THE RECEPTION OF HYDROGEN BONDING BY THE CHEMICAL COMMUNITY: 1920-1937

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It is well known that hydrogen bonding as a generalized concept was first proposed in the literature by Wendell Latimer and Worth Rodebush in 1920 (1). A footnote in their paper credits "Mr. Huggins of this laboratory [who], in some work as yet unpublished, has used the idea of a hydrogen kernel held between two atoms as a theory in regard to certain organic compounds". At the time Wendell Latimer was a lecturer in G. N. Lewis' chemistry department at the University of California at Berkeley, Worth Rodebush, a postdoctoral fellow, and Maurice Huggins, a first-year graduate student, working on his masters degree. The "unpublished work" referred to was actually done a year earlier when Huggins was an undergraduate. He has given several accounts of this work; the most complete and definitive of which appeared in 1980 (2). He begins by describing his reaction to advanced courses in organic and inorganic chemistry taught by Professors T. Dale Stewart and William C. Bray. In these courses the students were introduced to the Lewis theory of chemical bonding (2):

Prof. Stewart and Prof. Bray also discussed some of the unsolved problems of chemistry. These problems intrigued me. Could some of them be solved by the application of the Lewis theory, perhaps with modifications? I thought a lot and made crude notes about problem solutions that seemed reasonable to me ... In early May of 1919, as graduation approached, I became worried ... I had not written the term paper that Prof. Bray required for his course and time was getting short ... I went to Prof. Bray and asked him if he would accept my crude notes, with a title and my name added. He did so.

Dr. Huggins, in 1978, was kind enough to send me a photocopy of parts of these notes (3). The copy sent me consists of pages numbered 1-7 and 15-17, with page 17 obviously not the end of the document. The clearest indication of what would be called hydrogen bonding today is a diagram on page 17 showing a hydrogen fluoride dimer, with the four atoms arranged in a square, each hydrogen bonded to both fluorines by electron pair bonds. On page 6 an explanation of the keto-enol tautomerism of acetoacetic ester postulates a transition state in which hydrogen is bonded simultaneously by electron pair bonds to a carbon atom and an oxygen atom. There is no indication given that the concept is generally applicable nor is any name given to the idea.

For that matter, Latimer and Rodebush themselves do not actually use the terms "hydrogen bond" or "hydrogen bonding" in their paper. The closest they come is to describe it as "the hydrogen nucleus held between two octets constitutes a weak 'bond'." The first use of the term in the literature was in Lewis' book, Valence and the Structure of Atoms and Molecules, in which the section headed "Bivalent Hydrogen" begins (4):

It seems to me that the most important addition to my theory of valence lies in the suggestion of what has become known as the hydrogen bond.

It is hardly surprising that the idea of hydrogen bonding should have occurred independently to several young chemists...
at Berkeley at that time. Lewis had been, since 1912, building a strong department and, in doing so, attracted scores of bright young chemists as faculty members and doctoral students (Rodebush and Latimer had obtained doctorates from Berkeley in 1917 and 1919 respectively; Huggins would receive his in 1922). His new ideas on bonding must have been exciting to these young men. The idea of hydrogen bonding would appear to have been a natural outgrowth of the Lewis theory. In hindsight it is somewhat surprising that the idea of the hydrogen bond met with resistance from the older faculty whose teaching had inspired it. Huggins recounts how Prof. Bray commented on his paper (2):

Huggins, there are several interesting ideas in this paper, but there is one you'll never get chemists to believe: the idea that a hydrogen atom can be bonded to two other atoms at the same time.

Latimer has stated that Lewis' first response to the Latimer-Rodebush paper was to suggest that the section on hydrogen bonding be deleted (5).

Accounts of the history of hydrogen bonding in monographs and textbooks leave the impression that the concept was immediately embraced by the chemical community. A statement of George Pimentel and Aubrey McClellan is typical (6):

From these early beginnings welled a rising number of studies of H-bonding. As the common occurrence and importance of this weak bond has become apparent, the volume of work using the concept of a 'shared' proton has grown tremendously and at an increasing rate.

Actually the Latimer-Rodebush paper was almost completely ignored for ten years.

Before discussing the complex history of how the concept came finally to be accepted, some preliminary distinctions must be made. Latimer and Rodebush introduced the concept of hydrogen bonding to explain certain phenomena which were already well known: the anomalous boiling point of water (7), the vapor phase density of hydrogen fluoride (8), the anomalous freezing points (9) and vapor density curves (10) of various liquid mixtures, the basicity constants of ammonia and the substituted amines (11). Certain other phenomena now associated with hydrogen bonding were discovered soon after: the crystal structures of ice (12) and the HF²⁻ ion (13,14); and the change in stretching frequencies of the -OH bond (15).

Chemists tended to adopt four attitudes toward these "anomalies": some just determined, as precisely as possible, the physical constants or structural parameters and did not worry about their meaning; some attributed these anomalies to "association", without speculating on the nature of the forces causing the association; some proposed theories about the nature of these forces different from the Latimer-Rodebush concept of hydrogen bonding; and finally, some accepted the Latimer-Rodebush picture, often at second or third hand, although there was little unanimity as to the name to be given the concept. The number of chemists adopting this last attitude was small during the 1920's but became greater during the early and middle 1930's. By 1937 the concept was so widely accepted that it could be mentioned without giving a citation, and the term "hydrogen bond" had also become by far the most common name. In the remainder of this paper I hope to trace the web of influences by which this general acceptance was achieved, using biographical data, citation analysis, and preferred terminology as tools.

The first citation of the Latimer-Rodebush paper in connection with hydrogen bonding was by Irving Langmuir of the General Electric Company in 1921 (16). Langmuir had been instrumental in calling the attention of the chemical community to Lewis' ideas about chemical bonding (17). Rather than accepting the Latimer-Rodebush proposal, Langmuir put forth a competing idea (16):

In double molecules such as H₂O₂ (in ice), H₂F₂, and in compounds such as KHF₂, etc., it seems that the hydrogen nuclei instead of forming duplets with electrons in the same atom, form duplets in which the two electrons are in different atoms. The hydrogen nucleus itself thus acts as a bond in such a case. Latimer and Rodebush have made a somewhat similar suggestion in regard to hydrogen nuclei acting as bonds. They consider that the hydrogen nucleus acts on two pairs of electrons: one pair in each of the two atoms... Since the first layer of electrons in all atoms contains only two electrons, it seems probable that the hydrogen in this case also holds only two electrons and that these form the definite stable group which we have termed the duplet.

This idea is similar to the "liaison monoelectronique" pro-
posed, probably independently, by Jean Perrin in 1927 (18) and maintained by some French spectroscopists till 1937.

Maurice Huggins published two papers in 1922 (19) in which he expanded on the ideas presented in his 1919 term paper. Reference to the Latimer-Rodebush paper is made in the second paper, but more in the context of their applications of Lewis theory than specifically to hydrogen bonding. One diagram, the same in both papers, shows a hydrogen atom bonded to two other atoms (in NH₂OH). In both papers this form of bonding by hydrogen is not given any special name but is included, along with examples taken from boron and transition metal chemistry, as an example of what we would now call the coordinate-covalent bond. In the second paper, Huggins gave his first indication that he was proposing this form of bonding by hydrogen as a general concept (19).

It is also this kind of reaction which often produces polymerization and the formation of molecular aggregates (e.g., of H₂O).

Only two research groups, both English, made use of the concept of hydrogen bonding in the early 1920's. The first, that of Thomas Lowry of Cambridge University, began publishing on this subject in 1923 (20). The initial paper from this group is a survey of the evidence for hydrogen bonding. It is much more extensive than that given in the Latimer-Rodebush paper, which is cited, along with Lewis' then forthcoming book. Lowry had corresponded with Lewis in connection with an invitation for the latter to speak at a Faraday Society Symposium in June 1923 on "The Electronic Theory of Valence" (17) and presumably was shown the page proofs on this occasion. The term used to describe this concept (as will be true of future papers by this group during the 1920's) is "coordinated hydrogen".

The second group, that of Nevil Sidgwick at Oxford, published their first paper in 1924 (21). In this paper the "coordination of hydrogen" is used to explain the "abnormal" solubilities and boiling points of certain benzene derivatives. The difference in properties between groups capable of being hydrogen bonded ortho to each other, rather than meta or para, is explained in terms of "chelation". This is what would today be called intramolecular hydrogen bonding. Reference is given to the Latimer-Rodebush paper, Lewis' book, and the earlier paper by Lowry.

In the meantime, the X-ray determination of the crystal structures of ice (12), NaH₂F₁ (13), and KHF₂ (14) had been published. Huggins has claimed that (3):

Further evidence [for hydrogen bonding] came from the structure of ice. I predicted that hydrogen bridges would force ice to have a structure in which each oxygen is surrounded tetrahedrally by four others, with the hydrogens on the oxygen-oxygen center lines. In 1922, William H. Bragg showed that oxygen atoms are indeed in such an arrangement.

No such prediction appears in any of Huggins' early published papers, and if it appeared in his term paper, it had to be in a section I have not seen. Bragg himself considered that his work demonstrated that ice was an ionic structure with O²⁺ surrounded tetrahedrally by H⁺ ions. Friedrich Rinne and coworkers and Richard Bozorth established that the H₂F⁺ ion in NaH₂F₁ and KHF₂ was linear with the hydrogen atom between two fluorine atoms, but no speculation was attempted as to why these atoms adopted such a peculiar arrangement.

The most commonly accepted theory of the structure of water during the 1920's was that of Henry Edward Armstrong. An account of the current version of his theory can be seen in one of his papers from 1923 (22):

Water is a complex mixture, in proportions which vary with the temperature, of the fundamental molecule, hydron (OH₂), with molecules of various polymorphs, perhaps:

As can be seen from the diagrams, the association between molecules is assumed to be by way of O-O bonds.

Armstrong was born in 1848 and retired from teaching at Imperial College of Science and Technology in London in 1911. From 1890 till a few years before his death in 1937, he was considered one of the leading lights of British chemistry. He was noted for his love of controversy and ridiculed the theories of Arrhenius, van't Hoff and Ostwald for what he felt was their lack of consideration for the uniqueness of water (23). Naturally, hydrogen bonding did not escape his scorn. In a letter to Nature in 1926 Armstrong wrote (24):

I notice that in the lecture ... which Prof. Lowry gave recently in Paris ... he brought forward certain freak formulae for tartaric acid, in which
hydrogen figures as a bigamist... I may say he but follows the loose example set by certain USAeans, especially one E. N. Lewis [sic] a Californian thermodynamics, who has chosen to disregard the fundamental canons of chemistry - for no obvious reason other than that of indulging in premature speculation upon electrons as the cause of valency.

What may have made Armstrong so vehement was that Lowry had been one of his own students (17).

In 1927, Harris Chadwell, in his review of the molecular structure of water (7), under the heading of "Recent Theories", discussed various modifications of Armstrong's theory. The Latimer-Rodebush theory is mentioned, incongruously, under the heading "X-ray Analysis of Liquid Water". Incongruously, since when Latimer and Rodebush wrote, there were no X-ray data, and Chadwell does not discuss any X-ray evidence for their approach. The paragraph appears to be an afterthought, inserted at the last minute, possibly to meet a referee's comments.

The lecture by Lowry to which Armstrong referred had been recently published in Nature (25). The work described had also appeared in an earlier preliminary communication (26). In this work Lowry attributes anomalies in the optical rotary dispersion of tartaric acid to what now would be called intramolecular hydrogen bonding. The citation is to Lewis' book and attributes to Lewis the term "bivalent hydrogen" for the phenomenon. Intramolecular hydrogen bonding is also invoked about the same time by Sidgwick (27), under the name "chelation" to account for anomalous solubility data for \( \beta \)-keto-esters and \( \beta \)-diketones.

In 1927, Sidgwick published his influential book, The Electronic Theory of Valency (28), which did perhaps more than even Lewis' book to spread the new ideas about bonding to the chemical community. In it, Sidgwick presented what is essentially Lewis' theory, but developed more systematically and with a greater wealth of examples. He also had the advantage, as an experimental organic chemist, of being able to speak more directly to that audience than did Lewis. In this book, Sidgwick used the term "coordinated hydrogen" for what is now called intermolecular hydrogen bonding and "chelation" for intramolecular hydrogen bonding. The following shows how he represented coordinated hydrogen in water:

As a result of this work, Sidgwick's book (or papers from his group) became the most likely citation given for hydrogen bonding, and the most used term for the phenomenon became "coordinated hydrogen". This is particularly true of British chemists, but also, to a lesser degree, for Americans. For example, John Williams, of the University of Wisconsin, in a 1928 discussion of the relationship between molecular polariza-

zation and association, contrasted the "chemical" theory of Sidgwick, in which association consists of the formation of coordinate linkages, with the "physical" theory of Debye, in which association is due to the mutual interaction of dipoles. Williams concluded that the "physical" approach, while promising, is not able to account satisfactorily for all the data (29).

In 1932, James Speakman, of Sheffield University (30), cited a paper by Sidgwick's group in pointing out that the paracrystalline liquid hydrogen fluoride supports the assumption that it is a liquid in which association results from the coordination of hydrogen. In 1934, H. M. Glass, W. M. Madgin, and F. Hunter, of the University of Durham, cited Sidgwick's book in arguing that the "coordination of hydrogen" accounts for the heat of dissociation of quinoline o-chlorophenoxide in benzene solution (31).

Despite the influence of Sidgwick's book, explicit references to hydrogen bonding, whether under the name of coordinated hydrogen or any other name, are rather infrequent during the late 1920's and the early 1930's. Citing all the papers during this period in which the expected mention of the hydrogen bonding concept was absent, would expand the list of references to unmanageable size. Most of the papers previous to 1934, and a good proportion even for the period 1934-7 listed in the bibliography in Pimentel and McClellan's book (32) are of this character. It will suffice to mention the redetermination of the crystal structure of ice by William Barnes (33), in which he came to the conclusion that "The structure for ice proposed in this paper is practically identical with those of Dennison and Sir William Bragg."

In 1925, Sterling Hendricks and Linus Pauling determined the structures of \( \text{Na}_2\text{CO}_3 \), \( \text{KN}_2\text{CO}_3 \), and \( \text{KNCO} \) by X-ray diffraction (34). In the discussion they pointed out that the linear structure of the triminotride and cyanate ions is the same as that of the acid fluoride ion, \( \text{HF}_2^- \). For this ion they proposed the structure:

\[ \text{H} : \text{F} : \text{F} : \text{H} \]

No reference is made to the Latimer-Rodebush paper in connection with this structure, nor to Lewis' book, but the structure clearly indicates hydrogen bonding.

Pauling had received his Ph.D. degree from the California Institute of Technology (Caltech) in 1925, and when this paper was written he was a National Research fellow. According to Pauling (35):

I consider Sterling Hendricks to have been my first graduate student. He started his graduate work with Roscoe Dickinson, who then in 1924 went to Europe, leaving Sterling Hendricks in my care. We wrote some interesting papers together.

Not long after Pauling himself went to Europe, where he studied with Sommerfeld and learned about the new developments in quantum theory (36).

In 1928, Pauling wrote the first paper (36) in a series that would lead eventually to his book, The Nature of the Chemical Bond. In this paper we see the first use in the literature of the
term “hydrogen bond” since it was used in Lewis’ book. Pauling, however, had changed his views about the nature of the hydrogen bond since the appearance of the paper with Hendricks, apparently as a consequence of his exposure to quantum theory:

Calculated and observed values of the hydrogen-halogen distances in the hydrogen halides are in agreement only for HF, from which it can be concluded that HF is a polar compound formed from H⁺ and F⁻ and that, as London had previously stated, HCl, HBr, and HI are probably non-polar. The conclusion regarding HF is further supported by the existence of the hydrogen bond. The structure [\(\text{F}^-\text{H}^-\text{F}^-\)] for the acid fluoride ion and a similar one for \(\text{H}_2\text{F}_6\) are ruled out by Pauli’s principle, if the shared pairs are of London’s type. The ionic structure [\(\text{F}^-\text{H}^-\text{F}^-\)], in which the proton holds the two fluoride ions together by electrostatic forces (including polarization) is, of course, allowed. This conception of the hydrogen bond explains the observation that only atoms of high electron affinity (fluorine, oxygen, and nitrogen) form such bonds.

No reference is given to any earlier workers for the concept of the hydrogen bond.

An alternative candidate for the first mention in print of the term hydrogen bond since Lewis’ book is a volume by Arthur Buswell of the University of Illinois entitled *The Chemistry of Water and Sewage Treatment* (37):

Latimer and Rodebush in an extension of the Lewis theory of valence have made a plausible suggestion as to the way in which these molecular aggregates may be built up. They cite several instances in which a hydrogen nucleus act as a valence bond by sharing two pairs of electrons with different atoms. Their suggestion would be to consider dihydrol as formed thus:

\[
\begin{array}{c}
\text{H} \\
\text{H}\cdot\text{O}\cdot\text{H} \\
\text{H}\cdot\text{O}\cdot\text{H}
\end{array}
\]

If we consider the four electron pairs of the oxygen shell disposed toward the corners of a tetrahedron, it would appear that a double or triple ‘hydrogen bond’ might exist... It is hoped that this theory of the constitution of water will be subjected to experimental investigation.

Buswell had obtained a Ph.D. from Columbia University in 1917 and since 1920 held joint appointments as Professor of Sanitary Chemistry at the University of Illinois and as Chief of the State of Illinois Water Survey. At Illinois he was a colleague of Worth Rodebush, with whom he would later collaborate on some papers on hydrogen bonding. It is doubtful that Buswell’s book exerted much influence on academic chemists; I have found only one citation to it with reference to hydrogen bonding. The citation is from a review article by Rodebush.

A more complete presentation of Pauling’s views on the nature of the chemical bond was published in 1931 (38). The discussion of the hydrogen bond was essentially the same as in the 1928 paper, with the added point that the presence of OHO groups in many crystal structures indicates hydrogen bonding involving [\(\text{O}^-\text{H}^+\text{O}^-\)]. This strictly electrostatic view of the hydrogen bond was held by Pauling for several years and does not appear to have been definitely repudiated but gradually abandoned. In this paper, Pauling credited the discovery of the hydrogen bond to Huggins, and to Latimer and Rodebush.

Jack Sherman of Caltech, at the time one of Pauling’s graduate students, and previously an undergraduate at Berkeley, wrote a review of the thermochemistry of ionic compounds in 1932. In it he states (39):

The high value for the proton affinity from ammonium fluoride is surprising, but may be explained in the following way. Pauling has pointed out in his lectures that the unexpected occurrence of wurtzite structure for ammonium fluoride is probably due to the formation of hydrogen bonds.

Pauling covered hydrogen bonding in lectures on the nature of the chemical bond from 1927–1928 at Caltech and in lectures on the applications of quantum mechanics at Berkeley beginning in the spring of 1929. The view of hydrogen bonding in these lectures, at least from the period 1929−1931, is the same as that presented in his 1928 and 1931 papers (35,40).

In 1933, Pauling analyzed the X-ray diffraction data on \(\text{NH}_4\text{HF}_4\) (41):

In predicting a structure for \(\text{NH}_4\text{HF}_4\) we make the following assumptions:

1. We expect linear HF₂ groups as in NaHF₂ and KHF₂ with the H-F distance equal to 1.2 ± 0.1 Å.

2. We further expect hydrogen bonds between nitrogen and four surrounding fluoride ions. The fluoride ions should be approximately tetrahedrally arranged about the nitrogen ion, at a distance of 2.63 Å, as in NH₃F.

The hydrogen bond in this compound is assumed to be completely ionic.

Pauling and L. O. Brockway determined the structure of formic acid by X-ray diffraction in 1934 (42). Formic acid and other carboxylic acids had long been known to form dimers, and Latimer and Rodebush had suggested in 1920 that this was due to hydrogen bonding. The results of this determination confirmed this suggestion. In this paper Pauling retreated slightly from the purely ionic picture of the hydrogen bond, indicating that resonance between ionic and covalent forms of the carboxylic acid group may contribute to the stability of the hydrogen bond.

In 1935, Pauling published a paper on the structure and entropy of ice (43). In it he pointed out that the residual entropy of ice can be accounted for by a structure in which each oxygen
atom is attached to two hydrogen atoms in the same molecule, and to two other hydrogen atoms in other water molecules by hydrogen bonds, such that the hydrogens in the O-H-O linkage are not symmetrically located between the two oxygens. Since the discussion implies discrete water molecules, rather than ionic bonding between H⁻ and O⁺, it would appear that Pauling had quietly abandoned his insistence on the purely ionic nature of the hydrogen bond.

In 1936, A. E. Mirsky and Pauling (44) proposed that protein molecules are held in definite configurations by hydrogen bonding between amino and carboxylic side chains; the process of denaturation would be one in which these hydrogen bonds are broken. William Astbury and H. J. Woods (45) had previously proposed that bonding between protein chains is due to the attraction between =NH and =CO groups. The following diagram shows their proposed structure:

The dotted lines between the CO and NH groups might indicate that they had hydrogen bonding in mind, even though they do not use any of the names then current for the concept. The fact that the same dotted lines are used between the alpha-hydrogens in CHR groups, leaves some doubt that they intended anything so specific.

Several of the pioneers of hydrogen bonding returned to the concept in the 1930's, after a decade or more of pursuing other research interests. In 1931, Huggins proposed a mechanism for the high specific conductances of the hydroxide and hydrogen ions in liquid water involving the transfer of protons from one water molecule to another through the formation of temporary hydrogen bonds. This paper is the first use by Huggins of the term hydrogen bond (46). In 1936 he wrote reviews of hydrogen bridges in ice and liquid water (47) and in organic compounds (48). In the second paper he repudiates the accepted name for the concept (48):

The writer prefers the term "hydrogen bridge" to the expression "hydrogen bond" introduced by Latimer and Rodebush, believing it best to use the word 'bond' (in chemistry) only for a system consisting of one or more (nearly always two) electrons holding together two atoms. 'Hydrogen bond' is also confusing since it suggests the electron pair bond between two atoms in the H₂ molecule...

In this Huggins was fighting a lost cause, as by that year almost everyone else who was making use of the concept had adopted the term "hydrogen bond".

Lewis, by 1934, had turned his attention to the preparation of deuterated compounds. Differences between the vapor pressures of deuterobenzoic acid (49), deuterohaloic acid (50), and deuterocyanic acid (51), and the vapor pressures of the corresponding "light" compound were attributed to stronger hydrogen bonding in the deuterio compound. Thus, there is a 5% difference in the vapor pressure of the acetic acids, for which hydrogen bonding is important, and little difference for HCl and HCN, where hydrogen bonding is much weaker.

Rodebush, in 1936, published a review on the subject of hydrogen bonding and coordination (52), pointing out the similarities and differences (mainly that the hydrogen bond is much weaker than the coordination of metal ions) between the two concepts. He pointed out that it was only then, 15 years after the introduction of the concept, that definite proof of the hydrogen bond has appeared, pointing specifically to the X-ray studies of Pauling and the disappearance of the O-H vibrational frequency in the IR in hydrogen bonding situations (of this more later).

William Claussen and Joel Hildebrand (53) reported on the vapor pressures of hydrogen and deuterium fluoride in 1934, citing the above-mentioned papers (49-51) of Lewis:

Since the hydrogen bond has been regarded by Lewis as largely responsible for the differences in vapor pressure between the corresponding light and heavy compounds, it occurred to us that a comparison of the two hydrogen fluorides, in which this bond is particularly strong, would be interesting.

The results of this investigation supported Lewis' contention. Four years earlier, G. H. Cady and Hildebrand (54) had studied the freezing points of water-hydrogen fluoride mixtures and explained the results in terms of molecular compounds between H₂O and HF without reference to hydrogen bonding.

Hildebrand had been a faculty member at Berkeley since 1913. He was one of the first of the young faculty members brought in by Lewis to build up the department, and had collaborated with Latimer on the Reference Book of Inorganic Chemistry. Consequently it is surprising to find that it took Lewis' renewed interest in hydrogen bonding for him to accept the concept in his own work. Considering that it took 14 years for the hydrogen bonding concept to cross the hall (figuratively) at Berkeley, it is perhaps understandable that it took as long as it did to win acceptance from the chemical community at large.

In 1933, John D. Bernal and K. H. Fowler discussed the theory of water and its ionic solutions. Bernal, a crystallographer at Cambridge University (in 1937 he would move to Birbeck College, University of London) is probably best known for his work on the structures of proteins. Their explanation for the high mobility of the H₂O⁺ and OH⁻ ions was essentially the same as that proposed by Huggins in 1931, but no citation of Huggins' article was given. In comparing the association of water with that of other liquids, they stated that:
"In HF the cohesion is better regarded as due not to dipoles but to 'the H-bond'." In concluding they state (55):

It is clear that the ideas here developed, if they are at all correct, will lend themselves to a number of further applications particularly in physical and chemical applications of the hydrogen bond.

The term "hydrogen bond" does not otherwise occur in the main discussion of the structure of water and ice, but it is clear that this is what they have in mind. No citation of previous workers is given for the concept, but Lewis’ work with deuterium compounds is mentioned in a discussion of the mobility of D+ in heavy water.

In 1935, Bernal and H. D. Megaw published a major paper on the function of hydrogen in intermolecular forces (56). In it they attributed the "so-called hydrogen bond" to Huggins and Pauling. The major thrust of the paper was a distinction between ordinary hydrogen bonding and bonding between two hydroxyl groups, which they consider different enough to give a separate name: "the hydroxyl bond". Bernal’s papers influenced many British and Continental chemists during the middle 1930’s, as judged by the number of citations. The conception of the hydroxyl bond was much commented on and debated. Rodebush (52) remarked that the "hydroxyl bond" did not appear to differ in any significant way from the hydrogen bond, and after the initial impression caused by Bernal’s papers died down, this view came to be generally accepted.

Other crystallographers were, in the meantime, following Pauling’s lead, finding hydrogen bonding in various crystal structures. As early as 1930, J. West, of the University at Manchester (57), suggested that the X-ray analysis of potassium dihydrogen phosphate could best be fit by placing the hydrogen atoms on a line joining two oxygen atoms of adjacent PO₄²⁻ groups, giving each hydrogen a coordination of two. There is, however, no suggestion in this paper that this conclusion can be generalized to other structures.

In 1933, William H. Zachariasen of the Physical Laboratory of the University of Chicago came to the same conclusion with regard to the position of the hydrogen atoms in sodium bicarbonate (58). In this paper Zachariasen suggested that this arrangement is due to the hydrogen bond and credits Pauling with the idea. In 1935, Zachariasen reported the X-ray analysis of liquid methyl alcohol (59):

Our analysis thus strongly indicates the presence of hydrogen bonds between oxygen atoms of neighboring molecules... Every hydrogen atom is thus linked to two oxygen atoms; undoubtedly it is linked more strongly to one of the oxygen atoms than to the other, so it would still be justifiable to talk about hydroxyl groups. Naturally if we wish to characterize the nature of these hydrogen bonds, we should employ the term dipole bonding.

This is the first clear indication of the current view that the hydrogen bond is due primarily to unusually strong dipole interactions (60).

The current view also allows for some contribution from covalency in stronger instances of hydrogen bonding (such as HF₂⁻). These days this is generally described in terms of three-center orbitals. The equivalent for the chemist of the 1930’s would be "resonance". We have already seen that Pauling invoked resonance as contributing to the stability of the formic acid dimer (42). Siddig, in 1934, on quantum mechanical grounds, abandoned the theory that the hydrogen atom in the hydrogen bond has four shared electrons (61):

The solution of this difficulty is provided by the theory of resonance, the hydrogen atom being covalently attached to one and another of the two atoms in the two structures.

Bernal and Megaw (56) suggested that oscillation of the hydrogen atoms between positions in which it is bonded to each oxygen in turn might be equivalent to electronic exchange. They proposed this speculation rather tentatively, however, and concluded that the hydrogen bond is primarily due to electrostatic attraction.

In 1937, Albert Sherman (62), a Berkeley graduate and the twin brother of Jack Sherman who had worked with Pauling, considered that the hydrogen bond is stabilized by resonance structures in which the hydrogen atom is bonded to either oxygen, and that this stabilization energy should show up in thermochemical data for compounds in which it occurs. He pointed out that such stability is not found in thermochemical data for nitro derivatives of benzene and argued that hydrogen bonding is not present in these compounds, despite the indication from IR spectra that it is present. This analysis is flawed by the fact that he did not allow for the possibility of intermolecular as well as intramolecular hydrogen bonding, but the value (about 2 kcal/mole) that he predicted for the effect is of the right order of magnitude. IR and Raman spectra of water, the alcohols, amines, and related compounds were studied intensively in the 1920’s and early 1930’s. It was recognized that the characteristic stretching frequency of the OH or NH group appeared in the spectra of these compounds in the vapor phase, but was absent, or displaced, in the liquid phase or in solutions. In the condensed phase it had long been recognized that the position and intensity of this band varied with the temperature and the solution concentration. These effects in water were often interpreted in terms of Armstrong’s model for water, in which changes in temperature or solute concentration were attributed to the changing proportions of the various polymers of "hydrone". For the alcohols and amines the equivalent explanation in terms of different degrees of association was offered. Some workers, noting the fact that changes were seen in the OH or NH vibrational frequencies, drew the conclusion that association was through these bonds, but before 1935, no connection was made with the Laümer-
Rodebush concept of hydrogen bonding (63).

The first clear recognition that these changes were due to hydrogen bonding appeared in 1935. A paper (64) published in Nature on 26 January 1935 by a research group in the Bureau of Chemistry and Soils of the Department of Agriculture in Washington, D.C., attributed the lack of the characteristic OH absorption in such molecules as salicyaldehyde, o-nitrophenol, and 2,6-dinitrophenol to the presence of "chelated" hydrogen. Reference is given to Sidgwick's book. It is noteworthy that one of the members of the group, Sterling Hendricks, had previously worked with Pauling on the crystal structure of the HF₂⁻ ion (34). Independently, in a paper presented to the Academy of Sciences in Paris on 18 February 1935, Jacques Errera and Pol Mollet of the University of Brussels (65) came to the same conclusion with regard to the IR spectra of salicyaldehyde and o-chlorophenol. They also cited Sidgwick's book for the concept, calling it "covalence de coordination".

At about the same time (paper submitted 20 March 1935), Hendricks reported the results of an X-ray diffraction determination of the structure of oxalic acid. He concluded (66):

The separation O-O... = 2.55 Å... is probably associated with a "hydrogen bond" between two oxygen atoms.

The following year the group at the Bureau of Soils (67) adopted the term "hydrogen bond" for the concept, citing Huggins, Latimer and Rodebush, Sidgwick, and Pauling for the previous history of the concept. The absence of the characteristic OH stretching frequency is proposed as a definite test for the presence of hydrogen bonding. A paper (68) from the same group later that year, extending the application of the criterion to phenols, states that "The authors are much indebted to Professor Linus Pauling for discussion of this type of spectra and helpful advice as to its interpretation." It is tempting to speculate that it was the presence in the group of Hendricks and Oscar Wulf, both of whom had worked with Pauling, which led them to look at hydrogen bonding as a possible explanation of the anomalies.

By 1936, Errera (69) was also using the term "hydrogen bond", though he was still citing Sidgwick's book for the concept. Before the papers of Errera and the group at the Bureau of Soils, papers using the concept of hydrogen bonding had largely been confined to crystallographers, British physical organic chemists of the Sidgwick school, and a few chemists with associations with Berkeley. During 1936 and 1937 an increasing number of spectroscopists, both chemists and physicists, began publishing papers making use of the concept.

Another significant event leading to general acceptance of the concept was a Meeting of the Faraday Society on the Structure and Molecular Forces in Liquids and Solutions held at Edinburgh on 24-26 September 1936 (70). Hildebrand gave the keynote lecture for the section on the structure of solutions, in the course of which he stressed the importance of hydrogen bonding (71):

It is becoming evident, again, that the term "association" under which we have lumped all departures from normal behavior, must be subdivided into association arising from the interaction of dipoles, and that due to the formation of definite chemical bonds. Of these, perhaps the most interesting are the hydrogen bonds or 'bridges' between oxygen, nitrogen, or fluorine atoms, a species of chemical interaction.

Among the scientists who also gave papers at this meeting were Bernal (72) and Errera (73). The record of this meeting, appearing in print early in 1937, was much cited by chemists and physicists during the remainder of the year. Interestingly, the citations are as often to the "General Discussions" following the papers as to the papers themselves (74).

As an example of the shift of opinion during 1937, we might point to two French spectroscopists, René and Marie Freyumann. They had been working on the IR spectra of alcohols, amines, and related compounds since 1931, and René Freyumann had written his doctoral thesis (75) on the subject. In one of René's earlier papers (76), he studied the spectra of alcohols in non-polar solvents and attributed the shift in the OH stretching frequency on changing concentration or temperature to "les associations moléculaires", envisioned as in the following diagram:

\[
\begin{align*}
\text{R}^+\text{OH}^- & \\
\text{R}^+\text{OH}^- & \\
\text{R}^+\text{OH}^- & \\
\end{align*}
\]

In a paper presented to the Academy of Sciences in Paris by René on 28 December 1935 (77), he considers association as involving "des liaisons monoélectroniques" of Perrin:

\[
\begin{align*}
\text{R} & \\
\text{O} & \ldots \text{O} & \ldots & \text{H} & \ldots & \text{O} & \ldots & \text{R} \\
\text{R} & \ldots & \text{O} & \ldots & \text{H} & \ldots & \text{O} & \ldots & \text{R} \\
\end{align*}
\]

Another paper, by Marie, presented 25 January 1937 (78), also proposes "liaison monoélectronique" to account for shifts in IR spectra of amines. However, in a joint paper submitted on 25 February 1937 (79), they review the evidence for "liaison hydrogéne". Although the papers presented at the Faraday Society meeting are not cited as references, the timing of this paper and the abrupt shift in their view of the nature of association makes it likely that they were influenced by reports from other French scientists who had attended the meeting.

The Freymanns were not the first French scientists to use the term "hydrogen bond": it appeared (untranslated from English) in a paper submitted a month earlier (30 January 1937) by Ch. Sannié and V. Poremski (80) on the Raman spectra of organic acids.

By 1937, the term "hydrogen bond" was also used by Japa-
nese chemists. The earliest use of the term I have been able to find is in a paper by S. Mizushima, Y. Uehara, and Y. Morino (81) of the Imperial University of Tokyo. The first instance I have found of the occurrence of "Wasserstoffbrücke", the German equivalent of "hydrogen bond", is in a book published in 1938 (82). However, at the Edinburgh meeting, K. L. Wolf of the University of Würzburg wrote (83):

... it follows that the work required to separate completely the -OH bindings (due essentially to the dipole forces) from the state of pure alcohol to complete dissociation is ca. 8 kcal per mol. alcohol.

Since many participants at the meeting (including Hildebrand) were drawing distinctions between hydrogen bonding and dipole forces, it cannot be claimed that Wolf would have agreed that he was talking about hydrogen bonding. But his estimate of the heat of dissociation shows that he recognized that the forces between -OH dipoles are greater in magnitude than ordinary dipole forces.

Why did the acceptance of the hydrogen bonding concept by the chemical community take as long as it did? Rodebush gave one answer in his 1936 review (52): that it was only after 15 years that definite evidence for hydrogen bonding was forthcoming. The group at the Bureau of Soils proposed another explanation (67):

Bonding of hydrogen to two atoms has been recognized and described under such various terms as partial valence, secondary forces, hydrogen bond, chelate ring, coordination, Dimroth ring, association, intermolecular association, and the "ortho effect". This very multiplicity of naming reflects the amorphous character of the concept and its partially uncorrelated appearance in the literature during the past twenty-five years.

These explanations may be partially true; still, most of the textbook examples for the existence of hydrogen bonding were already known when Latimer and Rodebush wrote their paper, or were discovered soon afterwards. And most chemists who used the terms "association" or "intermolecular association" or "secondary valence" do not appear to have anything as definite as the hydrogen bond in mind.

It is more likely the case that the true explanation lies in two factors: first, despite the general acceptance of the Lewis theory by the late 1920's, most chemists were not yet accustomed to think in terms of electronic effects; they had learned early in their chemical education that "association" explained the properties now explained by hydrogen bonding, so that they did not question whether the concept of association had any real content. This is similar to the unthinking acceptance of the octet rule by chemists in the 1950's, so that the synthesis of xenon compounds came as a shock.

A second reason is similar to that proposed by Robert Kohler (17) to explain the delay in the acceptance of the Lewis theory: namely that Lewis, Latimer, Rodebush, and Huggins did not have any program of experimentation which made use of hydrogen bonding and consequently did not influence the greater number of chemists who were experimentalists rather than theorists. We see this influence of an experimental program in spreading acceptance of hydrogen bonding repeatedly during the 17 year history described in this paper. Lowry, and particularly Sidgwick, primarily influenced the new British school of physical organic chemists; Pauling influenced crystallographers; Lewis, when he began research on deuterium, where he could apply the concept of hydrogen bonding to his own work, influenced Hildebrand. Hendrickx, a crystallographer and Pauling's student, probably influenced the spectroscopists at the Bureau of Soils, who in turn, influenced other spectroscopists. Finally, the Edinburgh meeting of the Faraday Society, bringing together theorists and experimental scientists using different techniques, diffused the "new" ideas throughout the community of chemists and chemical physicists.

References and Notes

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32. Reference (6), pp. 387-447.
40. Pauling Archives, Oregon State University: Box 904, Advanced Inorganic Chemistry Lecture Notes, California Institute of Technology, 1930-31; Box 201, Berkeley Lectures on Applications of Quantum Mechanics, 1929-1933.
51. G. N. Lewis and P. W. Schults, “The Vapor Pressure of Liquid
63. See references 64-65, 67-69, and 75-82 for references to the earlier work.

The Editor regrets to report that Dr. Denis Quane passed away on 21 September 1990 shortly after correcting the final proofs for this article. Dr. Quane was an Associate Professor of Chemistry at East Texas State University, where he had been teaching a course in the history of science since 1982.

Joseph William Mellor (1869-1938)

Fathi Habashi, Université Laval

Today most students of chemistry have probably never heard of Joseph William Mellor, though his monumental 16-volume *Comprehensive Treatise on Theoretical and Inorganic Chemistry* is still to be found on the shelves of most chemistry libraries and he was, without a doubt, one of the most prolific and influential textbook authors of his time. His biography in the *Obituary Notices of the Fellows of the Royal Society* appears to have been accidentally overlooked by the standard biographical indices (1) and he does not appear in any of the standard biographical dictionaries of prominent scientists (2,.