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JOHN GAMBLE KIRKWOOD
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A Biographical Memoir by

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BY STUART A. RICE AND FRANK H. STILLINGER

IT IS A DISTRESSING fact that many of the most creative individuals suffer premature death, thereby robbing humanity of unrealized contributions. Examples abound in literature, music, and the graphic arts, as well as the fields honored by the National Academy of Sciences. John Gamble Kirkwood was one of these individuals; his remarkable career was compressed into just fifty-two years of life. During this shortened interval he managed to create a solid theoretical underpinning for many aspects of modern physical chemistry, with ramifications that still provide compelling directions for investigation forty years after his death. His legacy also includes a group of students and collaborators who developed into outstanding scientists, and whose research activities bear the imprint of the unmistakable Kirkwood style.

John Gamble Kirkwood (“Jack” to his family, friends, colleagues, and students) was the first child born to John Millard and Lillian Gamble Kirkwood in the small town of Gotebo, Oklahoma. His father had worked his way through college and law school in Chicago, and with a good business sense became a successful independent distributor for the Goodyear Corporation in the Midwest. Two sisters completed the immediate family: Caroline, born two years after Jack, and Margaret, who was fourteen years his junior.

The Kirkwood family moved to Wichita, Kansas, in 1909. Jack attended public school in Wichita through the third year of high school. He was recognized early as a remarkable student, excelling in science and mathematics, as would be expected from his later professional attainments. He also demonstrated considerable proficiency in foreign languages. In fact, he remained fluent in French throughout the remainder of his life and avidly displayed a continuing fascination with all aspects of French culture.

In the summer of 1923, while still a high school student, Jack visited California. As a consequence, he became attracted to the opportunity for a first-class scientific education at the California Institute of Technology. Cal Tech chemist A. A. Noyes (NAS, 1905) suggested that he skip the last year of high school, and so encouraged, Jack enrolled that fall at Cal Tech. This arrangement lasted two years, but it apparently caused some conflict with Jack's strong-willed father, who had a different concept of an ideal college education. To resolve the problem, Jack transferred from Cal Tech to the University of Chicago, from which he graduated with an S.B. degree in December 1926.

Jack entered the Massachusetts Institute of Technology as a graduate student in the chemistry department in February 1927. He received a Ph.D. in June 1929. His dissertation, under the direction of Frederick Keyes (NAS, 1930), involved measurement of the static dielectric constants of carbon dioxide and ammonia as functions of temperature and density. This research formed the basis for his first two published papers, coauthored with Keyes. Kirkwood's interest in the dielectric properties of matter persisted throughout his later career. In his classic 1939 paper "The Dielectric Polarization of Polar Liquids," he introduced for the first time the concept of orientational correlations for neigh-

boring molecules and showed how these control the dielectric behavior of liquids.

Upon completion of his Ph.D., Kirkwood became a National Research fellow for the period 1929-30. He remained in the Cambridge area to complete work with Keyes at MIT and to collaborate with John C. Slater (NAS, 1932) at Harvard. His research interests widened to include intermolecular forces and their influence on equations of state as expressed through theoretical analysis of gas-phase virial coefficients.

This early Cambridge period also included meeting the former Gladys Lillian Danielson, previously wife of the electrochemist Theodore Shedlovsky (NAS, 1953). They were married in 1930. A son, John Millard Kirkwood, was born in 1935. The couple was divorced in 1951.

In the 1920s and early 1930s it was logical for young American scientists to complete their professional training in Europe. An International Research Fellowship provided Kirkwood that opportunity, and the academic year 1931-32 was spent with Peter Debye (NAS, 1947) in Leipzig, with a visit to Arnold Sommerfeld in Munich. Four research papers born during this sojourn were written in German and published in *Zeitschrift für Physik*. The Debye-Hückel theory for strong electrolyte solutions was still less than a decade old and its significance and validity were sources of lively debate. Not surprisingly, Kirkwood initiated then what was to become a lifelong research interest in ionic solutions, ultimately producing studies of the structure of concentrated ionic solutions and their electrical double layers.

Jack Kirkwood returned to MIT as a research associate in the Physical Chemistry Research Laboratory, a position he held during the years 1932-34. His scientific interests during that period included quantum effects on equations of state, and he carried out seminal investigations of the general statistical mechanics of fluid mixtures and the rigorous theory

of electrolytic solutions. The last of these theoretical developments was honored in 1936 by the American Chemical Society Award in Pure Chemistry, which at the time was called the Langmuir Prize, and he was one of its youngest recipients.

The next three years (1934-37) saw Kirkwood as assistant professor in the Cornell University chemistry department. This arrangement was interrupted for a year (1937-38) during which he became associate professor at his second undergraduate institution, the University of Chicago. He returned to Cornell as Todd Professor of Chemistry for the years 1938-47.

The liquid state theory that Kirkwood pioneered during the 1930s and early 1940s continues, sixty years after its introduction, to exert a major scientific influence. The recognition that calculation of the properties of liquids in terms of interactions between the molecules involves solution of a coupled hierarchy of equations laid the foundations for a variety of approaches that exploit intuitive approximations. The first and most famous of these, known as the Kirkwood superposition approximation, was invoked to render solvable the fundamental equations satisfied by molecular distribution functions. Although now replaced by better approximations, the superposition approximation captures the essence of many of the physical effects that dominate the structure and properties of liquids and it continues to resonate throughout many aspects of condensed matter chemistry and physics. But, and more important, the formalism of the theory of distribution functions developed by Kirkwood remains a key part of the theory of liquids.

Another seminal contribution from Kirkwood's Cornell years is the theory of fusion, published in three papers with Elizabeth Monroe in the period 1940-42. This set of papers ranks as one of the major classics in the theory of phase change and has generated a large number of subsequent

variants and reinterpretations by other authors. These and other notable contributions to the molecular foundations of physical chemistry formed the basis of Kirkwood's election to the National Academy of Sciences in 1942.

The Second World War produced a major, albeit temporary, shift in Kirkwood's scientific direction. Military requirements of the time made it clear that basic understanding of explosives needed great improvement. Kirkwood took up the challenge and contributed to the war effort as a member of the National Defense Research Committee of the Office of Scientific Research and Development (1942-45) and as a member of the Basic Research Group, which was advisory to the chairman of the Defense Department's Research and Development Board. Kirkwood formulated quantitative theories of detonation and shock waves in air and water, some of which was accomplished in collaboration with H. A. Bethe (NAS, 1944), a colleague from Cornell and coauthor of a paper on order-disorder phenomena. A portion of the studies of explosions was published after the conclusion of the war. The U.S. Navy presented Kirkwood a Meritorious Civilian Service Award in 1945 as recognition for his contributions. In addition, he received a Presidential Certificate of Appreciation in 1947.

The phenomena that concerned most of Kirkwood's research attention prior to 1940 would be considered by chemists as involving low-molecular-weight substances. Subsequently, his attention began to turn to polymeric materials, both synthetic and biological. This trend began with collaborative work with R. M. Fuoss (NAS, 1951), explaining the dielectric loss mechanisms in polar polymers, and was a natural extension of his prior studies of the dielectric properties of polar fluids. Kirkwood's interest in polymers continued to grow and later it led to the development of theories for mechanical relaxation in polymers and hydrodynamic

flow and rheological behavior of polymer solutions. Furthermore, in 1941 he devised a new method for the fractionation (and thus separation) of proteins in solution, using electrophoresis-convection. Following World War II this method was applied, with modifications, to the isolation and purification of several significant proteins, including diphtheria antitoxin, and gamma globulin.

The year 1946 was especially notable for the appearance of the first paper in a long series devoted to the fundamental statistical mechanical theory of transport processes. This series of investigations was to remain a major theme in the thinking of Kirkwood and many of his students for the remainder of his life. A key element in this work was the concept of time-averaged molecular distribution functions and their dynamical equations; this was envisaged as a necessary component of any theory that was consistent with physical measurement protocols, and was inextricably connected to irreversibility. While subsequent studies have revealed the necessity of refinements to this point of view, it nevertheless provided a powerful technique for the deeper understanding of Brownian motion, of the Boltzmann and Enskog equations for gas-phase kinetics, and of the viscosity, thermal conductivity, and heat of transport coefficients in pure liquids. Furthermore, it led to derivation of the first autocorrelation function representation in transport theory, for the "friction coefficient," anticipating the later Green-Kubo-Mori-Zwanzig results of the same generic form.

Kirkwood moved from Cornell to Cal Tech in 1947 to become the Arthur A. Noyes professor of chemistry. He remained in that position until 1951. This period witnessed the appearance of the Kirkwood-Buff general theories of liquid solutions and of liquid surface tension. It was also the time when the Kirkwood-Riseman theory of macromolecular motions in solution (determining viscosity, diffu-

sion, relaxation) was developed. The first of these theories is one of a tiny group of exact representations of the properties of mixtures in terms of molecular distribution functions and molecular interactions. It was only slowly appreciated, but now is widely used to help interpret experimental data. The last of these theories was, at the time of its introduction and despite the use of some approximations, the most realistic representation of the character of molecular motion of polymers, including both chain connectivity and the influence of the surrounding medium. It has influenced all subsequent developments in the field.

In 1951 Kirkwood accepted the position of Sterling Professor of Chemistry and department head at Yale, where he remained until his death in 1959. He became director of science at Yale in 1958. He also served as foreign secretary of the National Academy of Sciences from 1954 to 1958, a role that no doubt appealed to his early interest in diplomatic service and that must have benefited from his linguistic talent. As foreign secretary, he was involved in scientific contacts with the former Soviet Union at the height of the Cold War, and he monitored the cooperative arrangements required by the International Geophysical Year 1957-58.

Jack Kirkwood remarried in March 1958, to Platonía Kaldes. The couple had first met during July 1955 in Washington, D.C. During their few months together they occupied an old house built in 1762 in Guilford, Connecticut, not far from the Yale campus in New Haven.

Early in 1958 Kirkwood was diagnosed as a cancer victim with an estimated survival period of roughly one year. He resolved to make the most of his remaining days and in spite of increasing physical pain managed to maintain scientific activities at a high level. For his students and collaborators in this period, watching this confrontation between the physical disease and his intellectual resolve was both

uncomfortable and inspiring. In this last year of his life he spent several weeks at the University of Chicago, and he was Lorentz visiting professor at Leiden in early 1959.

The struggle finally ended on August 9, 1959, in Grace-New Haven Hospital. John Gamble Kirkwood was buried in the Grove Street Cemetery next to the Yale campus, also the final resting site for two other giants of statistical mechanics, Lars Onsager (NAS, 1947) and Josiah Willard Gibbs (NAS, 1879).

Following his death, Jack Kirkwood was honored by a three-day memorial symposium, held September 12-14, 1960, in New York City in conjunction with the 138th national meeting of the American Chemical Society. Many of his former students and collaborators contributed papers to this symposium, with many others in nostalgic attendance. The proceedings of this Kirkwood Memorial Symposium appear in the November 1960 issue of the *Journal of Chemical Physics*, with an historical introduction by George Scatchard (NAS, 1946).

Since 1962, the Yale University chemistry department and the New Haven section of the American Chemical Society have administered the John G. Kirkwood Award for outstanding theoretical or experimental research in the physical sciences. It has been conferred approximately every two years. The first recipient was Kirkwood's former colleague at Yale, Lars Onsager.

An eight-volume *John Gamble Kirkwood Collected Works* under the senior editorship of I. Oppenheim was published by Gordon and Breach Scientific Publishers during 1965-68. These volumes reprinted the majority of his 181 published scientific papers, collected into topical subsets with prefatory comments by former collaborators. A complete chronological bibliography is available at the National Academy of Sciences archives.

We close this memoir with a few personal notes. One of the authors was a doctoral student and the other a post-doctoral student of Jack Kirkwood at Yale. During these relationships we knew him as a straightforward individual who would speak his mind directly, and sometimes brusquely, but who would never intentionally wound another. We also knew him as an individual who would counsel his coworkers and work to help them find positions and to advance their careers. We learned from him how to balance rigorous analysis with approximations that render a theory useful, and we learned some of the important elements that constitute taste in the creation, execution, and evaluation of science. Along with his other students and colleagues we profoundly regret the brevity of our association with Jack Kirkwood.

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