

A Hydrogen Isotope of Mass 2

Before the publication of this definitive paper on the discovery of deuterium [1,2], the existence of a heavy isotope of hydrogen had been suspected even though Aston [3] in 1927, from mass spectrometric evidence, had discounted the presence of the heavier isotope at a hydrogen abundance ratio ${}^1\text{H}/{}^2\text{H} < 5000$. (The modern best estimate of that ratio is 5433.78 in unaltered terrestrial hydrogen.) Harold Urey, however, continued to suspect the existence of the heavier isotope, based upon evidence from the sequence of properties of known nuclides and from faint satellite peaks in the Balmer series of the atomic hydrogen spectrum in the visible region. Birge and Menzel [4] had gone further by estimating the abundance ratio ${}^1\text{H}/{}^2\text{H}$ at about 4500 from the difference in the atomic weight of hydrogen measured by chemical versus mass spectrometric means.

Still, the world of science was unwilling to acknowledge the existence of a hydrogen isotope without direct experimental proof. Thus Urey solicited the collaboration of a physicist he had known well at Johns Hopkins University, Ferdinand Brickwedde, who had moved to the National Bureau of Standards after completing his graduate work and had begun to assemble an unexcelled center for thermodynamic measurements, especially at low temperature.

This was a time when isotopes, because of their identical configuration of extra-nuclear electrons, were believed to be chemically inseparable. Prout's old hypothesis of atomic weights being whole-number multiples of that of hydrogen now applied more satisfactorily to isotopes than to elements, but—apart from the effects from some radioactive processes applicable exclusively to elements of high atomic number—all atomic weights were still regarded as constants of nature.

Urey, Brickwedde, and their colleagues evidently did not share that contemporary viewpoint. These scientists had knowledge of the differences in nuclear spins, as well as magnetic and quadrupole moments, between isotopes of the same element. They had mastered quantum physics and thermodynamics, so surely they expected differences in physical and chemical properties and hence would have anticipated some differences in reaction dynamics and equilibria. They probably estimated the chemical differences among isotopes to be small, perhaps too small to be measured by contemporary experiments. Any successful separation, therefore,

was likely to be achievable largely by virtue of the difference in masses of isotopes of the same element. A suspected isotope of hydrogen had a mass two or three times that of the predominant ${}^1\text{H}$. The search for a hypothetical hydrogen isotope caused great excitement and led to a high-stakes competition among laboratories. None exceeded Urey and his coworkers in understanding and determination to find proof for the existence of an isotope of hydrogen by a clear-cut measurement. Actually, Urey and George Murphy had found, but not yet published, spectrographic evidence for the lines of ${}^2\text{H}$ obtained from samples of commercial tank hydrogen. These lines, however, were seen only after long photographic exposures. The suspicion persisted that these extra lines could have arisen from irregularities in the ruling of their grating or from molecular hydrogen.

Urey and Brickwedde recognized that the proportional mass difference of a possible hydrogen isotope ${}^2\text{H}$ or ${}^3\text{H}$ was most likely to show in molecular hydrogen (H_2). A fractional distillation near the hydrogen triple point (about 14 K) gave the best chance of achieving a high concentration of the hypothesized ${}^2\text{H}$. Despite the considerable experimental difficulties, Brickwedde at NBS undertook the attempt to separate partially the hypothetical isotope by fractional distillation of liquid hydrogen [1,2].

Murphy much later [5] recalled the fear of being beaten in the race for priority in a proof for the existence of ${}^2\text{H}$ at a time when Brickwedde reported a manufacturing delay in the large NBS hydrogen liquifier. The delay, however, appears to have been well used. The authors attempted a quantitative calculation of the enrichment to be expected. By making use of the equality of free energy of gas and solid in equilibrium and the Debye theory of the solid state, they calculated, with minor additional assumptions, the ratio of the vapor pressures $p({}^1\text{H}_2)/p({}^1\text{H}{}^2\text{H})$ at the triple point as 2.688.

For the actual experiment Brickwedde started with 400 ft³ of hydrogen gas which was liquefied after precooling with liquid air boiling at reduced pressure. Liquid hydrogen was then fed into a 1.6 L evaporation flask. Evaporation took place until about 1/3 of the hydrogen remained, which was then fed into sample tubes and transported to Columbia University for atomic spectroscopic comparison with normal hydrogen by Murphy [1,2]. Assuming the above-quoted abundance ratio to be 4500 [3], the mole fraction left in the still should by their calculation have increased by a

factor of 4000. (It would have been higher, if ^3H were involved.) Although the concentration factor of 4000 was never achieved, the ^2H concentration was so greatly enhanced that its existence could be demonstrated from the spectroscopic measurements without any remaining doubt. A Letter to the Editor [1] narrowly achieved the desired priority and alerted the scientific community to the upcoming full paper [2], which was recognized as much for the low-temperature advances—the first of a series of similarly significant low-temperature measurements related to superconductivity at NBS [6]—as for the scientific significance of a separable stable hydrogen isotope. This full paper [2] earned Urey the 1934 Nobel Prize for Chemistry.

Although he refrained from stealing the limelight and the priority from the Urey, Brickwedde, and Murphy classic experiment, Edward Washburn of NBS, in association with Urey [7], published in 1931 a demonstration of the existence of ^2H based upon a simpler and subsequently much more important method of enrichment. Washburn and Urey argued that chemically unbonded $^2\text{H}^+$ might have a lower mobility and/or higher cathodic potential in electrolysis. In fact, such concentration was demonstrated in a number of samples, including those from residual solutions from commercial electrolytic cells that had operated continuously for two to three years. These samples were examined spectroscopically by Murphy at Columbia, and the quantification of the enrichment was also carried out at NBS using water density measurements. The high accuracy of these measurements stands as a great tribute to NBS. This work is recorded in many papers authored or co-authored by E. R. Smith. In a very elegant experiment, for example [8], the authors compared the densities of four kinds of samples: natural water, water prepared by combining hypothetically enriched hydrogen with normal oxygen, water prepared by combining natural hydrogen with enriched oxygen, and water prepared by combining hypothetically enriched hydrogen with enriched oxygen. Thus they were able to show not only that the ^2H enrichment is real, but that the enrichment of the higher isotopes of oxygen is also measurable. Washburn showed great ingenuity in searching out waters that were enriched or denuded in ^2H . In one experiment he and his son compared water from sap taken from the top of a tree with water from the roots. The results showed conclusively that ^2H existed and that isotopic compositions, and also atomic weights, could no longer be regarded as invariable.

The ^2H isotope, as early as in 1934 [9], was named by Urey as deuterium (symbol D) with a nucleus called deuteron (symbol d). As is common to many significant discoveries in science, this event was widely anticipated but, in contrast with most other discoveries, its

applications followed swiftly. Within a year, an NBS group had used isotopic composition in an electrolytic process control. A Cambridge group under Rutherford [10] had prepared deuterated compounds such as D_3PO_4 , bombarded them with deuterons, and correctly identified the reaction: $\text{D}+\text{D} = \text{T}+\text{H}$ (T is the symbol for the new radioactive isotope of hydrogen of mass 3, called tritium). The nuclear reaction type (d,n) was also identified, in which the neutron that is produced carries off the excess energy in the deuteron (the excess energy over that of a neutron separated from the nucleus of ^1H). Within a decade of the discovery of D, the thermodynamic properties of the hydrogen isotopic species had been measured (see, for example, Fig. 1) and definitive values published by NBS [11]. Furthermore, the application to a fledgling nuclear industry was realized, and the cosmological significance began to be appreciated.

The literature resulting from the discovery of deuterium grew very fast. As early as 1935, Urey with Gordon Teal [12], who much later became Director of the NBS Institute for Materials Research, wrote a comprehensive review of the methods of separation of deuterium, its properties in gas, liquid, and solid phases, the chemical kinetics of deuterated compounds, analytical applications for deuterium, the nuclear spin and

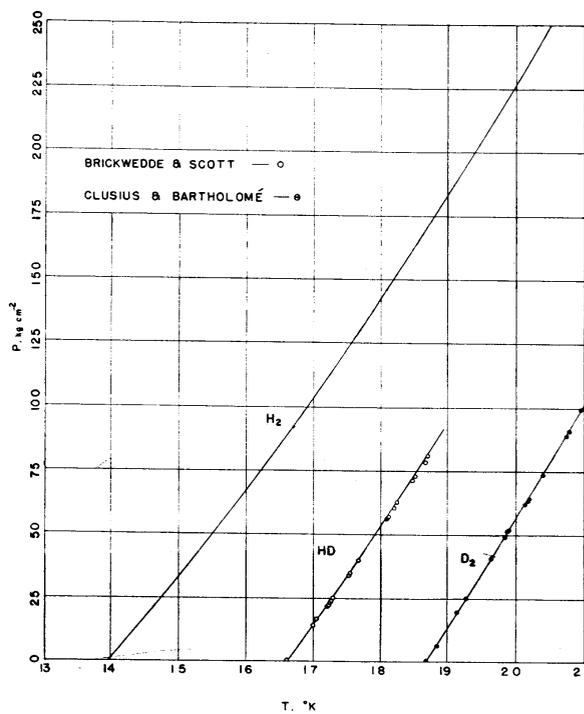


Fig. 1. Melting point pressure as a function of temperature for H_2 , HD, and D_2 (from [11]).

moments, and the atomic and molecular spectra. The discovery of deuterium had started a whirlwind of change in science.

The above description may give the false impression of a straightforward, orderly path to the discovery of deuterium. To correct that illusion, the reader might enjoy reading Brickwedde's memoirs [13] written after all the dust had settled and after Urey, Murphy, and Washburn had died. In that article Brickwedde first pays great tribute to Urey "who proposed, planned, and directed the investigation. Appropriately, the Nobel Prize for finding the heavy isotope of hydrogen went to Urey." Brickwedde then points out that the work stumbled on by a succession of errors, some detrimental, some accidentally fortunate to furthering progress. One such error was made on authoritative, but false, advice that electrolysis could not alter significantly the hypothetical isotopic composition of hydrogen, so that the first sample of hydrogen used by Brickwedde for fractional distillation by the above described *tour de force* was already denuded in deuterium! At that juncture, Washburn at NBS was again the hero who suggested the preparation of the hydrogen sample was faulty.

After receiving the degree of AB (chemistry) and PhD (physics and mathematics) from Johns Hopkins University, Ferdinand Graft Brickwedde started at NBS in 1925 as postdoctoral Mansell Research Associate. In 1926 he became Chief of the Low Temperature Laboratory. In 1946 the Heat and Power Division was restructured and Brickwedde was appointed its Chief in recognition of his leadership potential. At the same time Brickwedde organized and led the Thermodynamics Section, one of the component parts of the new Division. Besides his key contributions to the discovery of deuterium, his research covered a diversity of topics including measurement of thermodynamic properties, the liquefaction of gases, the superfluidity of liquid helium II, the absolute temperature scale, applications of refrigeration, solar energy, rheology, octane rating, and the properties of deuterium compounds. Simultaneously with his appointment at NBS, Brickwedde served as a part-time physics professor at the University of Maryland, where he gave graduate courses in statistical mechanics, relativity, electrodynamics, and quantum mechanics. He organized the University of Maryland Extension Program in physics at NBS. This program was important in that it gave opportunities for NBS staff to keep abreast of current developments in specialized fields, to acquire knowledge in new fields, and to satisfy interests to teach while at a non-academic establishment. It also enabled many young staff members at NBS and

other Federal agencies to satisfy their course requirements towards advanced degrees by attending classes at NBS after working hours. He also was consultant to Los Alamos Scientific Laboratory, the University of California Lawrence Livermore Laboratory, and a commission member of the International Institute of Refrigeration and the International Union of Pure and Applied Physics. Brickwedde won the Hillebrand Prize of the Chemical Society of Washington and was Associate Editor of *The Physical Review*. As NBS expanded in the early 1950s, he helped recruit young PhDs for the new programs. He and his wife, Langhorne Howard Brickwedde, an NBS electrochemist, were gracious hosts to many of the new arrivals. In 1956 Brickwedde, when only 53 years old, left NBS to accept the post of Dean of Physics and Chemistry at Pennsylvania State University and, in 1978, the Evan Pugh Research Professorship there. He died in 1989 at the age of 86.

Prepared by Walter J. Hamer and H. Steffen Peiser.

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