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JOEL HENRY HILDEBRAND

1881—1983

A Biographical Memoir by
KENNETH S. PITZER

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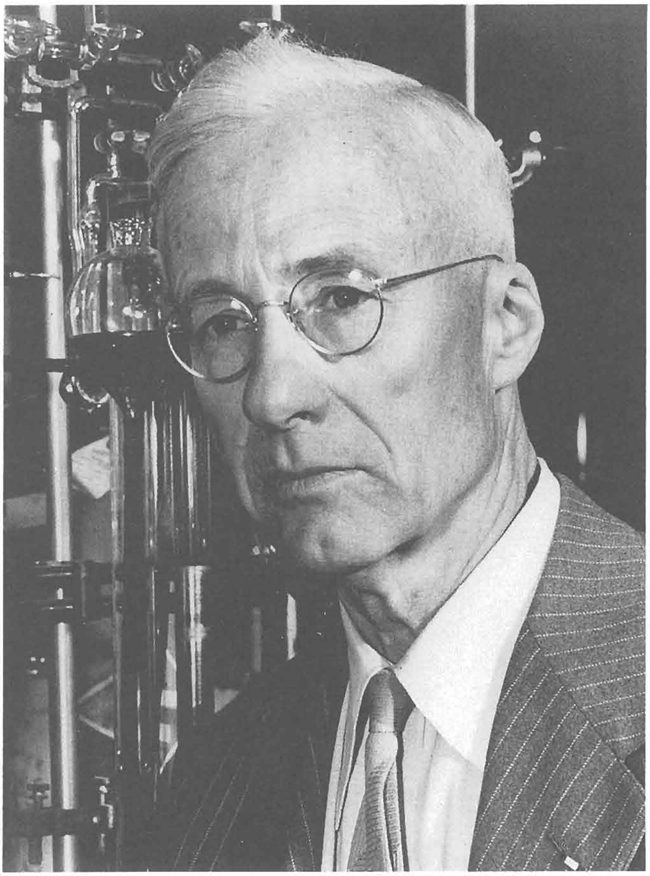
Biographical Memoir



Joel H. Hildebrand

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November 16, 1881–April 30, 1983

BY KENNETH S. PITZER

THIS BIOGRAPHICAL SUMMARY differs from that for a typical scientist in many respects. First, there is the remarkable diversity of fields in which Joel Hildebrand made major contributions. To research scientists and engineers, his contributions to our knowledge of liquids and nonelectrolyte solutions are most important. But a substantially larger group recognize him as their outstanding teacher of freshman chemistry and often as the most inspiring teacher of their college experience. Others know him as mountaineer, lover of the outdoors, president of the Sierra Club, and coauthor with his daughter Louise of a charming little book, *Camp Catering*. There was his effective leadership in a variety of educational and scientific organizations far beyond chemistry, involving service as a member of the Council of the National Academy of Sciences (1949–52), dean of men and dean of the College of Letters and Science at the University of California, and member of the Citizens Advisory Committee on Education to the California Legislature. And, finally, he continued his active professional life past age 101.

It is a special pleasure to me to have the opportunity to write this biography. I first met Joel Hildebrand when I entered graduate school at Berkeley in 1935. His cordiality to young people was immediately apparent. Although I did not do my thesis research with him, I did consult him frequently and the discussion was always helpful. With my appointment to the faculty, the association with Joel continued and expanded to a wide range of activities and to personal friendships including our families—with mine of the generation of his children.

Joel Henry Hildebrand was born on November 16, 1881, in Camden, New Jersey. His ancestors came to America before the revolution from the upper Rhine valley. When asked about his longevity, Joel replied, "I chose my ancestors carefully" and frequently added that most, if not all, lived well past eighty. His father, Howard Onid Hildebrand, was in the insurance business near Philadelphia, and Joel attended local schools. His intellectual interests were particularly stimulated by a grandfather who, although of limited schooling, had read widely and accumulated an excellent library. With his interest in natural phenomena aroused, Joel acquired and studied Dana's *Geology*, Newcomb's *Astronomy*, and similar books. After his high school mathematics was completed with solid geometry and trigonometry, he discovered independently the power and beauty of calculus. After he had learned as much chemistry as his teacher (the principal) knew, he was given the key to the laboratory, a college laboratory manual, and encouragement to learn more on his own. Joel told with justified pride about his experiment proving that nitric oxide gas was NO rather than N_2O_2—a result that demolished a theory in a book by a Harvard professor that he had been given. It is clear that this high school principal was a great source of encouragement also for opening to Joel broader horizons of interest in various cultural areas, including music.

Hildebrand entered the University of Pennsylvania in 1899 and wisely chose a double major in chemistry and physics in the College of Arts and Science rather than a more "professional" course in chemistry that emphasized recipes for analysis and similar details. He thereby had the opportunity to learn not only more physics but also history, literature, and mathematics while avoiding details of chemistry that were unimportant and sometimes even untrue.

After receiving his Ph.D. in 1906 in chemistry at Pennsylvania, Hildebrand was encouraged to spend a postdoctoral year in Germany learning the new science of physical chemistry before returning to teach it. He went to Berlin, where he attended lectures by J. H. van't Hoff and by Walter Nernst. He also did some research under Nernst and then returned to the University of Pennsylvania to serve on its faculty until 1913. In that year Gilbert N. Lewis invited Hildebrand to join the remarkable group of young chemists whom he selected and led in transforming the Chemistry Department at the University of California into a center of international eminence.

Hildebrand's doctoral thesis of 1906 was entitled "The Determination of Anions in the Electrolyte Way," and he continued with several papers on electrochemical methods in analysis. Herbert S. Harned was his first research student, and Harned's thesis was in this area. But Hildebrand soon shifted his primary interests to physical rather than analytical topics (as did Harned, who proceeded to a very distinguished career at Yale and was elected to the National Academy of Sciences).

The color of iodine solutions fascinated Hildebrand throughout his career; his first paper on that topic, "Uber die Farbe von Jodlosungen," was published in 1910. He soon noted (1920) that the deviations from Raoult's law of various violet solutions of I_2 formed a regular pattern. However, the curve for I_2 in benzene differed from this pattern, and the solution had a somewhat different color. This color difference suggested a more intimate interaction of the iodine with benzene.

These ideas were extended in many directions through the years. The concept of a regular pattern of positive deviations from Raoult's law grew into a general theory of "regular solutions." Such systems involve no specific solvation or association and the mixing of their molecules is essentially random. Equations for the activities of the components of such solutions had already been developed by several scientists, but these suffered either from the absence of relationships to the properties of the pure components or, in van Laar's case, to making these connections through an approximate equation of state. While the van der Waals equation was a great advance at the time and it gives a reasonable representation of gas imperfection, the quantitative deviations in the liquid region are large, and it is the liquid region that is pertinent to liquid solutions.

Scatchard published a paper in 1931 which, in his words, "may be regarded as a quantitative development of the treatment of Hildebrand, although it disagrees with his ideas in some important details, or as a method of freeing the van Laar treatment from the inadequacies of the van der Waals equation." Hildebrand and Wood derived the same equation two years later by a very different and modern method—by integrating the intermolecular pair potentials throughout the liquid weighted by the radial distribution function.

Both Scatchard's and Hildebrand's results yield the same working equation relating the deviation from ideal solutions (Raoult's law) to the cohesive energy density of the pure components, that is, $\Delta E/V$, where E is the energy of vaporization of a volume V of the pure liquid. More precisely, it is the square of the difference in the square roots,

$[(E_1/V_1)^{1/2} - (E_2/V_2)^{1/2}]^2$, that determines the departure from ideality.

In recent years, this quantity, $(E/V)^{1/2}$, has been called the solubility parameter (or Hildebrand's solubility parameter) and given the symbol δ. The Scatchard-Hildebrand equation is quite successful—better than any other equation of comparable simplicity and generality. But it is not surprising that there are departures from perfect agreement, and from time to time Hildebrand presented tables of adjusted solubility parameters that yield improved agreement. These are always discussed in relation to aspects of the intermolecular forces that might explain the need for adjustment. Joel's effort to improve the theory of regular solutions continued with a final paper in 1979.

Hildebrand, always the effective teacher, summarized the current status of knowledge about nonelectrolyte solutions in monographs designed to interest and instruct chemists. Initially, these were general reports on the status of knowledge in the field and carried the title *The Solubility of Nonelectrolytes.* The successive editions of 1924, 1936, and 1950 (the last with R. L. Scott) grew in size along with the rapid advance of knowledge in this area. Opposite the title page of the third edition is a picture of a tube containing seven incompletely miscible liquids (heptane, aniline, water, perfluorokerosene, phosphorus, gallium, and mercury)—a beautiful example of Joel's flair for generating interest in and enjoyment of his topic for discussion. After 1950, Joel left to others the task of general review of knowledge concerning nonelectrolyte solutions, and he prepared smaller books concentrating on the areas of his particular interest. These were *Regular Solutions* in 1962 with R. L. Scott and *Regular and Related Solutions: The Solubility of Gases, Liquids, and Solids* in 1970 with J. M. Prausnitz and R. L. Scott.

The relationship of the color of iodine solutions to their other characteristics was noted. Joel maintained a continuing interest in the changes of color (or new spectral features) as an indication of bonding. The one case where I was coauthor with Joel of a published paper arose from a series of discussions in this general area; it is entitled "Color and Bond Character" and appeared in 1941. Hildebrand's most important discovery in this area came in a series of papers with H. A. Benesi in 1949–50 that related an intense ultraviolet absorption to the formation of electron donor-acceptor complexes. This type of complex, now more commonly called a charge-transfer complex, has been investigated extensively by others, is well understood theoretically, and is an integral part of our body of organized knowledge.

The "rule" that carries the Hildebrand name concerns the entropy of vaporization of a normal liquid. In 1915 he showed that, for a typical group of "normal" liquids boiling near or below room temperature, the entropy of vaporization was more nearly constant if compared at a constant vapor volume rather than on the constant pressure basis of Trouton's rule. With this considerably higher precision of agreement, the Hildebrand rule became a much more useful criterion of a normal liquid. In comparison, hydrogen-bonded or other highly polar liquids have larger entropies of vaporization than do "normal" liquids.

Another idea of Hildebrand's that has great practical as well as theoretical importance concerns the use of helium in deep diving. A diver at depth experiences high pressure and correspondingly increased solubility of breathing gases in his blood. The problem of the "bends"—the release of this gas as a bubble in a blood passage when the diver emerges—was well known. In the mid-twenties Hildebrand suggested that this problem could be ameliorated by substituting helium for nitrogen in mixture with oxygen for the diver's breathing gas. Not only is the solubility of helium much less than that of nitrogen at a given pressure, but also the diffusion rate is faster. These basic ideas have had a major role in improving diving capability and safety ever since.

Also in the mid-twenties, Hildebrand initiated precise physical-chemical studies of anhydrous hydrogen fluoride and fluorine. Among other studies, he and Simons measured the anomalous P-V-T behavior of HF and interpreted it on a polymerization basis. Simons proceeded from this beginning to a fruitful career of specialization in fluorine chemistry.

Through the years Joel took pleasure in demolishing concepts that he regarded as spurious or misleading. He was not fooled by "polywater." He was severely critical of theories of liquids that were based on complex assumptions about structural features for which there was no direct verification. With the deeper insight of molecular dynamics calculations, these complex assumptions have now been disproved in many cases. But Joel had refused to accept these theories, even if they were reasonably successful in representing the experimental data available at the time. Several of these situations are described in his 1977 paper, "Operations on Swollen Theories with Occam's Razor."

Another case of this type is the "hydrophobic effect" or, worse, the "hydrophobic bond." Joel objected to these terms because "phobic" implies repulsion. It is true that in aqueous solution a solute containing both alkyl (or other nonpolar) groups and polar groups will arrange itself in a manner to favor water contact with the polar groups of the solute and alkyl group contact with other alkyl groups. But this does not mean that an alkyl group is actually repelled by a water molecule. Rather, as Hildebrand concludes, "There is no hydrophobia between water and alkanes; there is only not enough hydrophilia to pry apart the hydrogen bonds of water so that the alkanes can go into solution without assistance from attached polar groups."

In the period 1970–77 Joel gave considerable attention to the viscosity of liquids or, as he prefered, the fluidity that is the reciprocal of viscosity. These papers are collected in a small monograph, *Viscosity and Diffusivity: A Predictive Treatment,* published in 1977 with an introduction by J. O. Hirschfelder. In the introduction Hirschfelder writes of Hildebrand, "Somehow, he has the ability to sweep away all of the complexities and discover simple relationships which will take theoreticians another generation to derive." Indeed, Joel often presented new empirical relationships that were simpler and more accurate than those in common use. And he presented them in a simple qualitative theoretical framework that was free from inconsistencies or the complexities often contrived to circumvent inconsistencies. This book often elicited the comment that "Hildebrand is a genius in finding ways to present data so that they fall on a straight line." But Joel's were not merely functions yielding straight lines; he also required conformity to general ideas of molecular structure and behavior. Indeed, he was a genius in research of this type.

Hildebrand's impact as a teacher was just as important and in many respects more remarkable than his role in research. His freshman chemistry lectures, given regularly from 1913 until his "retirement" in 1952, were legendary. Thousands of alumni recall his vivid descriptions and dramatic demonstrations as well as his enlivening digressions into music, art, and mountaineering.

A single course was offered at Berkeley with total enrollment usually somewhat over 1,000, with lectures in a room seating about 500, but with laboratory, quiz, and discussion in groups of twenty-five. William Bray and Wendell

Latimer (both members of the Academy) took primary responsibility for the laboratory and wrote the book for it. Most of the regular faculty supervised freshman sections (in addition to other teaching) and thereby initiated the graduate students into their teaching assistant duties in an apprenticeship pattern. Thus, there was extensive involvement of most of the faculty with the general chemistry course and general agreement concerning its character. But Hildebrand gave the lectures, wrote the quizzes and examinations, and was in general charge of the course. He also wrote the central text, *Principles of Chemistry*, which was revised several times.

The course at Berkeley, as developed by Hildebrand, Bray, Latimer, and others, departed from the pattern of that time by much greater emphasis on principles, with reduced attention to memory of specific factual material. It was only after about twenty-five years that other textbooks began to appear that reflected a similar emphasis. Of course, the "Berkeley" books were used elsewhere in the intervening years.

As is often the case, the pattern has recently shifted farther (probably too far) toward dominance of theory and general principles and the near exclusion of "factual" material. The "Hildebrand" course maintained a balance; the student learned that, while important aspects of chemistry could be related to general principles through relatively simple equations, other experimental facts were best remembered, if important enough, or looked up when needed. To promote the habit of quick and convenient reference to this body of knowledge, Latimer and Hildebrand prepared their *Reference Book of Inorganic Chemistry* (1928). It was revised several times and was available combined with *Principles of Chemistry* in a single volume.

Joel was superb as a lecturer and thoroughly enjoyed it. There were many lecture experiments with an entertaining aspect and lots of humorous comments that the students enjoyed. But Joel never lost sight of the primary purpose of the lectures, and most of these entertaining features were tied into the primary lesson of the day. Joel's enthusiasm, combined with thorough knowledge and excellent lecture technique, was almost irresistible. There was never a problem of slack attendance at Hildebrand lectures.

From 1913 through 1952, Hildebrand had about 40,000 students in his freshman lectures. While only a moderate proportion followed chemistry professionally, many became engineers, physicists, or other scientists. Others became lawyers, business executives, and leaders in various fields, and they have a clearer picture of the role of science in the modern world because of their contact with Joel Hildebrand. His impact as a teacher was great indeed.

This fame as a teacher of chemistry gave Joel the credentials and brought invitations to influence educational matters more broadly. His former students, now in a multitude of positions of responsibility and influence, urged his inclusion on committees, boards, and conferences. A notable example was the Citizens Advisory Committee to the Joint Education Committee of the California legislature.

Joel had all of the qualifications of a good administrator or organizational leader. He never shirked such responsibilities when they were pressed upon him, but he never let such duties draw him permanently away from his primary interests in teaching and research. His preferences in this respect fitted very comfortably with the policies of the University of California, wherein academic administration was in the hands of distinguished professors, but there was no implication that a given individual would continue indefinitely as a department chairman or a dean. Indeed, the status of ex-dean was most highly regarded at the Berkeley Faculty Club.

Thus, Joel accepted appointments and served a few years in each case as dean of men (1923–26), dean of the College of Letters and Science (1939–43), chairman of the Department of Chemistry (1941–43), and dean of the College of Chemistry (1949–51). He also played a major role in the Academic Senate and served as chairman of important committees of the Senate.

In making an administrative decision, Joel collected and digested the pertinent information, consulted other individuals as appropriate, and then reached his conclusion promptly without emotional trauma. When he left his administrative office, he left those problems behind and was ready to discuss a problem in chemistry or to give a freshman lecture with full vigor and enthusiasm.

Other organizations frequently called on him to take positions of leadership, and he accepted when he believed he could make a significant contribution without undue interference with his work in chemistry. Thus, he became interested in the Sierra Club and was soon asked to be president (1937–40). He held various positions in the American Chemical Society but declined nomination as president until after his retirement from regular teaching; then he was elected and served in 1955. He also managed the U.S. Olympic Ski Team in 1936.

Hildebrand was elected to the Council of the National Academy of Sciences for a three-year term (1949–52) and to its Executive Committee for 1950–52. He also served by appointment as chairman or member of several important committees.

In both world wars Hildebrand was asked to undertake special duties. In 1918–19, he directed the chemical warfare laboratory of the American forces in France, with the rank of major and later of lieutenant colonel, and was awarded the Distinguished Service Medal. In 1943–44 he was a liaison officer in London for the Office of Scientific Research and Development. The British government also took advantage of Joel's presence in London to obtain his personal advice on many problems and awarded him their King's Medal for Service in the Cause of Freedom in 1948.

In 1908 Joel married Emily Alexander, whose continued good health and vigor were as exceptional as Joel's. Emily also lived to age 101. Their seventieth wedding anniversary in 1978 was a great occasion for all of their many friends. They had four children: Louise, Alexander, Milton, and Roger. Two are professors in the sciences—Milton in zoology at the University of California at Davis and Roger in physics at the University of Chicago. Both have been very successful in their own research and have held broader leadership roles within their universities. After outstanding research for the Standard Oil Company of California (now Chevron) in the area of oil discovery and production, Alexander took an early retirement and has been an active and successful farmer in the central valley of California. All of the children are married; there are twelve grandchildren and at least thirteen great-grandchildren. In their later years Joel and Emily frequently had a grandchild living with them while attending the university or beginning some new activity in the area.

In 1953, when Joel Hildebrand received the Willard Gibbs Medal, his son Roger was invited to help introduce him. The result was a most amusing and interesting insight into the Hildebrand family. Joel was always the enthusiastic teacher. As Roger tells it, "We were encouraged and instructed in any worthwhile pursuit. The most confirmed blockhead could hardly have withstood the assault of intellectual enthusiasm which we enjoyed. Any flair for science, athletics, music, arts or crafts on our part was noticed and the spark was fanned by a powerful hand. As a result, enough bonfires lit the sky to reduce any mother but mine to a cinder."

Another paragraph from Roger's introduction: "We learned a lot by watching him. He worked and played hard. He is justly proud of his physical condition. He once entered a grandfathers' swimming race. Now it takes him a quarter mile or so to get really warmed up, so he dove in and swam a few laps each of breast stroke, back stroke, and crawl. His competitors, who were watching from the bank, gradually disappeared and it is said that by starting time not a one of them could be found."

Among my multitude of memories of happy associations with Joel, I recall particularly the skiing trips of the mid-fifties. He was a member of a ski club with a lodge in the Sierra Nevada. All of the other members had given up skiing, even though many were younger than Joel. Thus, he had, in effect, a private ski lodge, and he invited his younger colleagues and sometimes their spouses on many occasions. Our skiing was primarily cross-country, which was also my preference, and most enjoyable. Equally wonderful were the evenings around the fireplace when we discussed all sorts of interesting topics. Joel had a stimulating comment on any topic, and we learned much from his rich experience.

An interesting Hildebrand story arose when the editor of *Who's Who in America* decided in 1975 to transfer Joel to the compilation "Who Was Who." This elicited a spirited response, of course, in which Joel listed five research publications from 1974 as well as others in press for 1975, together with copies of several comments about his current activities from others, including President Handler of the National Academy of Sciences. He concluded by saying: "Leave me out of *Who's Who,* if you must—*Europa* still lists me, but please postpone till a more appropriate time including me in Who *Was* Who. People would be writing to learn what happened to me." Needless to add, Joel continued to be listed in *Who's Who*—not "Who *Was* Who."

Nearly innumerable honors of various types came to Joel Hildebrand through the years. The more important honors are listed elsewhere, so I will comment only briefly. From the American Chemical Society came the award of the Nichols Medal in 1939; its teaching award in 1952; the Willard Gibbs Medal in 1953; and its highest recognition, the Priestley Medal, in 1962. Joel was elected to the National Academy of Sciences in 1929 and to the American Philosophical Society in 1951. He received an honorary doctorate after retirement from the University of California in 1954. I had the pleasure of presenting Joel on that occasion. When the citation was read, the audience immediately applauded Joel so enthusiastically that President Sproul at first forgot to confer the degree. After that omission was remedied, Joel received a second ovation. The warmth and enthusiasm of that occasion symbolize beautifully the high regard in which Joel was held by students, alumni, professional colleagues, and all others who had come to know him. Hildebrand's one hundredth birthday was celebrated by a special university convocation followed by a well-attended luncheon; it was a truly remarkable occasion.

CHRONOLOGY OF MAJOR ACTIVITIES AND HONORS

1881	Born November 16 in Camden, New Jersey
1903	B.S., University of Pennsylvania
1906	Ph.D., University of Pennsylvania
1906–07	Postdoctoral fellow, University of Berlin
1907–13	Instructor in Chemistry, University of Pennsylvania
1913–17	Assistant Professor of Chemistry, University of California, Berkeley
1917–18	Associate Professor of Chemistry, University of California, Berkeley
1918–52	Professor of Chemistry, University of California, Berkeley
1923–26	Dean of Men, University of California, Berkeley
1939	Sc.D., University of Pennsylvania
1939–43	Dean, College of Letters and Science, University of California, Berkeley
1941–43	Chairman, Department of Chemistry, University of California, Berkeley
1949–51	Dean, College of Chemistry, University of California, Berkeley
1952	Professor Emeritus, University of California, Berkeley
1954	LL.D., University of California

PROFESSIONAL SOCIETIES

1929	Member, National Academy of Sciences
1934	President, Pacific Division, American Association for the Advancement of Science
1946	Member, Royal Society of Edinburgh
1951	Member, American Philosophical Society
1953	Honorary Life Member, Faraday Society
1955	President, American Chemical Society
1957	Honorary Life Member, American Institute of Chemists
1960	Honorary Life Member, California Academy of Sciences

NATIONAL AND OTHER SERVICE

1917–18	Lieutenant Colonel, U.S. Army, Chemical Warfare Service
1922	Distinguished Service Medal, U.S. Army
1936	Manager, U.S. Olympic Ski Team
1937–40	President, Sierra Club
1942–43	Expert Consultant, Military Planning Division, Quartermaster Corps
1942–43	Member, Chemical Referee Board of Production Research and Development, War Production Board
1943–44	Scientific Liaison Officer, Office of Scientific Research and Development, American Embassy, London
1948	King's Medal for Service in the Cause of Freedom, United Kingdom
1958–60	Member, Citizen's Advisory Committee to the Joint Education Committee of the California Legislature

AMERICAN CHEMICAL SOCIETY AWARDS

1939	New York Section, William H. Nichols Medal
1949	Maryland Section, Remsen Award
1952	Scientific Apparatus Makers Association Award for the Teaching of Chemistry
1953	Chicago Section, Willard Gibbs Medal
1961	Northeastern Section, James Flack Norris Award in Teaching of Chemistry
1962	Priestley Medal

OTHER AWARDS AND LECTURESHIPS

1936	Faculty Research Lecture, University of California, Berkeley
1944	Guthrie Lecture, Physical Society, London
1944	Walker Memorial Lecture, University of Edinburgh Chemical Society
1952	Reilly Lectures, Notre Dame University
1953	Romanes Lecture, Royal Society of Edinburgh

1953	Spiers Memorial Lecture, Faraday Society
1954	Treat B. Johnson Lectures, Yale University
1956	Bampton Lectures in America, Columbia University
1957	W. A. Noyes Lecture, University of Illinois
1963	William Procter Prize, R.E.S.A.
1965	Joseph Priestley Award, Dickinson College
1971	Gilbert Newton Lewis Memorial Lecture, University of California, Berkeley
1974	S. C. Lind Lecture, Oak Ridge National Laboratory
1978	Clark Kerr Medal for "distinguished service to higher education," University of California Academic Senate

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