BIOGRAPHICAL MEMOIRS

Royce W. Murray

January 9, 1937–July 6, 2022
Elected to the NAS, 1991

A Biographical Memoir by R. Mark Wightman

Royce W. Murray was a faculty member in the Department of Chemistry, University of North Carolina at Chapel Hill, for fifty-seven years. He was an analytical chemist who pioneered several research areas, including chemically modified electrodes and the development of methods to synthesize and characterize metal nanoparticles. He described his research in more than 440 refereed publications. Murray was named Kenan Professor in 1980, a prestigious rank at his home institution. His research program was recognized by his induction into the National Academy of Sciences in 1991. He received numerous national and international awards and medals. For twenty-one years, he served as editor-in-chief of *Analytical Chemistry*, the premier journal in his scientific discipline published by the American Chemical Society (ACS).

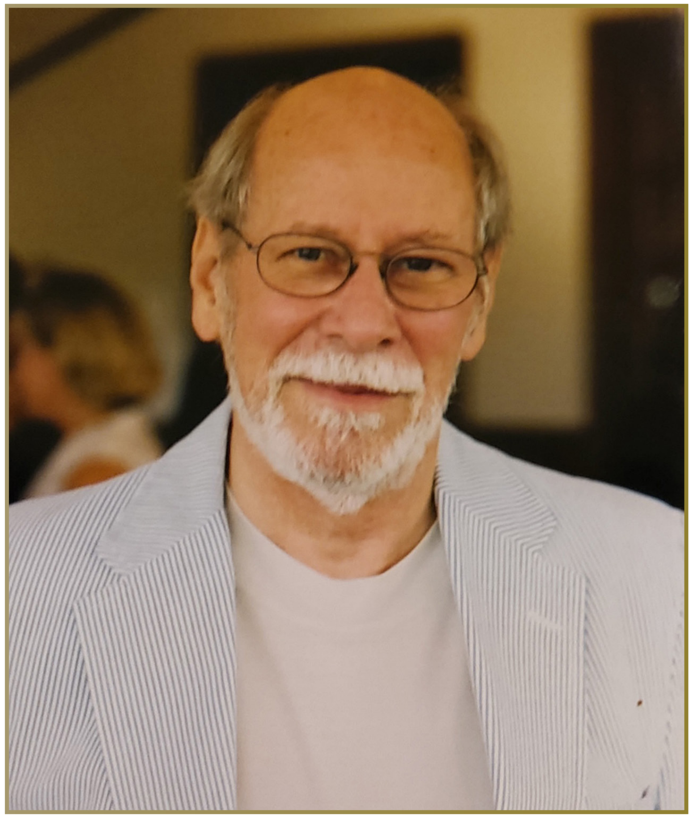

Figure 1 Royce Murray at the celebration of his 40th anniversary at the University of North Carolina at Chapel Hill.

Royce Murray was born on January 9, 1937, in Birmingham, Alabama, to parents Royce Leeroy Murray and Louisa Justina Herd Murray, and he had one older sister, Amelia. In high school, he was a good student and also a state mile champion in track. His father was a high-voltage electrician, and because he grew up in this environment, Royce became comfortable using a variety of machines and tools. Royce entered college in 1954, attending Birmingham-Southern College. His first-year chemistry teacher inspired him to major in chemistry, and this initial decision was reinforced by his analytical chemistry professor. He rapidly completed the chemistry curriculum at Birmingham-Southern and graduated in 1957 at age twenty.

That same year, he married Judy Studinka, and they would have five children. His eldest, Kathy, became a medical technologist. Stewart, his only son, became a pilot for the U.S. Navy, then a commercial pilot, and then owned a farm in California. Debra earned a Ph.D. in entomology and became a researcher at Duke University Medical Center. Melissa became a large-animal veterinarian working in upstate New York. She is the mother of Royce's only grandchild, Levi, born in 2007. Daughter Marion became a horticulturist with Utah State University.

Royce joined the Department of Chemistry at Northwestern University as a graduate student in 1957. There, he pursued a Ph.D. in analytical chemistry under the direction of Richard C. Bowers, an electrochemist who later became president of the University of Montana. Don Deford, inventor of the three-electrode potentiostat and a chemical instrumentation specialist, also played a significant role in his graduate education. Royce received his Ph.D. degree in 1960.

This was an exciting time for analytical chemistry because it was evolving into new domains. The heart of analytical chemistry has always been its focus on measuring various aspects of chemicals and their reactivity. The focus in the early part of the twentieth century was on the use of careful measurements of precise amounts of chemical reagents to learn more about the concentration and speciation of a chemical sample. But the instrumentation that evolved during World War II provided new, nonchemical ways to monitor chemical reactions and thus to achieve these goals. Electronics were inexpensive, and chemical transducers became more reliable. Thus, the development of the three-electrode potentiostat during this period was a natural consequence of the increasing role of instrumentation in chemical analysis. Similar advances in optical spectroscopy, nuclear magnetic resonance, mass spectrometry, surface analysis, and many other fields led to the term "instrumental analysis," the title of a course that is still an important part of the modern chemical curriculum. Royce's research at Northwestern used these instrumental approaches to probe the chemistry of the permeation of inorganic ions into cellulose acetate membranes. Although it did not achieve much acclaim at that time, that research would prove to be an interesting predictor for his future directions.

After graduation from Northwestern, Royce launched himself into the professorial market. He was offered positions at the University of Arkansas and Vanderbilt University but decided that the University of North Carolina at Chapel Hill (UNC) was where he wanted to be. Royce later recalled that the facilities there were lousy (many remember the 1925 vintage Venable Hall that was torn down in 2007), the salary was low ($6,000), and startup funds were nonexistent. Nonetheless, Royce was drawn to the attractive village of Chapel Hill in 1960 for two reasons: the faculty were collegial, and the best analytical chemist in the country, Charles N. Reilley, was a faculty member. Thus, Reilley could serve a role akin to a postdoctoral advisor as Royce embarked upon his professorial career.

Murray collaborated with Reilley in his initial research at UNC, and it involved the use of chronopotentiometry, a form of electrochemical titration in which the applied current is the titrant and the time of the transition of the electrode potential to a new value indicated the end point. These experiments were well suited to Royce, who was expert in instrumentation and electrochemistry. In this early phase, Reilley and Murray shared research grants as well as research space. But Murray soon started attracting graduate students to his own group and began exploring new aspects of electrochemistry, especially for the analysis of surface adsorbed species. Royce's group was also active in the pursuit of ways to optically monitor products of electrolysis. This gave rise to the optically transparent electrodes that allowed both precise spectral and coulometric measurements. Meanwhile, Reilley's group was exploring the use of the then-new digital computers for logging data and controlling experiments. Because the groups occupied the same space, these approaches also permeated Royce's experiments, facilitating much more detailed analysis of data.

A real turning point for Royce came in 1971, when he went to the National Science Foundation as part of the organization's rotator program in analytical chemistry. There he was exposed to hundreds of research proposals from all around the country, and the experience expanded his horizons and gave him a broader view of analytical chemistry. This was the era when chromatographic stationary phases were being prepared with attachment of chemical moieties to surfaces of solids using well-characterized chemistry. He realized that chemical modifications of electrode surfaces could similarly steer specific molecules to the electrode, which would enable desired electrochemical reactions and suppress unwanted results. But research in this area awaited methods to quantitate surface attachment of chemical substances.

Royce's dreams of chemically modified electrodes came to fruition in 1974, when he and Reilley obtained funding for an X-ray photoelectron spectroscopy instrument. This device allowed the surface attachment of monolayers of chemical species attached to solid surfaces to be measured and confirmed. Now the electrochemical experiments could be executed with a firm knowledge of how the electrode surface had been changed by surface modification. Murray's group first explored single monolayers and later moved to polymer attachments on electrode surfaces. The polymer modified electrodes were particularly interesting because they could be built so that they incorporated all the elements of a classical electrochemical cell. This realization led to a large body of work that transformed the way electrodes were designed as sensors or as electrocatalysts. Importantly, the polymer film electrodes allowed investigation of the way in which electrical charge propagates through these materials. The group successfully explored electron hopping, as well as electron self-exchange reactions, charge balance equations, and electron transfers in the absence of solvent. A particularly important outcome of these experiments was that the Murray group learned how to decorate the conductor surface in a variety of ways. They used stable chemical linkers, such as thiols on gold, to anchor electroactive molecules. Other molecules were designed with spacers that confined them to the electrode of the conductor but at a precise distance from the surface. In this way the

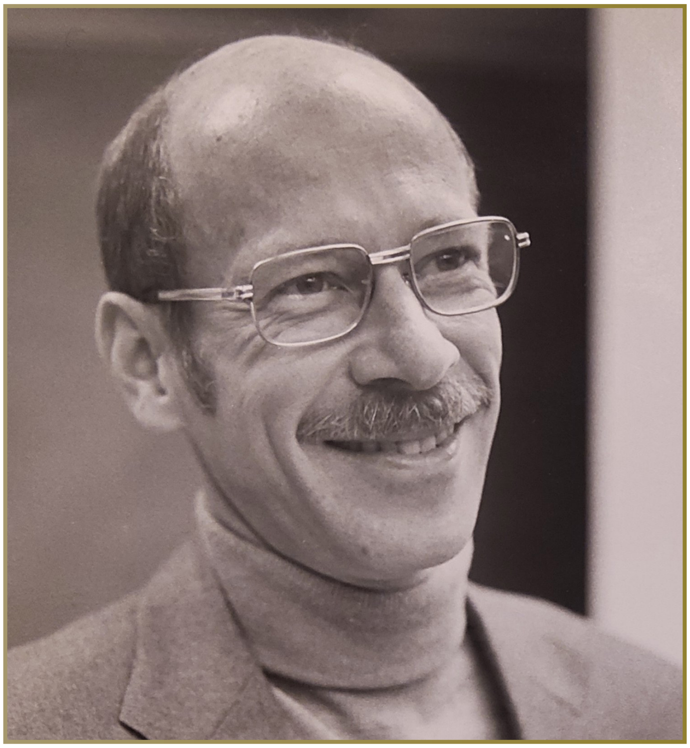

Figure 2 Royce Murray circa 1980.

distance dependence of the rate of electron transfer could be explored, and the group obtained good agreement with Marcus theory. These procedures formed a toolbox of techniques to test a variety of electrochemical phenomena.

In 1991, Murray accepted the position of editor-in-chief of *Analytical Chemistry,* an ACS journal that had a long history of publishing state-of-the-art research in the area of its title. He retained that position for twenty-one years, and this service further enhanced his view of the discipline. As editor, he quickly realized that he was not leading the discipline. Instead, as he clearly described in an editorial, he "was 'leading from behind,' watching with pleasure as researchers plow ahead, and occasionally yelling 'turn left,' or trying to rescue an aberrant direction of effort, or pointedly declining manuscripts that are 'beating the proverbial dead horse.'" He also had to deal with a variety of issues common to science then and now, including ethical and other issues that required handling through firm but noncompromising actions. The journal steadily improved its rating during the time of his editorship.

In his research, Royce often made forays into areas that were unexpected but provided interesting information. He characterized ionic liquids with Holden Thorpe, future editor of *Science*. He and his group did electrochemistry at exceptionally low temperatures. Because the molecules were connected to the electrode with chemical spacers of known lengths, he was able to measure heterogeneous rate constants of electron transfer and use such methods to verify existing electron transfer theories. He and his group designed experiments with diffusional mass transport that was incredibly slow. And they also investigated the electrochemical properties of superconductors at these low temperatures.

Metal colloids have been used for centuries in a variety of applications. including to colorize glass. But the properties and composition of these materials were only quantifiable when they were made by precisely controlled synthetic techniques. In the mid-1990s, Brust and coworkers at the University of Liverpool in the United Kingdom fabricated Au nanoparticles made with organothiolates. The Murray group realized that their work at modifying metal surfaces had generated a broad range of reagents that would be useful in the generation of nanoparticles of known dimensions and structure. But the conditions of the Brust synthesis had to be adapted to yield a monodisperse set of nanoparticles. After this was achieved, they could experimentally address a broad range of questions. For example, what are the differences in properties when individual atoms are compared to small nanoparticles containing a finite number of atoms? When do nanoparticles become distinct from bulk metals? The Murray group set out to improve the synthetic routes to nanoparticles and to develop analytical methods to characterize their unique properties.

Other characterization problems arose besides the issue of monodispersity. Should the particles be characterized according to their size, as measured by transmission electron microscopy? Alternatively, should the particles be characterized by the stoichiometry of the reagents that were used in their fabrication? The stoichiometry approach is much more specific from a chemical point of view but involves careful use of mass spectrometry. Murray's group was instrumental in these types of molecular characterization and produced reproducible data for gold nanoparticles. After these problems were solved, researchers could make some broad conclusions about nanoparticles. In gold nanoparticles larger than three or four nanometers, their properties approached those of bulk metals. In nanoparticles with sizes of two nanometers or less, quantized double-layer charging was observed during voltammetry. One can actually see in the voltammogram distinct peaks as electrons are sequentially added to the nanoparticles in solution. For even smaller nanoparticles, the voltammograms of these reagents show the behavior of discrete molecules. This arises because, like a molecule, the nanoparticle has a distinct band gap that can be measured both voltammetrically and spectroscopically.

Clearly, Royce and his group accomplished a great deal of research. But Royce's interest was not solely focused on research. He also was a gifted teacher who exerted considerable effort to improve the teaching of science at UNC. He set about improving the existing inadequate facilities that chemistry had when he arrived. In 1967, he was named chair of a departmental committee that planned a new chemistry research building, Kenan Laboratories. Not only did this building provide much needed space and fume hoods for chemical experiments, it also was the first UNC chemistry building to have air conditioning. This temperature regulation allowed research during the hot Chapel Hill summers, dramatically increasing the number of departmental publications. In this era, he was director of undergraduate studies and department chair. Later, he chaired the Curriculum in Applied Sciences and Materials Program, which evolved into the Department of Applied Sciences.

Additionally, Royce improved undergraduate instruction at UNC through planning Morehead Laboratories, the site of undergraduate laboratories that replaced Venable Hall. In 2000, to improve space for all of science at UNC, he chaired a university committee to shape a science complex for physical sciences. Several new buildings ensued, including one named after Royce, Murray Hall. Another, named Caudill Laboratories, was named after one of his undergraduates who founded a pharmaceutical analysis firm located in Research Triangle Park. The others were Chapman Hall, Genomic Sciences, and a reincarnation of Venable Hall.

Royce had numerous interests outside of chemistry. At lunchtime, he was frequently found on the trails through the woods that surround the Chapel Hill campus. Running remained important to him throughout his career. While a young man, he built a sailboat in his basement and enjoyed using it on Kerr Lake near Chapel Hill. He was well known for his annual fishing trips along the Canadian border with Jim Coleman of Stanford University. He was an ardent Tar Heel basketball fan and had seats on row twelve of the Smith Center. He also was a car buff. While a young father, he drove a Volkswagen minibus. This evolved into a Porsche 914 in his middle years. Still later he drove pickups that he used to haul manure to his annual vegetable garden. Royce loved to travel and experience the world. He especially enjoyed trips to the southern regions of Chile with his second wife, Mirtha, a Chilean native. Together they traveled extensively around the world. Royce married Mirtha Umaña, a fellow chemist, in 1982 and they were happily married for forty years until his death on July 6, 2022, after a lengthy illness.

The part of work Royce most enjoyed was his interactions with students, postdoctoral fellows, and faculty colleagues. More than 160 graduate students, undergraduates, and postdoctoral fellows did research in his laboratory. Many of them obtained prestigious faculty positions or made major contributions in the chemical industry. A large part of his success in teaching arose because he was a patient listener. I first met Royce in the summer of 1968 (during his minibus phase) as a prospective graduate student. I joined his research group, and then, after receiving my degree in 1975, I was a postdoc with Ralph Adams, who was exploring neurochemistry. I started my research program at Indiana University. In 1989 (his Porsche phase), I became Royce's colleague on the UNC chemistry faculty. Trying to keep up with his example (while teaching, doing research, or running) challenged me to greater exertions in all these areas. It is hard to imagine a better mentor and colleague than Royce W. Murray.

Note

Many of the personal details of Royce's life were taken from his published work and editorials. See especially R. W. Murray, 2004, "'Cadmium Horses' and Glucose" (*Anal. Chem.*76:149a); R. W. Murray, 2001, "Biography and Reminiscences of a 40-Plus Year Career as a Chemistry Faculty Member" (*J. Phys. Chem. B* 105:8642–8647); and Royce W. Murray, 2006, "Charles Norwood Reilley Biographical Memoir" (National Academy of Sciences Biographical Memoirs https://nap.nationalacademies.org/read/11807/chapter/17).
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