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OLIVER REYNOLDS WULF

1897—1987

A Biographical Memoir by

HAROLD S. JOHNSTON

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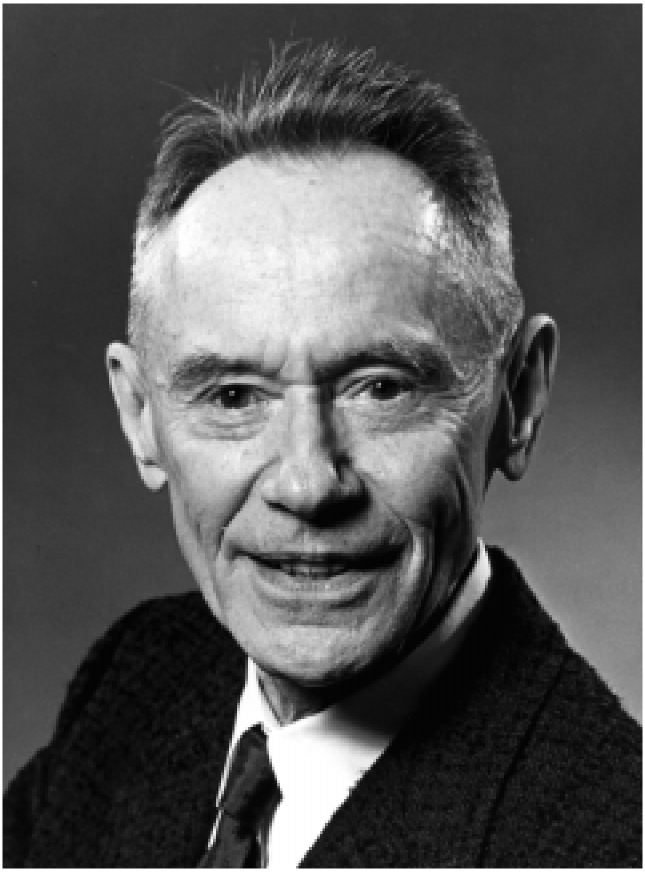

Oliver R. Wulf

OLIVER REYNOLDS WULF

April 22, 1897-January 11, 1987

BY HAROLD S. JOHNSTON

OLIVER REYNOLDS WULF was a chemist, physicist, and meteorologist. He was an expert in the chemistry of ozone and the oxides of nitrogen in the laboratory and in the atmosphere; infrared spectra of molecules as related to their molecular structure; photochemistry and physics of the atmosphere; and the relation of solar activity and geomagnetism to large-scale circulation of the atmosphere. He was elected to the National Academy of Sciences in 1949.

Oliver Wulf was born in Norwich, Connecticut, on April 22, 1897. He was the son of Otto Ernest Wulf and Grace Reynolds Wulf; he had an older sister and a younger sister. His father, a businessman, co-managed the largest department store in Norwich.

The family home at 120 Laurel Hill Avenue in Norwich had a basement with a cement floor. The basement was kept quite livable by a coal-burning furnace for heating the house. His father had installed a long workbench of 2-inch-thick plank along one side of the basement, and the workbench played an important role in Oliver's scientific development. Excited by early radio and wireless telegraphy, Oliver, in the third grade, built a 1-inch induction coil and a simple galvanometer. Noting his interest in the subject, his father bought him a book entitled *How Two Boys Made Their Own Electrical Apparatus*. While still in grammar school, he built a spark radio station with crystal detector and using Morse code, he played chess with a man who lived on the other side of town. He cleaned used photographic glass plates, stacked them with tin foil between, and obtained a large condenser. His father bought him a 15,000-volt Thordarson half-kilowatt transformer. With this and other equipment, Oliver built a large Tesla coil and a two-electrode spark gap for his wireless transmitter. His system operated at high frequencies. He studied glow discharges, and he attained heavy brush discharges with a Geisler tube, which he made from a discarded light bulb.

Oliver found greatly increased opportunity upon going from grammar school to high school, the Norwich Free Academy. He found and read serious scientific books in the library on subjects related to electricity and magnetism. From the start, the high-school chemistry and physics teacher took an interest in him. This allowed him free access to the science stockroom, which had originally been well stocked but not used a great deal. He especially enjoyed using a large induction coil, which had been used for an X-ray tube. In his home laboratory, he constructed a high-temperature electric-arc furnace, with which he melted zinc, brass, and iron. Occasionally he blew out the 35-ampere master fuse in his home. The Tesla coils he built produced the distinctive odor of ozone. He read about ozone in chemistry books in the library, and he developed a method specifically to detect ozone in his laboratory.

Oliver graduated from Norwich Free Academy in 1915 and received the science award. In his home basement laboratory, from the third grade through high school, Oliver did experimental work in chemistry and physics, largely concerned with the effects of high-frequency, high-voltage electrical discharges.

After high school, Oliver went to Worcester Polytechnic Institute. He had a good time taking freshmen chemistry and freshman physics courses, but his grades were neither good nor bad. Professor Farrington Daniels, who became one of the foremost physical chemists of the time, took a good deal of interest in him to the point of great kindness. Daniels was studying the fixation of nitrogen by the discharge produced by a large Tesla coil. The apparatus was similar to what Oliver had used in high school, but it was much bigger than those he had before. The research that Daniels was doing could equally well have been carried out in either a physics department or a chemistry department. Oliver's past interest and experience had been more nearly physics than chemistry, but because a chemist, Daniels, was doing research in his favorite field, Oliver became a chemist.

There was on campus a small stone structure, a geophysical and geomagnetic laboratory. Robert H. Goddard, the Goddard of rocket fame, was carrying out some experiments. Oliver's physics instructor was working with Goddard in that building, and he explained the research to Oliver, who found it extremely interesting. (Oliver Wulf received the Robert H. Goddard Award from Worcester Polytechnic Institute in 1962.)

Oliver entered Worcester in 1915 and would have graduated in the class of 1919, but he went into the Navy in June of 1918 and was at the officer school at Harvard when the war ended in late 1918. He received an honorable discharge from the Navy in April 1919. He returned to finish schooling at Worcester Polytechnic Institute, and he received his B.S. degree in chemistry in 1920. He filed his undergraduate thesis on "The Action of High Frequency Silent Discharge on Gases." It was unusual for an undergraduate student to do research to the extent that Oliver did with Farrington Daniels at Worcester.

During World War I, Farrington Daniels left Worcester to become director of the Fixed Nitrogen Research Laboratory in Washington, D.C. After Oliver graduated, Daniels invited him to join that laboratory, where he worked as a junior chemist at the U. S. Department of Agriculture (1920-22). Oliver worked with Daniels in parallel with another student who was studying a famous chemical reaction, the first-order decomposition of nitrogen pentoxide, the first clear-cut case of a first-order reaction.

Accepting an offer from the University of Wisconsin, Daniels left the Fixed Nitrogen Research Laboratory. A staff member of the laboratory, Richard Chace Tolman, was appointed the new director. Later Tolman was professor of theoretical chemistry at Caltech, and he achieved great distinction, for example, writing the heavy, thick book entitled *Relativity, Thermodynamics, and Cosmology*, which graduate students at Caltech fondly called “The Three Little Words Book.”

Tolman assigned Oliver Wulf to work under Sebastian Karrer, a physicist. Wulf’s work then became the production of ozone, and determining for sure, if possible, the molecular weight of ozone, which is the work he did up to the time he left the Fixed Nitrogen Research Laboratory. In those days, no one was quite sure that what one called ozone was all O_3. Some had proposed an N ozone and an O_4 ozone. In view of these uncertainties, Wulf’s question was: “What is the molecular weight of what WE call ozone?” Wulf concentrated on preparing pure ozone, and he weighed bulbs of that gaseous material on a sensitive balance. He found the molecular weight of ozone to be indeed 48, establishing that it was O_3. This procedure sounds simple, but it had difficulties. He flowed oxygen from a commercial tank through a high-temperature furnace to burn up any methane and other hydrocarbons; passed the stream through chemical traps to remove water, carbon dioxide, and nitrogen oxides; sent the pure dry oxygen between two concentric glass cylinders; and applied a silent electric discharge, which broke oxygen (O_2) apart to give two oxygen atoms (O). Each oxygen atom added to an oxygen molecule to form ozone (O_3). Wulf passed the gaseous mixture of oxygen and ozone through a liquid-air cold trap to condense the ozone. He slowly removed the liquid air container to let the oxygen boil off and leave behind deeply purple liquid ozone. He let the ozone evaporate into an evacuated glass bulb of about 1/2 liter volume and at a pressure of about 1/20 atmosphere. Such a bulb would weigh about 200 grams. If ozone were O_4, the mass of the bulb and gas would be 200.07143 grams; if ozone were O_3, the mass of the bulb and gas would be 200.05357 grams. The difference is 0.0089 percent of the total weight. A good chemical analytical balance can be used to make such measurements, but it requires great attention to details to achieve the necessary precision.

One may ask, “To increase precision, why not go to higher pressures of ozone?” The answer is that pure ozone gas at room temperature readily explodes at pressures above about 1/20 atmosphere. Pure liquid ozone readily detonates, shattering glass apparatus and throwing off pieces of glass at high velocities.[1] If ozone is prepared from gaseous oxygen containing traces of hydrocarbons, the probability of explosion greatly increases. If ozone is prepared from gaseous oxygen containing traces of nitrogen, the final product is contaminated by oxides of nitrogen. If the reactor contains traces of water vapor, the yield of ozone is greatly decreased.

Early in 1922 Tolman left the Fixed Nitrogen Research Laboratory in Washington, D.C., to be a full professor at the California Institute of Technology. The next 12 months were eventful for Wulf. He became engaged to be married.

He decided that his salary as a junior chemist was not enough to support a family. In the summer of 1922 he obtained a job from the Bristol Company in Waterbury, Connecticut, makers of recording instruments. Shortly afterward, he received a letter from Professor A. A. Noyes inviting him to accept a scholarship and be a graduate student at Caltech. Noyes was chairman of the chemistry department at Caltech, in fact, he was one of the main founders who converted the provincial Throop Institute of Pasadena into the California Institute of Technology. Undoubtedly, Tolman had recommended to Noyes that he make this offer.

His fiancée, Beatrice (Bea) Jones, urged Wulf to go to Caltech. His father and all the men in Wulf's family were businessmen of some kind, and he was obsessed with the idea of becoming a good businessman. He wrote to Noyes, thanking him but declined, saying he felt he ought to go to work full time to support a family. In the summer and early fall of 1922 he was alone, a bachelor in Waterbury going daily to work on a long trip by trolley car to the Bristol Company. He was an apprentice working under a very excellent machinist in the heavy-machinery brass works.

Oliver Reynolds Wulf and Beatrice Mae Jones were married on October 21, 1922. They lived in an apartment in Waterbury. By January 1923 Wulf recognized that the work in the Bristol brass works was not suitable for him. At Bea's strong recommendation, he wrote to Professor Noyes, asking if his offer still held. Noyes warmly renewed the offer. Mr. and Mrs. Wulf crossed the country by train and arrived at Caltech in March 1923.

Professor Noyes met the Wulfs at the Pasadena station and introduced them to advanced graduate student Richard Bozorth, later famous at Bell Labs. On Bellevue Drive between Euclid and Marengo they found living quarters on the second floor of a rather large garage, where they lived until Wulf obtained his Ph. D. degree in 1926. Fellow graduate students in 1924 were Linus Pauling, Ernest White, Reinhardt Schuhmann, Bill Houghton, Joseph Mayer, Paul Emmet, and Merle Kirkpatrick.

Wulf spoke of a feeling of excitement around Caltech at that time. Professor Hendryk Anton Lorentz was present in the physics department. Wulf recalled a lecture by Professor Ehrenfest in which he placed an imaginary ensemble on the laboratory bench, and as he walked across the speaking area he very carefully went around the imaginary ensemble he had left there. Professor Raman, a tall figure with arms frequently folded, was an excellent lecturer. There was the Astronomy-Physics Club with participation by Hubble and his staff, and Wulf was fascinated by the unfolding of Hubble's famous work. In a visit there, Professor Michelson gave a very interesting seminar concerning the Michelson-Morley experiment.

Wulf took a kinetic theory course given by Professor Robert Millikan, president of Caltech. Other chemists in the course were Linus Pauling, Rudolph Langer, and Don Loughridge. Hearing that the Nobel Prize had been awarded to Millikan, Wulf and the other students gave him a standing ovation when he came into the classroom on the third floor of East Bridge Hall.

When Wulf took up graduate work at Caltech under Professor Richard Tolman, he studied the kinetics of the thermal decomposition of ozone by two methods: (1) a static method with manometric determination of the rate of decomposition and (2) a flowing method with chemical analysis of ozone. He flowed ozone through a coil of glass tubing where ozone decomposed at a rate depending on the concentration of ozone in the tubing and the temperature of the glass. His Ph. D. thesis and the three articles he co-authored with Tolman were based on the thermal decomposition of ozone as measured by the flow method. Wulf started his research in the spring of 1923 and continued through half of 1926.

At the end of his graduate studies at Caltech, Wulf received a National Research Fellowship, one of the few sources of support for postdoctoral research at that time. During his last year as a graduate student at Caltech, he started some work on the photochemistry of ozone. He was interested in the structure of the ozone molecule with respect to its absorption of light, and that interest led him to the general question of the absorption of light by molecules. Professor Raymond Birge in the physics department at Berkeley had an active program in spectroscopy, including infrared spectroscopy of molecules as related to their shapes, ultraviolet spectroscopy of diatomic molecules, and hydrogen atom emission. During 1926-27 Wulf took his NRC fellowship to the University of California to work in collaboration with Birge. He extended his study of ozone to include its molecular spectroscopy. Later, he made significant contributions to molecular spectroscopy by studying the infrared and ultraviolet spectra of other molecules, simple and complex.

The Fixed Nitrogen Research Laboratory in Washington, D.C., where Wulf had worked as a junior chemist (1920-22), had become the Bureau of Chemistry and Soils, a laboratory for fertilizer investigations in nitrogen, phosphorous, and potassium, and he was offered a position there. After Wulf completed his fellowship at Berkeley, he and Bea spent three weeks driving their model-T Ford from Berkeley to Washington. Wulf progressed from associate chemist to senior physicist at the Bureau of Chemistry and Soils in the U. S. Department of Agriculture (1928-39).

Frederick Gardner Cartrell, inventor of the electronic smoke precipitator, was head of the Bureau of Chemistry and Soils, and he strongly supported Wulf and his work.

Wulf carried out further studies of the oxides of nitrogen, and he retained a strong interest in ozone. He studied photochemical destruction of ozone and photochemical production; the combination of these two processes gives the ozone photochemical steady state. He set up a simple laboratory experiment to illustrate that the photochemical steady state depended on movement of the gas relative to the source. In his words,

> Flow away from the source may bring ozone formed where radiation is being strongly absorbed to regions where photochemically it is dark, the ozone is stable and thus stored, while flow toward the source, any such stored ozone would be erased in the region of strong absorption of radiation. It was thus apparent that the winds of the upper atmosphere could affect its ozone content.

Wulf did substantial work on the vertical distribution of ozone in the atmosphere, as set up by photochemistry and air motions.

In 1932, while in Washington, Wulf received a Guggenheim Fellowship. He spent the first half-year in Berlin, where he said he "received a tremendous education," including an inspiring association with Professor Michael Polanyi. He and Bea were in Berlin when they heard that the bank in which they had deposited almost all their money had failed and gone into bankruptcy, a widespread event during the depression. During their second half-year, they went to Göttingen to associate with James Franck at the second institute of physics at the university; Max Born had the first institute of physics upstairs in the same building. They later did additional travel in Europe, Mexico, and the Caribbean.

In 1935, Wulf received the Hillebrand Prize sponsored by the American Chemical Society.

Solar radiation at shorter wavelengths (and thus higher energy) than the wavelengths that form ozone is absorbed by air at much higher altitudes to photo-ionize air to form the ionosphere, which was responsible for long distance radio communication.

Wulf's interest in how air motions move ozone in and out of the ozone formation region in the stratosphere, the temperature structure of the atmosphere, and how solar radiation produces ions in the upper atmosphere led him into the study of meteorology and atmospheric dynamics. In 1939, at the recommendation by Carl Rossby, famous meteorologist and atmospheric dynamicist, Wulf was appointed senior meteorologist in the U. S. Weather Bureau. He remained a member of the Weather Bureau from 1939 until he retired in 1967, even though the Weather Bureau assigned him to do independent work at places other than Washington, D.C. Again at the recommendation by Carl Rossby, the Weather Bureau assigned him in 1941 to the Institute of Meteorology at University of Chicago to teach meteorology to Air Force cadets, which he did until the end of the war.

In 1945 the Weather Bureau assigned Wulf to Caltech as a research associate with rank of full professor in the Division of Chemistry and Chemical Engineering, a position he held until he retired in 1967.[2]

Wulf found it especially interesting that ionized air, set in motion by winds in the upper atmosphere, moved across lines of force in Earth's magnetic field to produce small but observable magnetic signals at the surface of Earth. Wulf's major research at Caltech after he returned in 1945 was collaboration with Seth Nicholson, a solar astronomer and leading authority concerning sunspots. They worked together with the solar telescope and other equipment at the Mount Wilson observatory, and they published several articles together, studying the relation between solar activity, geomagnetic activity, and Earth's magnetic field. They also examined the effects of the Moon in perturbing recurrent Sun-induced geomagnetic activity. One interesting project was their study of global atmospheric tides as induced by the Sun and the Moon .

In a short speech at his retirement dinner in 1967 Wulf summed up his recent and future research.

> The realization that the movement of this photochemical ionized air reacted on the earth's magnetic field, in very small degree it is true, led to very great interest in the circumstance that probably this reaction to air motion in the lower ionosphere was being measured daily and not at one point occasionally, but at many magnetic observatories over the surface of the earth. Thus the realization that information concerning winds in the upper mesosphere and lower thermosphere, that is the lower ionosphere, was probably contained in the daily continuous records of the earth's magnetic field, led to a strong feeling that here was a field in the atmospheric sciences holding great promise, and it is in the midst of work in this field that we are at present and planning to continue.

To summarize, Oliver Wulf in his childhood carried out serious self-educational construction of devices and experiments with high-frequency, high-voltage electrical discharges. Later, this experience led his research, step by step, to nitrogen fixation by electric arcs, ozone chemistry, ozone photochemistry, ozone in the atmosphere as affected by photochemistry and air motions, atmospheric dynamics, meteorology, and ions and winds in the ionosphere, causing induced magnetic signals at the ground. His childhood fascination with electricity and magnetism at his basement workbench grew to become major contributions toward understanding electricity and magnetism in the global atmosphere.

THIS BRIEF REVIEW of Oliver Wulf's personal and professional life is based in part on my recollection of a pleasant and profitable association with him from 1946, but in large measure it is based on material from the Archives of the California Institute of Technology: (1) an interview with Oliver Reynolds Wulf by Tom Apostol, Oral History Project, Pasadena, California, copyright 1987; (2) an inter-

view with Mrs. Oliver Reynolds Wulf by Harriet Lyle, Oral History Project, Pasadena, California, copyright 1982; (3) a four-page summary and list of items in the Wulf archives; and (4) a five-page transcript of an address Wulf made at his retirement dinner at the Pasadena Huntington Hotel on April 29, 1967. Statements I make in this memoir concerning his feelings and opinions are based on his words in the oral history and his talk at the retirement dinner.

NOTES

1. When I (H.S.J.) was a graduate student at Caltech in 1945-47, Professor Don Yost and I wanted to study the rate of reaction between ozone and nitrogen dioxide. Oliver Wulf instructed me how to prepare pure ozone, including the safety warnings. Later in my laboratory at Stanford, my graduate students and I made and used ozone for several studies. We had only one explosion. Fortunately, following Wulf's advice, we carried out the experiment inside a hood and behind heavy steel plates, and no one was hurt, but all adjacent apparatus was demolished.

2. It was at this time (1946-47) that Wulf taught me (H.S.J.) how to make and handle ozone in the laboratory. He also taught me about Sydney Chapman's mechanism for ozone formation and destruction in the upper atmosphere; about G. M. B. Dobson's measurement of ozone and its vertical distribution in the atmosphere by means of ground-based spectroscopy of scattered sunlight during sunset or sunrise; and about ions and winds in the ionosphere.

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