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Louis Plack Hammett
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LOUIS P. HAMMETT WAS one of the founders of physical-organic chemistry, and a major contributor to it. Together with Arthur Lapworth and Christopher Ingold he created a new branch of chemistry, a new discipline. The ideas and principles of physical-organic chemistry changed the world's teaching and practice of chemistry and, in particular, changed the way synthetic organic chemistry is performed, with enormous practical consequences.

All important practitioners of synthesis today make extensive use of mechanisms of reactions and the stereochemistry of reactions. The understanding of mechanism and stereochemistry was strongly advanced not only by Hammett's research but especially by his famous textbook *Physical-Organic Chemistry*.[1] The concepts on which chemists today depend include an acidity function that Hammett invented and a famous equation named for him that allows a quantitative understanding of chemical reactivity.

PERSONAL

Louis Hammett was born in 1894 while his parents were visiting Wilmington, Delaware, so that this most quintessential New Englander managed to begin his life south of the Mason-Dixon line. He grew up, however, in Portland, Maine. His father, a native New Englander whom Hammett described as "intellectually brilliant," was educated as an engineer and had an outstanding record at both Harvard and MIT. From his father and a maternal uncle, Hammett learned to use and love tools and drawing instruments. The Portland schools were hardly superior, as illustrated by the fact that the primary function of the chemistry instructor was that of a basketball coach.[2] Hammett had no talent for sports, but, perhaps despite the teacher, he fell in love with laboratory work, and the school did drill him well in German, English composition, and elementary math.

Following his father to Harvard, Hammett studied analytical chemistry under Gregory Baxter and organic chemistry under E. P. Kohler, whose "intense enthusiasm for unraveling the mysterious principles which controlled the . . . practical operations of the

synthetic organic chemist"[2] put Hammett on the path he followed for the rest of his life. At Harvard he met James Bryant Conant, who was a graduate student and teaching assistant while Hammett was an undergraduate and who also contributed to physical-organic chemistry. Hammett graduated summa cum laude, won a Sheldon Traveling Fellowship, and in 1916 in the middle of World War I went to Zurich to work with Hermann Staudinger.

On his return to the United States in 1917 he expected to be inducted into the Army; he found instead that he was assigned to laboratory work and at the age of twenty-three was put in charge of a group investigating paints and varnishes and especially "dopes" for the fabrics of airplane wings. Hammett wrote, "We did some respectable developmental research . . . none of which ever got published." Research that Hammett would describe as "respectable" must have been very good indeed.

Shortly after the end of World War I, Louis Hammett had the remarkable good judgment and good fortune to marry Janet Marriner, also from Portland. They had a long and happy married life, raised two successful children, and were blessed with five grandchildren. Janet also entertained Louis's graduate students and postdoctorals, and kept him from becoming too intense. Louis listed "good company" as his leisure interest, and so it was. Janet reported on one occasion that Louis had been born two drinks under par, and although sometimes he did seem a bit formal, a bit stiff, he was always good company, with or without a drink, and Janet was too.

SCIENCE

Hammett did not begin his spectacular career immediately after the war, but started with a mundane industrial job. In the spring of 1920, however, he accepted an instructorship at Columbia, where he taught and simultaneously carried out research on the hydrogen electrode under the supervision of Hal Beans. He wrote that he could not have managed financially without a subsidy from his father-in-law, a situation that anticipated that of some graduate students today. When he received his Ph.D. in 1922 he was not "besieged with offers of highly remunerative positions." On the other hand, his work at Columbia had progressed nicely. He was especially influenced by four men, two he never met and two he met only much later: A. Hantzsch, A. Werner, G. N. Lewis, and J. N. Bronsted. Appropriately, he noted too that you did not have to work as a postdoctoral in someone's lab to be influenced by that person; thousands have been strongly influenced by Hammett, usually because of *Physical-Organic Chemistry*, even though they never met the man himself.

THE ACIDITY FUNCTION

Hammett's first great contribution to chemistry was the concept of superacidity and his acidity function. In 1928 he suggested that HCl is a stronger acid in solution in benzene,[3] where it cannot ionize, than in water, where it is fully ionized. Today we accept as obvious the leveling effect of water and similar basic solvents on acidity, but when Hammett advanced this idea it was considered paradoxical at best. Incidentally, James Bryant Conant was also interested in superacid solutions, however he was less successful than Hammett in developing the concept.

The chemistry of concentrated sulfuric acid is startlingly different from that of more dilute acid. Hammett grasped the essential fact that concentrated sulfuric acid and similar acids have acidities out of all proportion to their concentrations. With A. H. Deyrup he set up an acidity scale[4] based on the indicator properties of aromatic amines, a scale that measures 100% sulfuric acid as 10^{10} times as strong (that is, ten billion times as strong) as 10% acid, and then showed that this acidity scale was relevant to chemistry.

The measurement scheme of Hammett and Deyrup was as follows. They found an indicator (p-nitroaniline) that functioned in dilute aqueous acid, where the ordinary pH scale is valid, and determined its pK. They then defined an acidity function, H_o, as $H_o = pK + \log (B)/(BH^+)$, where (B) and (BH^+) are the concentrations, not the activities, of the basic indicator (here p-nitroaniline) and its conjugate acid. In solutions where the acidity was too great to allow a meaningful determination of pH, the ratio of (B) to (BH^+) could still be determined colorimetrically, and so define H_o.

Of course, this scheme could not be carried very far, because when the ratio of (B) to (BH^+) becomes especially small, it becomes experimentally impossible to measure it accurately. But if the ratio of $(B)/(BH^+)$ is first obtained when it is, say, 10 to 1, and then obtained again in a more acidic solution where it is, say 1 to 10, an investigator will have a solution 100 times, or 2 log units, more acidic, as defined by H_o. One can then try another, less basic coloro-metric indicator, one that is perhaps only 1/10 protonated in this second, more acidic solution, and from this fact and the H_o of the solution determine its pK. Now in still stronger acid, one can determine H_o and then determine the pK of a third indicator and so on, leapfrogging across the acidity scale. It was in this way that Hammett showed that his new acidity function measured 100% sulfuric acid as stronger than 10% acid by a factor of 10^{10}.

It behaves that way in chemical synthesis. With Martin Paul, Hammett pointed out the relationship between his acidity function and the rates of acid-catalyzed reactions.[5] Similar functions based on Hammett's principles even provided other acidity scales, including one that changes 3000-fold between 80% and 90% sulfuric acid, corresponding to the chemical fact that the nitration of nitrobenzene proceeds 3000 times as fast in 90% as in 80% sulfuric acid.[6] One needs such acidity scales to understand the enormous change in rate of reaction that occurs with relatively small changes in the concentration of sulfuric acid. Similar scales have been extended beyond 100% sulfuric acid into true superacidic media, such as fuming sulfuric acid, or solutions of HF in BF_3. George Olah won the 1995 Nobel Prize in chemistry for his demonstration of the catalytic effects of such superacid

solutions.[7]

Finally, R. P. Bell showed that Hammett's acidity function really measures the activity of water in superacid solutions. Water binds strongly to protons and reduces their activity. With this work the concept of superacidity and the measurement of superacidity become readily comprehensible.[8]

Hammett and others also expanded the concept of basicity to superbasic solutions and invented an H_ function to describe them.[9]

PROTONATION OF CARBONYL GROUPS

The protonation of a carbonyl group has been postulated as the first step in the mechanisms of many acid-catalyzed reactions. Such mechanisms can be supported by measuring the extent of protonation of aldehydes, ketones, acids, esters, and amides. The ultraviolet spectrum of a carbonyl group markedly changes when it is protonated, and the extent of protonation can be determined from the ultraviolet spectra of solutions of carbonyl compounds in strong sulfuric acid.[10] In fact, carbonyl compounds can be used as a set of Hammett indicators, different from but parallel to the aromatic amines used to set up the H_O function.

This work is experimentally easy today with electronic spectrophotometers, but Hammett and Flexser determined the pK of acetophenone and benzoic acid as bases before the Beckman DU spectrophotometer or any such instrument had been invented. Flexser did his ultraviolet spectroscopy photographically, using a grating spectrophotometer. The amount of work involved was considerable, but an important concept was established.

THE HAMMETT EQUATION

Hammett's second major contribution to physical-organic chemistry concerned his equation, commonly called the Hammett equation. This concerns the correlation of equilibria and rates for reactions of substituted aromatic compounds. Chemists had long realized that reactions with large negative free energies may nevertheless be extremely slow. For example, the equilibrium position for Egyptian sarcophagi and air is practically completely to the side of carbon dioxide and water, yet for millennia no detectable reaction has occurred with the samples now in our museums. Nevertheless, Hammett showed how, within certain limited sets of reactions, rates do follow equilibria. The standard to which he referred other reactions is the ionization of substituted benzoic acids, and he defined substituent constants, σ, by the equation:

$$\sigma = \log K_S/K_O$$

where σ is the constant for the substituent s, K_S is the ionization constant for the substituted benzoic acid, and K_O is the ionization constant for benzoic acid itself. He then demonstrated that the equation:

$$\log k_S/k_O = \text{}$$

holds with remarkable fidelity for the rate of a wide selection of reactions of meta- and para-substituted aromatic compounds, where a single constant ρ is adequate to define each reaction and the substituent constants are those defined above. The fact that the equation does not hold for ortho-substituted aromatic compounds presumably means that here steric effects complicate what are otherwise resonance and electrostatic ones.

The Hammett equation is an expansion--a large expansion--of the Brønsted equation. The latter relates acid and base catalysis to acid-ionization constants; the Hammett equation interrelates all sorts of reactions--saponification of esters, nucleophilic displacement reactions, bromination of substituted acetophenones, solvolysis of benzoyl chlorides, and many more.

PHYSICAL-ORGANIC CHEMISTRY

In 1940 Hammett published his revolutionary text *Physical-Organic Chemistry*. The book established the field and proved much more important than Christopher Ingold's *Structure and Mechanism in Organic Chemistry*.[11] The experimental underpinnings of those reaction mechanisms that were then known were clearly set out and the principles for the determination of mechanism were established. The large community of physical-organic chemists throughout the world--especially in the United States--that thrived over the next decade or two based its work largely on Hammett's *Physical-Organic Chemistry*. In 1970 he published a second, enlarged edition. But, necessarily, the second edition points out the difficulties as well as the triumphs of the acidity function and exceptions to general rules, and somehow had much less influence than the first. The first edition of Hammett's book stands as one of the great textbooks in chemistry, at least comparable in its impact to *Thermodynamics* by Lewis and Randall[12] or the first edition of *Biochemistry* by Fruton and Simmonds.[13]

In the second edition of his famous book Hammett recognized that "It would be . . . hypocritical humility for me to pretend that I

do not know that [the equation] is commonly called the Hammett equation, or that I am not grateful to those who have honored me in this way . . . . "

THE EXPLOSIVES RESEARCH LABORATORY

The Second World War had started by 1940, and Hammett's efforts were diverted from pure chemistry to national service. The National Defense Research Committee established an Explosives Research Laboratory outside Pittsburgh at Bruceton, Pennsylvania, on the site of the Bureau of Mines with George Kistiakowsky as director and Hammett as associate director. Later in the war when Kistiakowsky moved to Los Alamos, Hammett took on the job of director. The Bruceton lab was remarkably successful even though one industrial chemist predicted that a group of college professors would blow their own heads off and one admiral announced that he already knew what there was to know about explosives. The lab made several important inventions that were useful in the war and after, and it did not sustain a serious accident.

In particular, Kistiakowsky and his lieutenants developed the explosive lenses that effected the implosion needed for the plutonium bomb. Hammett, Frank Long, and their coworkers invented and developed a jet-assisted takeoff system based on a new ammonium perchlorate propellant that was used to help overloaded planes to get off the runway with their bombs and fuel. John Kincaid invented a method of making large "grains" of rocket propellant--grains of thousands of pounds--that permitted the manufacture of the solid rockets that propelled some of the ICBMs, and others at the lab made several minor inventions as well.

The laboratory under Hammett was friendly and productive, perhaps friendly because it was productive and vice-versa. In any event, under Hammett's management it functioned more than efficiently; it functioned imaginatively. The civil service employees of the Bureau of Mines were left behind on the property when the lab was turned over to Kistiakowsky, Hammett, and their new colleagues; and the civil service was responsible for the management of the property. In some instances they didn't seem fully aware that the lab was instituted to help with the progress of World War II. They certainly taught many of the academics some extraordinary and unwelcome lessons about the civil service. Nevertheless, the laboratory was unquestionably a huge success and that success was due in considerable part to Hammett's effective management.

THE POSTWAR YEARS

At the conclusion of the war Hammett returned to Columbia. He wrote[14] "Emotionally exhausted by my wartime experiences, I returned to a university which welcomed me with less than open arms." Joseph Mayer and Harold Urey, two of the superstars of the chemistry faculty at Columbia, had been lured away to the University of Chicago, and Hammett was not appointed chairman until 1951. He felt hurt and said so in a handwritten note filed in the archives of the National Academy of Sciences. In 1951, when he was finally appointed chairman, he supervised the buildup of the Chemistry Department at Columbia and in particular oversaw the professorial appointments of Gilbert Stork, Ronald Breslow, and Cheves Walling. Hammett took emeritus status in 1961 and in 1973 he retired to the Quaker community of Medford Leas. He died there in 1986 at the age of ninety-two.

Although Hammett's postwar years were not entirely happy ones, he received a number of signal honors during that period. He was of course elected to the National Academy of Sciences. He refused to stand for election for president of the American Chemical Society, but served as its chairman of the board. He received the National Medal of Science from President Johnson and a number of other significant honors, including the Chandler Medal, the James Flack Norris Award (twice), the Willard Gibbs Medal, and the Lewis Medal. He was elected an honorary member of the Chemical Society (British) and in 1962 received an honorary degree from Columbia. He served as visiting professor at several universities. These are numerous and splendid distinctions, but his real honor is the esteem in which he is held by his colleagues throughout the world, who rightly regard him as a true pioneer in physical-organic chemistry. Perhaps he sensed at least part of that great esteem.

NOTES

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