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HERBERT SPENCER HARNED

1888—1969

A Biographical Memoir by

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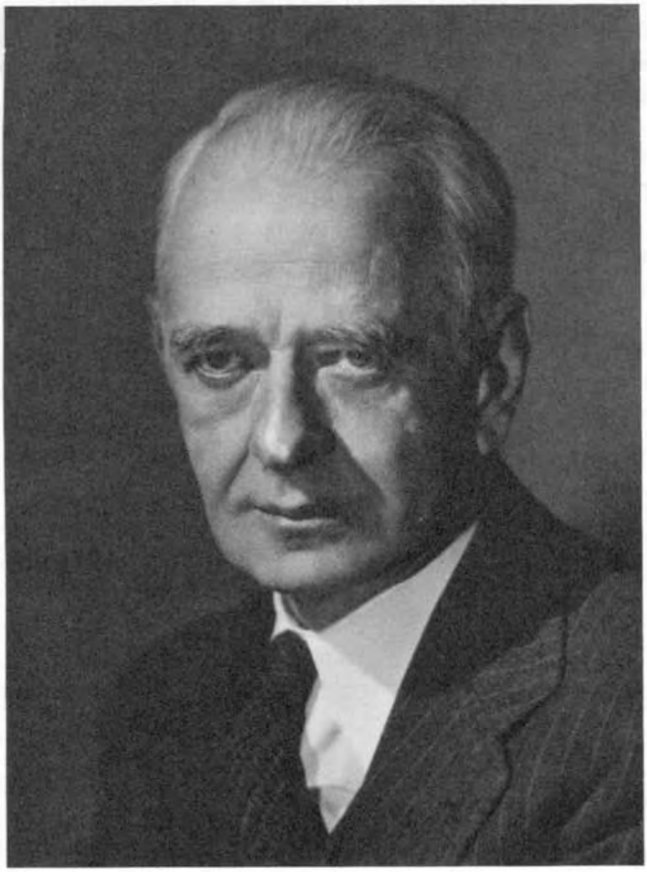
Biographical Memoir



Herbert S. Harned

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December 2, 1888—July 29, 1969

BY JULIAN M. STURTEVANT

HERBERT SPENCER HARNED started graduate work in chemistry at the University of Pennsylvania shortly after the introduction into this country of the theoretical and mathematical approach to chemical problems embodied in physical chemistry. His doctoral research was in preparative inorganic chemistry under the direction of Edgar F. Smith, but before he started this work, he spent a brief period in the laboratory of Joel H. Hildebrand. This apprenticeship with Hildebrand appears to have played a major role in steering his interests away from classical chemistry, toward the newer physics-oriented discipline.

Hildebrand, after obtaining his Ph.D. at Pennsylvania in 1906, had studied with Walther Nernst in Berlin, and after returning to Philadelphia, had instituted a program of research and instruction in physical chemistry. In Hildebrand's laboratory, Harned worked on a titrimetric method for the determination of magnesia in limestone, and a joint publication, Harned's first, resulted from this work in 1912. This research involved the use of the hydrogen electrode, with measurements of potential to an accuracy of only 10^{-2} volt. Harned was confident that measurements with this electrode could be carried to much better levels of accuracy, and an important part of his later scientific work consisted in showing that the hydrogen electrode could be utilized in a wide variety of electrochemical cells having potentials stable and reproducible to 10^{-4}, or even 10^{-5} volt. This drive toward experimental perfection and accuracy characterized Harned's long-continued studies of electrolytic solutions. His privately stated aim was to obtain thermodynamic data that could stand unchallenged for decades, and he certainly achieved this aim in abundant measure.

Herbie, as he was always known to his countless friends, was born on December 2, 1888, in Camden, New Jersey, the son of Augusta Anna Traubel Harned and Thomas Biggs Harned. Herbie was the youngest child in the family, with a sister, Anna, ten years older than he, and a brother, Thomas, six years his senior.

Herbie's mother and father, as well as other Harneds, had been very close to the poet Walt Whitman. Herbie's mother was hostess at the Whitman dinners which were held every Sunday night in the Harned home. She was the one who held the Whitman coterie together, and the hostess who sat next to the poet at his seventieth birthday party. Although Herbie was only four when Whitman died, and one of his few remembrances of Whitman was his being frightened by the poet's beard, he was always very proud of his parents' intimacy with the poet. Herbie's lifelong interest in literature was doubtless in large part due to the influence of parents and relatives who were intimate with literary figures such as Whitman.

When Herbie was five years old, the family moved to Germantown, an outlying section of Philadelphia. His father established a successful law business in downtown Philadelphia. The Germantown household was a lively place, with a succession of dinner parties and dances. Although Herbie, as the youngest member of the family, was for many years only a spectator of these events, the constant presence of guests, many of them distinguished individuals, made a deep impression on him.

Herbie was a boy of slight build, but under the tutelage of his brother Tom he developed early a knack for sports requiring sharp eyes and good coordination—to the point where he became a match for boys of larger physique, especially in tennis and cricket. The family lived close to the Germantown Cricket Club, where excellent instruction and facilities in a wide variety of sports were available. Among Herbie's playmates in Germantown were several boys, including William Tilden, who later became outstanding athletes. Herbie was fond of telling how he defeated Bill Tilden at tennis when he was fourteen years old, and Bill was eleven. At about this time, Herbie began to show a real talent for cricket, and he devoted much time to the sport until he was twenty-six. He played on various teams, in prep school and in college, and on first-class amateur teams organized at the Germantown Cricket Club. He played against numerous American teams, as well as against outstanding English, Canadian, Australian, and Bermudan teams, both in this country and abroad. Once in a match in Bermuda, he batted an entire inning, making 113 runs not out, his greatest achievement in the sport. Herbie felt that cricket taught him a great deal that carried over into his professional life. It emphasized fair play and good sportsmanship; it showed him that by hard practice with careful attention to form, he could overcome the disadvantage of his relatively small stature; and it required playing not only on the team, but also for the team.

Herbie's father became seriously ill in 1910, and never fully recovered his health, with the result that the family circumstances became very straightened. It is a good indication of the calibre of this man that although he was going heavily into debt to keep his family together, he nevertheless donated his very valuable collection of "Whitmania" to the Library of Congress. In 1914, Herbie's mother, to whom Herbie was most deeply attached, died of cancer. The home in Germantown and other properties were sold to retire debts, and the family moved to an apartment in Germantown. Since Herbie's elder brother had gone to Chicago, the responsibility of maintaining the family fell primarily on Herbie. It was this responsibility, according to his own account, that stimulated him to adopt a very serious and determined approach to his preparation for a professional life.

In the fall of 1915, Herbie met Dorothy Foltz of Chestnut Hill. A year later they became engaged, and they were married on September 8, 1917. Dorothy, who survives Herbie, proved to be the ideal wife for a young man deeply involved in establishing a scientific career, with the long hours of extra-familial activity involved in that pursuit. Herbie's father, by then nearly seventy, lived with the young couple, and a close relationship soon developed between him and his daughter-in-law.

Herbie became a captain in the Chemical Warfare Service in June 1918. After two months at the CWS establishment at the American University in Washington, during which he wrote a long report on phosgene, he was sent to France. A period of field training was followed by duty at the central research laboratory of the American Expeditionary Force near Paris. A number of lasting friendships were made with chemists stationed there. A study of the kinetics of adsorption of gases on charcoal which Harned started at this laboratory was completed after his return to the States. This was a pioneering effort in this field and has been frequently cited.

Herbie's father died in September 1921. A very close father-son relation had developed, most particularly since Herbie's return from France, and this was another keenly felt tragedy.

To return now to Harned's educational and professional careers, it is evident that he received much preschool training at home. He has particularly singled out as of incalculable value to him the instruction his mother gave him in arithmetic before he went to school at the age of nearly seven. His success in learning arithmetic gave him confidence in understanding any kind of school work. After three years at a small school run by two Misses Knight, he was sent to the Penn Charter School, an excellent Quaker preparatory school in Philadelphia, where his course was strictly classical, with no hint of science. He has stated that his teachers there were all excellent, and that after his strict training there, he found his college courses to be quite easy.

In 1905 Herbie entered the University of Pennsylvania, where in his freshman year, although he continued with his classical studies including Greek and Latin, he had his first contact with science. He took the course in chemistry and was immensely impressed by the accuracy of the measurements which fixed the composition of air and water—to the extent that he decided to pursue a career in science. By the time he became an upperclassman, his two major interests were chemistry and literature, the latter from an entirely nonprofessional point of view.

Harned graduated from college in 1909, and, as noted above, stayed on at Pennsylvania for graduate work in chemistry. Three of his teachers in graduate school he has singled out as having had an especially great influence on him. Two of these, Edgar F. Smith and Joel H. Hildebrand, have already been mentioned. The third was a philosopher, Edgar Singer. His course on the history of modern philosophy was considered by Harned to be the best seminar course he ever had, and led him to take several additional courses with Singer. His experience in these courses gave him a viewpoint which significantly motivated his later professional career:

search for the most fundamental quantity you can find and then measure it with the highest accuracy you can achieve. Some years later he discovered this quantity, the chemical potential, in the work of Josiah Willard Gibbs, and the major portion of his research career involved the accurate measurement of this quantity.

In summarizing his studies in philosophy, Harned wrote that after being tossed this way and that by the conflicting views of nineteenth century philosophical thought, there was only one mode of thought and action to which he could subscribe. This was the quantitative method of science, as exemplified in the work of Copernicus, Galileo, Kepler and Newton. There was beautifully illustrated here the importance not only of fundamental laws and theories, but also of accurate observations and measurements.

Harned obtained his Ph.D. in 1913. In that same year, Hildebrand left Pennsylvania to join the faculty at the University of California at Berkeley, and Harned was made an instructor and head of the Physical Chemistry Division at Pennsylvania. As was more frequently the case in those days than now, he was saddled with an extremely heavy load of undergraduate and graduate teaching. There were approximately forty students in his undergraduate course in physical chemistry, and since the laboratory only accommodated ten students, he had to divide the group into four sections, each of which spent many hours a week in the laboratory. All of this, combined with graduate lectures, constituted a tough assignment, carried with far less help from teaching assistants than is customary today.

It is a clear measure of the strength of Harned's dedication to research that within two years, despite these formidable teaching duties, and working entirely on his own, he was able to publish a pioneering twenty-two page paper on the precise ($\pm 10^{-4}$ volt) utilization of the hydrogen and calomel electrodes in the determination of the activities of hydrogen and hydroxide ions in neutral salt solutions. This paper, in which he showed without any doubt that the law of mass action was not applicable for calculating ionic equilibria in solutions of strong electrolytes, attracted much attention and spurred visits by chemists from other universities to his laboratory. All of this served to bolster his self confidence at the threshold of his career, and to confirm his belief that he had initiated an important program of research.

It was evident to Harned that a definitive interpretation of the results obtained in this first work was hampered by the presence of small but unknown liquid junction potentials. In the following year, 1916, he published his first paper on electrolyte activities determined using cells without liquid junction, and he continued using such cells, in a steadily expanding diversity of applications, over the next forty-odd years.

Harned wished to avoid too narrow a specialization at this period in his career. His papers on conductimetric titrations (1917 and 1918) constituted the first utilizations in this country of a conductance bridge in chemical analyses. Also in 1918, just before entering the army, he published his first paper in the field of reaction kinetics in solution. He returned briefly to reaction kinetics several times in later years, but as one may infer from remarks he made, not as frequently as he would have liked.

Harned's remaining years at Pennsylvania became increasingly productive, and by the time he left there to go to Yale University in the fall of 1928, he had published thirty-four papers. After a long period of working alone, he finally began to have collaborators, both graduate students and people of more advanced standing. In 1924 Gösta Åkerlöf came from Sweden to his laboratory on the recommendation of Svante Arrhenius. He remained in close association with

Harned for more than twenty years at Pennsylvania and Yale, although he worked essentially independently after receiving his Ph.D. In 1927 Robert A. Robinson came as a Commonwealth Fellow from Birmingham, England. He and Harned maintained throughout the rest of Harned's career a close relation that culminated in the joint publication of a monograph on multicomponent electrolyte solutions in 1968.

During these years, he made systematic measurements of the activity coefficients of strong acids and bases, in both dilute and concentrated solutions, in the presence of neutral salts. He discovered useful regularities in these systems, one of which has come to be known as Harned's rule. This states that in solutions of constant total ionic strength, the logarithm of the activity coefficient of one solute is directly proportional to the concentration of the other. This was to be a matter of continuing interest to him, and three of his last papers, published between 1959 and 1963, are concerned with the effect of temperature on such systems. It should be added that Harned was well aware that this rule is not universal, and that caution must be exercised in its application.

In this period he initiated his work on the thermodynamics of electrolytes in mixed solvents with a study of hydrochloric acid in water-ethanol mixtures. This work was greatly extended in later years, culminating in a series of papers, published from 1936 to 1939, concerning hydrochloric acid in water-dioxan mixtures containing as much as 82 weight percent dioxan (dielectric constant about 10 at 25°).

Harned has written that he regarded the year 1927–28, his last year at Pennsylvania, as the most fruitful one in his scientific life. A graduate student, John M. Harris, Åkerlöf, Robinson, and he worked jointly on four separate topics: the use of amalgam electrodes in studying the thermodynamics of solutions of electrolytes; the thermodynamics of solutions of mixtures of electrolytes at high concentrations; the first application of cells without liquid junction to determine the ionization constants of weak electrolytes; and the investigation of neutral salt effects in homogeneous catalysis. During this year, ideas and methods were developed which were later widely employed not only in his laboratory, but in many others around the world.

Although his research was going very well, Harned decided to accept an offer from Yale. He felt that this move would significantly expand his research opportunities. There was available in the Sterling Chemistry Laboratory, then only five years old, what seemed like almost unlimited space for his laboratories; he was assured of initial financial support in his research which quite surpassed that to which he was accustomed; and it seemed probable that he could expect to have a good group of graduate students as colleagues.

Immediately on arrival at Yale, Harned, in harmonious cooperation with the other physical chemists on the staff, carried through revision of the graduate program in physical chemistry. He was determined that the orientation of this program should be exclusively toward pure research, with a firm basis in the mathematical and theoretical aspects of the subject. He eliminated everything in the nature of conventional undergraduate courses from the graduate program.

Harned's arrival at Yale coincided with the start of a vigorous university-wide expansion in plant and program. He has written very approvingly of what the president, James Rowland Angell, and the graduate dean, Wilbur Cross, accomplished for the university, particularly in bringing about a remarkable upgrading of the graduate school.

I shall take the liberty of inserting here some personal comments. I went to Yale as a graduate student in chemistry in 1927, and joined the staff in 1931. I therefore had frequent contact with Herbie until his retirement in 1957. There is no doubt that, despite the general growth of the University referred to above, his own initially promising situation at Yale began to deteriorate a few years after he arrived there as a result of decreasing financial and administrative support for his own research program and for physical chemistry in general. The Chemistry Department entered a period of decline relative to chemistry departments at other institutions and to other science departments at Yale. Fortunately, a goodly stream of graduate students continued in physical chemistry, most of whom worked with Harned. It is greatly to his credit that despite the difficulties inherent in the situation, he remained a very productive scientist.

This period of relative quiescence of the Chemistry Department was enlivened by a few very important events. The first of these Harned considered to be the single most important thing he accomplished at Yale. In 1931 he received a letter from Lars Onsager stating that due to financial exigencies, he was losing his post at Brown University. Within hours Harned had arranged the offer of a Sterling Fellowship to Onsager which, most fortunately for Yale, was accepted. Needless to say, this fellowship was soon converted to a permanent position on the faculty.

In 1945, largely through Harned's efforts, Raymond M. Fuoss was persuaded to leave the central research laboratory at General Electric to join the Yale faculty. His addition to the staff made certain the preeminence of Yale in the physical chemistry of electrolytes.

In 1951, after the retirement of Arthur J. Hill as chairman of the Chemistry Department, the university was most fortunate in persuading John G. Kirkwood to come from the California Institute of Technology to serve as chairman. There ensued a period of very healthy development of chemistry at Yale which markedly improved the atmosphere for Harned's last few years before retirement.

Shortly after setting up his laboratories at Yale, Harned, in collaboration with Benton B. Owen, undertook an extension of his earlier work on cells containing weak acids and bases, and developed a highly precise method for determining the dissociation constants of such substances. This method has been widely employed by many workers in other laboratories, particularly for obtaining dissociation data for weak electrolytes and ampholytes of interest in biochemistry. With various colleagues, notably Robert W. Ehlers, the method was adapted for measurements over a wide range of temperatures. This involved as the first step a careful determination of the standard potential of the silver-silver chloride electrode over the temperature range 0–60°C. The cell used in this work, composed of a hydrogen electrode, a silver-silver chloride electrode, and a solution containing a weak acid (in the Brönsted sense) in protonated and unprotonated forms, together with an appropriate neutral salt, has come to to known as the Harned-Ehlers cell. This cell has found important additional application in the establishment of a practical pH scale by Roger G. Bates and others, and it has been shown in several of Harned's papers to be well suited for the determination of dissociation constants in mixtures of organic solvents with water.

With the potential of the silver-silver chloride electrode well established over a wide temperature range, it became possible to use precise electromotive force measurements to determine the dissociation constant of water, also over a wide temperature range, and from these data to evaluate the enthalpy of dissociation of water. The cell measurements gave the value of 13.52 kcal mol^{-1} at 25°C, whereas several concordant direct calorimetric measurements gave 13.35 kcal mol^{-1}. The difference in these values, which is well above the apparent accuracy of the two methods, remains unexplained. It is an indication of the objectivity of Harned's approach to his research that, in view of the fact that enthalpy values are obtained directly by the calorimetric method but only indirectly by differentation with respect to temperature from electromotive force data, he was prepared to accept the calorimetric value in a situation such as this.

In 1932 Harned decided to write a comprehensive treatise on electrolytes, and asked Benton Owen, his first graduate student at Yale, to be his coauthor. Harned has emphasized in his "Memoirs"* that this was a most felicitous choice; his and Owen's approaches and talents complemented each other well, and the coauthorship produced a better work than either of them could possibly have achieved individually. The preparation of this book, which came to be known as the "Opus" around the laboratory, proved to be a very difficult task, and it was not until nine years later that a lengthy manuscript was finally completed. *The Physical Chemistry of Electrolytic Solutions* was published late in 1942 in the American Chemical Society Monograph Series, and was immediately accepted as the standard treatise in the field. The "Opus" appeared in a second edition in 1950, and a third edition in 1958, with an increase in length from 612 pages to 803 pages; these new editions were obviously more than routine revisions of the original.

In January 1942, Harned was named official investigator for a project on isotope separation supported by the Office of Scientific Research and Development. His assignment was to investigate the possibility of separating uranium isotopes by an electrophoretic procedure. Most of the physical chemists in the department were drafted into this enterprise, a large area of the laboratory was walled off and blacked out to meet security requirements, and a round-the-clock seven-days-a-week program was instituted with a large number of moving boundary cells under constant surveillance. Unfortunately, it

* Unpublished three-volume set.

eventually turned out that this method was impracticable. The group then investigated one or two other methods of separation which also turned out to be unsuccessful. The final task assigned the group was to devise a procedure by which very pure uranyl nitrate could be obtained from ore from the Belgian Congo. In this effort, success was achieved and the process was carried to pilot plant scale. All of this work was carried out under circumstances involving heavier than usual teaching loads because of the presence on campus of a Navy V12 educational program, and the continuation of graduate instruction and research in physical chemistry.

Shortly after the conclusion of this war work, Harned developed an ingenious conductimetric method for the determination of the diffusion coefficients of electrolytes. The first report on this method was published in 1945; from then until 1958 some nineteen papers detailed its broad application. This method gave sufficiently precise results to lead to the first quantitative experimental verification of the limiting Nernst equation relating diffusion coefficients to ionic conductances. Of even greater importance, striking support for the Onsager-Fuoss theory of conductivity was obtained, in particular with respect to the magnitude and sign of the electrophoretic term involved in this treatment.

Harned was closely associated with several important research efforts which do not appear in publications carrying his name. He persuaded Andrew Patterson to try to verify Onsager's theory of the Wien effect. In a classic experiment, Patterson and J. A. Gledhill established the validity of the theory, which relates the change in conductivity of electrolyte solutions to changing field strengths. Their method utilized pulsed fields, and in the case of weak electrolytes permitted the measurement of the rate of recombination of ions at the termination of the pulses, thus initiating the study of chemical reaction rates on a hitherto inaccessible time scale.

Another example of his wide influence is the following. L. G. Gosting was interested in investigating the equivalence of the Onsager coefficients L_{ij} and L_{ji} in multicomponent diffusion. Harned pointed out to Gosting that the information concerning the variation of ionic activity coefficients that is needed in obtaining the Onsager coefficients from diffusion coefficients is readily available on the basis of Harned's rule if the diffusion experiments are carried out at constant total molarity. Gosting's elegant work was the basis for the definitive test of the Onsager principle in diffusive processes.

From time to time during his career, Harned published review papers which summarized progress in fields to which he had contributed and discussed the the significance of his results and those of other workers. This very useful type of publication saw its greatest development in the "Opus" mentioned earlier.

In the course of his thesis work at Pennsylvania, Harned prepared the mixed chloride of niobium $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$ and showed that the complex ion $(Nb_6Cl_{12})^{++}$ carries two positive charges. This synthesis was published in 1913. Many years later, Linus Pauling saw this publication and became interested in the structure of the ion; he also thought that it might be useful as a heavy metal replacement in a protein single crystal for X-ray crystallographic study. He and his colleagues apparently had difficulty in preparing the compound in amounts large enough for the structural and protein studies, and in 1956 Pauling invited Harned to come to the California Institute of Technology to repeat the synthesis. At this time, Harned found that by using elevated temperatures and cadmium in place of sodium amalgam as reducing agent he could increase the yield from 6 percent to 60 percent.

Harned served as a consultant at the Oak Ridge National Laboratory for the period from 1950 to 1965. He felt that his long association with that laboratory was very profitable to him as well as to the people there with whom he consulted.

Yale had at that time a policy of mandatory retirement at the end of the academic year during which one reaches the age of sixty-eight, and therefore Harned had to retire on June 30, 1957. He published sixteen papers after that, including one giving a second important Harned's rule concerning activity coefficients of electrolytes in mixed solvents. He also published a monograph (with R. A. Robinson), and remained active in a consultative capacity not only at Oak Ridge, as mentioned above, but also with an Atomic Energy Commission contract at Yale.

Professor Harned's long and active life came to an end on July 29, 1969, at the age of nearly eighty-one. He is survived by his wife Dorothy and three daughters and a son.

I AM GREATLY INDEBTED to Mrs. Herbert S. Harned (Dorothy) for the opportunity to study various documents of Professor Harned's, in particular his three-volume handwritten "Memoirs of H. S. Harned." The task of preparing this biographical sketch was immeasurably facilitated by the availability of these memoirs.

Professor R. A. Robinson, of the University of Newcastle upon Tyne, delivered the opening address at a session dedicated to Harned at a meeting of the American Chemical Society in Chicago in 1970. Professor Robinson very kindly made available to me the manuscript of this unpublished address, and I have made much use of it.

I have received important help in the preparation of this sketch from several colleagues, including Philip A. Lyons, Andrew Patterson and Arthur M. Ross.

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