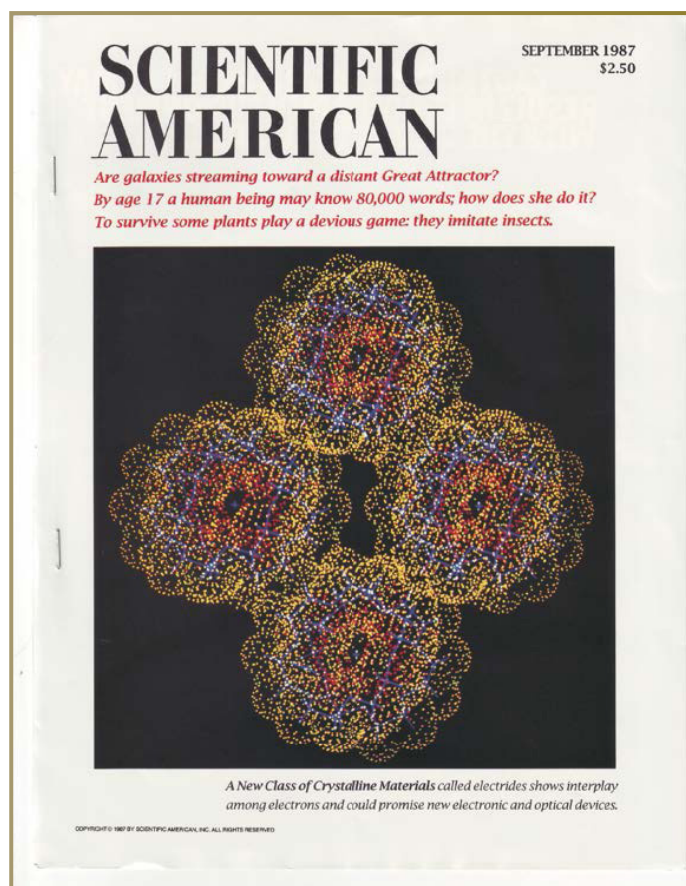
Jim in his one-room lab/office that he shared with two graduate students in Kedzie Hall at MSU.

overcome in 1970, soon after the discovery of crown ethers and cryptands, when Jim's group reported these complexants dramatically increased the solubilities of alkali metals in a range of solvents. For example, in the absence of a complexant, potassium is negligibly soluble in dimethyl ether; the addition of 15-crown-5 yields solutions with concentrations as high as 0.5 mol L^{-1} . Studies of complexed alkali metal solutions conducted in his lab found that the complexed cation Na^+ (cryptand[2.2.2]) was thermodynamically stable, exhibited slow decomplexation kinetics, and was relatively stable in the presence of the strongly reducing species Na^- or e^-_{solv} . Powders and films of a solid compound could be produced from these solutions by rapid solvent evaporation, and slow cooling of concentrated solutions resulted in brilliant gold crystals, metallic in appearance, suitable for structural determination. In 1974, Jim's lab reported the crystal structure of Na^+ (cryptand[2.2.2]) Na^- , the first known "sodide," providing irrefutable proof that sodium could exist in the -1 oxidation state, overturning a century of chemical dogma. His lab went on to solve the crystal structures of more than twenty-six additional sodides, four potassides, four rubidides, and three cesides, showing that all of the alkali metals except lithium (and francium) could form stable anions in salts. Furthermore, examples of alkali metal anion dimers and chains, as well as cation-anion contact pairs, have been identified in some of these structures.

Although alkali metal in solvents such as amines and polyethers contain both alkali metal anions and e^-_{solv} , Jim's lab showed that complexants could shift the equilibrium to exclude the former. Supported as a Guggenheim Fellow and Fulbright Research Scientist for a sabbatical leave in Strasbourg, France, from 1975–1976, with future Nobel laureate Jean-Marie Lehn, Jim found that evaporation of the solvent results in blue films, which he identified as "electrides,"

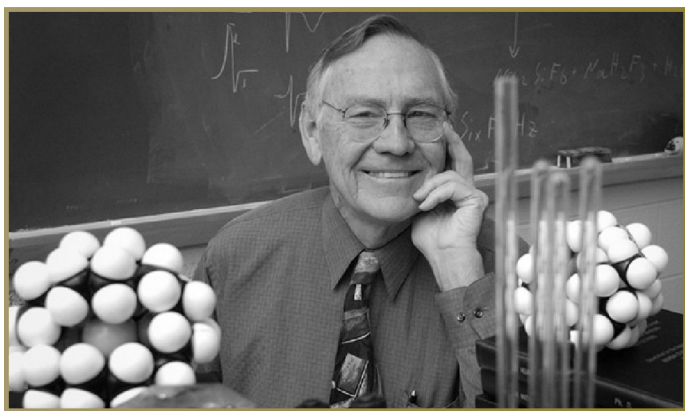


Crystals of $\text{Na}^+(\text{C}_{222})\text{Na}^-$, the first sodide. (J. L. Dye, J. M. Ceraso, M. T. Lok, B. L. Barnett, F. J. Tehan. *J. Am. Chem. Soc.* 1974, 96, 608.)



assuming that the anions in these salts were trapped electrons. His lab was later able to grow crystals of $\text{Cs}^+(\text{18-crown-6})_2e^-$ suitable for X-ray structure determination and showed that it was isostructural with the corresponding sodide, but remarkably with individual electrons serving as anions in the place of Na^- . In total, Jim's lab reported the crystal structures of eight electrides and the synthesis of powder samples of numerous others. As with the alkalides, the anions, trapped electrons, are found in isolated cavities or as dimers or in chains. Remarkably, the properties of these electrides appear to be determined by the interconnections of the anion cavities, the structure of the volume of the crystal structure devoid of atoms rather than that occupied by atoms as in conventional materials. Essentially, electrides are stoichiometric F-center salts, early examples of quantum confinement in which the electrons form a complex lattice gas.

For more than two decades, Jim's lab studied the properties of alkalides and electrides. As was the case with alkali metal solutions, both classes of materials are notoriously difficult to study as they are highly air sensitive and, even more troublesome, temperature sensitive and prone to rapid autocatalytic decomposition. The synthesis and study of alkalides and electrides is conceptually simple, but success in doing so required highly innovative approaches. Specialized glassware and techniques were devised for their synthesis, recovery, and



Jim in his office at MSU.

storage and also for their transfer and study. For example, Jim designed a grease-free vacuum manifold, reaction and storage vessels, and vacuum synthesis techniques to overcome these difficulties. When commercially available instruments were used, procedures had to be developed and, in some cases, significant ingenious modifications had to be conceived and implemented to allow loading and studying these highly sensitive compounds. In many cases, instruments were designed and built in his lab. His lab designed and built a vapor deposition apparatus to synthesize alkalides and electrider films in-situ and study their photophysical properties (fluorescence/lifetimes, optical absorption, and reflectance), and team members also built a photoelectron emission spectrometer, a single temperature-controlled crystal solid state NMR probe, two- and four-probe electrical conductivity measurement systems, and numerous other innovative instruments and apparatuses. Jim was never deterred by the time and effort it took to pursue difficult problems.

Jim retired in 1994, receiving emeritus status. He continued to study alkalides and electrides, seeking and finally synthesizing a thermally stable electrider and reporting its structure and that of the isostructural sodide in 2005. He also pursued the synthesis and study of all inorganic electrides, stabilizing alkali metals in porous silica and alumina, and creating “near” electrides. He co-founded SiGNa Chemistry Inc. to commercialize these materials for use in organic reductions and NaSi as a portable hydrogen source for hydrogen fuel cells and oil recovery, receiving a 2008 Presidential Green Chemistry Challenge Award.

Jim served as interim secretary of the Physical Chemistry Division of the American Chemical Society (ACS), chair of the Fellowship Committee of the National Research Council, member of the editorial board of the ACS journal *Inorganic Chemistry*, member of the Advisory Committee of the Division of Materials Research of the National Science Foundation (NSF), and chair of the Canvassing Committee for the ACS Award in Pure Chemistry. His accomplishments,

including more than 230 refereed publications, earned a Junior Sigma Xi Award (1968), Distinguished Alumnus Award (Gustavus Adolphus College, 1969), MSU Distinguished Faculty Award (1974), Senior Sigma Xi Award (1987), Michigan Association of Governing Boards Award (1990), Chemical Pioneer Award (American Institute of Chemists, 1990), ACS Award in Inorganic Chemistry (1997), John C. Bailar Jr. Medal (University of Illinois, 1997), Stauffer Lecturer (University of Southern California, 1998), Spedding Lecturer (Iowa State University, 2004), and four Camille and Henry Dreyfus Senior Scientist Mentor Awards. He was an NSF Science Faculty Fellow, a Fulbright Research Scientist (1975–1976), and a Guggenheim Fellow twice (1975–1976 and 1990–1991). In 1989, Jim was elected to the National Academy of Sciences, the recognition of which he seemed to be most proud. He stated, in his understated folksy way, that it was “quite an honor” to sign the “great book” and join the esteemed institution founded by Abraham Lincoln. The following year, he was elected to the American Academy of Arts and Sciences.



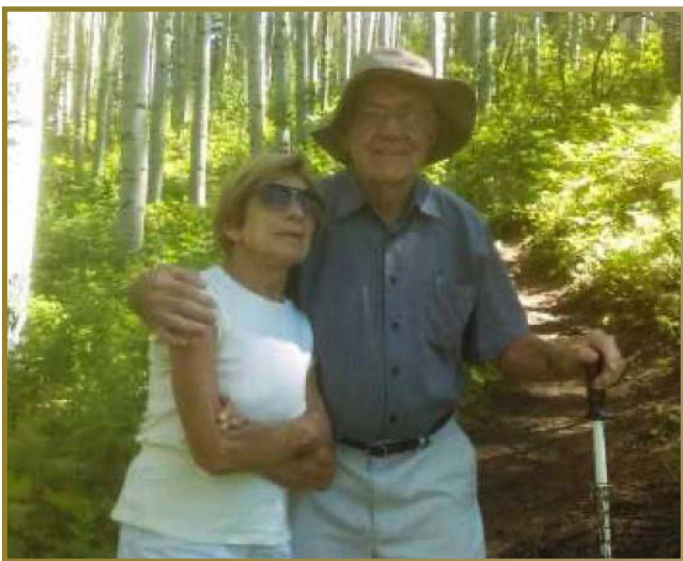
Jim signing the Great Book.

Jim’s attitude about his research was in my mind best summed up by a single-pane cartoon that he had posted on his office door: it depicted a chemist speaking to another in a lab, stating that he was on the “verge of a huge breakthrough,” but at the “point where chemistry leaves off and physics begins” so he’d have to end the project. Jim never let the artificial boundaries of fields confine his science. He was clearly proud to be a physical chemist who received the ACS Award in Inorganic Chemistry. He collaborated with a large number of researchers from a wide variety of disciplines around the world. He co-authored publications with twenty-three faculty and staff members at MSU alone: in chemistry, physics, biochemistry, biophysics, and geology. Jim’s influence will be felt across a wide swath of science and continue to be spread

by the fifty-six Ph.D. students, seventeen master's students, fifteen postdoctoral fellows, and thirty undergraduate researchers that he mentored.

Jim's mentoring style fostered critical thinking, rigor, and also community. He rented a cabin and a boat in upper Michigan each year, taking his entire research group on a weekend fishing and comradery trip. He kept in touch with his former students with a yearly Dye Group Letter, personal visits, and an open invitation to drop by and even stay the night at his home. He truly cared about his students as people, helping them when he could. This is perhaps best illustrated by the story of one of his students, Long Dinh Le (Ph.D., 1973), who returned to his native South Vietnam after graduation. In 1975, his homeland was overrun by North Vietnam, and he fled with his wife to Thailand. They had lost everything and life was difficult for them in a refugee camp. After learning of Long's situation, Jim wanted to send them money, but he was afraid that Long would not receive it. So, Jim sent an issue of a journal in which he had recently published an article with a note asking Long to read it very carefully. When Long received the magazine, he found that two of the pages had been glued together. Holding the pages up to the sun, he discovered desperately needed money hidden between the pages. Later, Jim sponsored Long and his wife to come to the United States, where Long joined the department at MSU, working there until retirement.

Jim was a man of faith and family, serving as a deacon at University Lutheran Church near his home in East Lansing, Michigan. He met the love of his life, Angie (Angeline Medure), in high school, walking with her at the head of the prom procession as senior class president and then down the aisle of matrimony on June 10, 1948, in Buhl, Minnesota. Their marriage remained strong for the rest of his earthly



Jim and Angie hiking in Colorado in 2016.

days, traveling the world together, fishing, golfing, gardening, and frequently seen walking hand in hand until declining health limited his activities in his final year. He will be dearly missed by his wife of more than seventy-three years, their three children, ten grandchildren, and twelve great-grandchildren, and by everyone who had the blessing of knowing him.

ACKNOWLEDGMENTS

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