Harold Urey and the discovery of deuterium

Chemistry, nuclear physics, spectroscopy and thermodynamics came together to predict and detect heavy hydrogen before the neutron was known.

Ferdinand G. Brickwedde

It was on Thanksgiving day in 1931 that Harold Clayton Urey found definitive evidence of a heavy isotope of hydrogen. Urey's discovery of deuterium is a story of the fruitful use of primitive nuclear and thermodynamic models. But it is also a story of missed opportunity and errors—errors that are particularly interesting because of the crucial positive role that some of them played in the discovery. A look at the nature of the theoretical and experimental work that led to the detection of hydrogen of mass 2 reveals much about the way physics and chemistry were done half a century ago.

Although George M. Murphy and I coauthored with Urey the papers reporting the discovery, it was Urey who proposed, planned and directed the investigation. Appropriately, the Nobel Prize for finding a heavy isotope of hydrogen went to Urey.

In this article we will look first at the research that led to the discovery, as that work was understood at the time. Then we will look at some of the same activity with the understanding that only hindsight can give. Throughout the discussion I will include fragments from my memory—illustrative episodes connected with the discovery.

Urey's career

Urey died last year at 87 years of age, after a remarkably productive and interesting life. He was a chemist with very broad interests in science, reminiscent of the natural philosophers of the eighteenth and nineteenth centuries. Murphy, who went on to become professor and head of the department of chemistry at New York University, died in 1968.

Urey was born on a farm in Indiana in 1893, and in childhood moved with his family to a homestead in Montana. After graduating from high school, he taught for three years in public schools, and then entered Montana State University as a zoology major and chemistry minor. Money was tight for him as a college student. During the academic year he slept and studied in a tent. During his summers he worked on a road gang laying railroad track in the Northwest.

Urey graduated with a BS degree in 1917, when there was a need for chemists in the war effort. He worked for the Barrett Chemical Company in Philadelphia on war materials. After the war, Urey taught chemistry for two years at Montana State University, and in 1921 entered the University of California at Berkeley as a graduate student in chemistry, working under the guidance of the renowned chemical thermodynamicist Gilbert N. Lewis. As a graduate student, Urey was a pioneer in the calculation of thermodynamic properties from spectroscopic data. He received a PhD in 1923 and spent the next academic year as an American-Scandinavian Foundation Fellow in the Physical Institute of Niels Bohr in Copenhagen.

After Copenhagen, Urey joined the faculty at Johns Hopkins University. Although in the chemistry department, he attended the physics department's regular weekly "journal" meetings for faculty and graduate students, and he participated in the discussions. It was at these meetings that I, as a graduate student in physics, became acquainted with Urey. While Urey was at Hopkins, he and Arthur E. Ruark coauthored the classic textbook, Atoms, Molecules, and Quanta, which was the first comprehensive text on atomic structure written in English. I proofread the entire book in galley for the authors.

Urey's work bridged chemistry and physics. In 1929 he was appointed associate professor of chemistry at Columbia University, and from 1933 to 1940 he was the founding editor of the American Institute of Physics publication, Journal of Chemical Physics. When the biographical publication "American Men of Science" took note of scientists selected for recognition by their peers, Urey was elected in physics. In 1934—only three years after the discovery of deuterium—Urey was awarded the Nobel Prize in chemistry.

Before the search

In 1913, Arthur B. Lamb and Richard Edwin Lee, working at New York University, reported a very precise measurement of the density of pure water. Their measurements were sensitive to $2 \times 10^{-7}$ g/cm$^3$. Various samples of water, which were carefully prepared using the best purification techniques and temperature controls, varied in density by as much as $8 \times 10^{-7}$ g/cm$^3$. They concluded that pure water does not possess a unique density.

Today we know that water varies in isotopic composition, and that samples of water with different isotopic compositions have different vapor pressures, making distillation a fractionating process. The Lamb–Lee investigation is interesting because it was the first reported experiment in which an isotopic difference in properties was clearly in evidence. It is the earliest recognizable experimental evidence for isotopes. (The existence of isotopes was proposed independently by Frederick Soddy, in England, and by Kasimir Fajans, in Germany, in 1913.) Think what the result might have been had Lamb and Lee pursued a progressive fractionation of water by distillation and separated natural water into fractions with different molecular weights.

Less than two decades later, by the time of the discovery of deuterium, isotopes were an active field of research. The rapid development of nuclear physics after 1930 was initiated by isotope research. It was a time of search for as-yet undiscovered isotopes,
especially of the light elements, hydrogen included, and Urey was very much a participant.

I remember a conversation in 1929 with Urey and Joel Hildebrand, a famous professor of chemistry at Berkeley. It took place during a taxi ride between their hotel and the conference center for a scientific meeting we were attending in Washington. When Urey asked Hildebrand what was new in research at Berkeley, Hildebrand replied that William Giauque and Herrick Johnston had just discovered that oxygen has isotopes with atomic weights 17 and 18, the isotope of weight 18 being the more abundant. Their paper would appear shortly in the Journal of the American Chemical Society. Then Hildebrand added, "They could not have found isotopes in a more important element." Urey responded: "No, not unless it was hydrogen." This was two years before the discovery of deuterium. Urey did not remember this remark, but I did.

At the time, answers were being sought to questions such as: Why do isotopes exist, and what determines their number, relative abundances and masses (packing fractions)?

Urey, along with others, constructed charts of the known isotopes to show relationships bearing on their existence. The figure on page 36 is one of Urey's charts. At the time, the neutron had not been discovered—it was discovered in 1932, the year after deuterium. The chart was based on the theory that atomic nuclei were composed of protons, plotted here as ordinates, and nuclear electrons, plotted as abscissae—the number of protons was the nuclear mass number, and the number of nuclear electrons was the number of protons minus the atomic number of the element. In Urey's chart, the filled circles represent the nuclei from H¹ to Si³⁰ that were known to exist before 1931. The open circles represent nuclei unknown before 1931. The chart's pattern of staggered lines, when extended down to H², suggested to Urey that the atoms H³, H⁴ and He⁸ might exist because they are needed to complete the pattern.

Harold Clayton Urey and a country schoolhouse in Indiana where he taught after graduating from high school. Urey taught for three years in public schools in Indiana and Montana before he entered Montana State University. (Schoolhouse photo from the Urey collection, AIP Niels Bohr Library.)

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Urey had a copy of this chart hanging on a wall of his laboratory. The isotope helium-5 does not exist, and the staggered line does not provide a place for the isotope helium-3, which was discovered later. The diagram is only of historical interest now, but it was an incentive to Urey to look for a heavy isotope of hydrogen.

Prediction and evidence

In 1931—the year of the discovery of deuterium—Raymond T. Birge, a professor of physics at the University of California, Berkeley, and Donald H. Menzel, professor of astrophysics at Lick Observatory, published a letter to the editor in Physical Review on the relative abundances of the oxygen isotopes in relation to the two systems of atomic weights that were then in use—the physical system and the chemical system. Atomic weights in the physical system were determined with the mass spectrograph and were based on setting the atomic weight of the isotope O¹⁶ at exactly 16. In the chemical system, atomic weights were determined by
bulk techniques, and the values were based on setting at 16 the atomic weight of the naturally occurring mixture of oxygen isotopes, O\textsuperscript{16}, O\textsuperscript{17} and O\textsuperscript{18}. Thus the atomic weights of a single isotope or element on the two scales should differ. The weight numbers should be greater on the physical scale.

However, in 1931 the atomic weights of hydrogen on the two scales were the same within the claimed experimental errors. The chemical value was 1.00777 ± 0.00002. Birge and Menzel pointed out that the near coincidence of these two atomic weights leads to the conclusion that normal hydrogen is a mixture of isotopes—H\textsuperscript{1} in high concentration and a heavy isotope in low concentration. The atomic weight was not higher on the physical scale because the mass-spectroscopic techniques saw only the light isotope.

To the heavy isotope they gave the symbol H\textsuperscript{2}, perhaps the first time this symbol occurred in the literature. Assuming the atomic weight of heavy hydrogen to be two, Birge and Menzel calculated its relative abundance from the supposed equivalence of the atomic weights of hydrogen-1 on the physical scale and the normal mixture of hydrogen isotopes on the chemical scale. They obtained 1/4500 for the abundance of H\textsuperscript{2} relative to H\textsuperscript{1}.

Within a day or two at most after receiving the 1 July 1931 issue of the Physical Review, Urey proposed and planned an investigation to determine if a heavy isotope of hydrogen did really exist.

Urey and Murphy, working at Columbia, identified hydrogen and its isotope spectroscopically, using the Balmer series lines. The atomic spectrum was produced with a Wood's electric discharge tube operated in the so-called black stage—the configuration of current and pressure that most strongly excites hydrogen's atomic spectrum relative to its molecular spectrum. They observed the spectra with a 21-foot grating, in the second order. The dispersion was 1.3 Å per mm. The expected shifts, then, were of the order of 1 Å, as indicated in the table below. The vacuum wavelengths of deuterium's lines were calculated using the Balmer series formula

$$\lambda_n = R_H (1/2^n - 1/n^2)$$

and the "best" values for the atomic constants. The Balmer a-lines of hydrogen and deuterium are separated by 1.8 Å, the b-lines by 1.3 Å, and the γ-lines by 1.2 Å. The concentrations of deuterium relative to hydrogen are determined by comparing the measured times required to produce plate lines of H and D of equal photographic densities. The exposure times for H\textsuperscript{2} and H\textsuperscript{1} were about 1 second.

Using cylinder hydrogen, Urey and Murphy found very faint lines at the calculated positions for D\textalpha, D\textbeta and D\textgamma. The lines were faint because of the low concentration of deuterium in normal hydrogen. There was a possibility that the new lines arose from impurities, or were grating ghost lines arising from the intensively hydrogen Balmer spectrum.

Clincing evidence

Urey decided not to rush into print to stake a claim to priority in this important discovery; he decided to postpone publication until he had conclusive evidence that the "new" spectral lines attributed to the heavy isotope were authentic and not impurity or ghost lines. This evidence could be obtained by increasing the deuterium concentration in the hydrogen filling the Wood's tube and looking for an increase in intensity of the deuterium Balmer lines relative to the hydrogen Balmer lines. After careful consideration of different methods for increasing the deuterium concentration, Urey decided on a distillation that would make use of an anticipated difference in the vapor pressures of liquid H\textsuperscript{2} and liquid HD. He made a statistical, thermodynamic calculation of the vapor pressures of solid H\textsuperscript{2} and solid HD at the triple point of H\textsuperscript{2}, 14 kelvins, where the liquid and crystal phases of H\textsuperscript{2} are in equilibrium and have the same vapor pressure. The calculation was based on the Debye theory of solids and the zero-point vibrational energy of the solid, 9R\textsuperscript{8}/8 in the Debye notation. At 14 K, the calculated ratio of vapor pressures, P(H\textsuperscript{2})/P(H\textsuperscript{1}), is 0.4, indicating a large difference in the vapor pressures of solid H\textsuperscript{2} and HD. On this basis, Urey expected a sizeable difference in the vapor pressures of liquid H\textsuperscript{2} and HD at 20 K, the boiling point of H\textsuperscript{2}.

Urey approached me at the National Bureau of Standards in Washington, inviting me to join the search for a heavy isotope of hydrogen by evaporating 5- to 6-liter quantities of liquid hydrogen to a residue of 2 cm\textsuperscript{3} of liquid, which would be evaporated into glass flasks and sent by Railway Express to Columbia University for spectroscopic examination. At the time, 1931, there were only two laboratories in the United States where liquid hydrogen was available in 5- or 6-liter quantities. One was the National Bureau of Standards in Washington and the other was Giauque's laboratory at the University of California, Berkeley. I was happy to cooperate, and I prepared—by distilling liquid hydrogen at the Bureau of Standards—the samples of gas in which the heavy isotope was identified.

The first sample I sent to Urey was evaporated at 20 K and a pressure of one atmosphere. It showed no appreciable increase in intensity of the spectral lines attributed to heavy hydrogen. This was unexpected.

The next samples were evaporated at a lower temperature—14 K at 53 mm of mercury pressure, the triple point of H\textsuperscript{2}, where the relative difference in the vapor pressures of H\textsuperscript{2} and HD was expected to be larger than at 20 K, and the rate at which heavy hydrogen is concentrated was expected to be more rapid.

These samples showed 6- or 7-fold increases in the intensities of the Balmer lines of deuterium. On this basis, it could be concluded that the lines in the normal hydrogen spectrum attributed to deuterium were really deuterium lines, but the clinching evidence was finding that the photographic image of the D\textalpha line—the most intense D-Balmer line—was a partially split doublet as predicted by theory for the Balmer series spectrum.

From measurements of the relative intensities of the H and D Balmer series lines, Urey estimated that there was one heavy atom per 4500 light atoms in normal hydrogen. Later measurements showed it to be nearer one in 6500.

Unraveling a comedy of errors

It is now clear why the first distilled hydrogen sent to Urey did not show the expected increase in the deuterium concentration, and maybe even showed

News story on the awarding of the 1934 Nobel Prize in chemistry. Article appeared 16 November 1934. (Copyright The New York Times. Reprinted by permission.)
a small decrease. The explanation came with the discovery of the electrolytic method for separating H and D, suggested by Edward W. Washburn, chief chemist at the National Bureau of Standards, and verified experimentally by Washburn and Urey just after the publication of our April 1932 paper.

When Urey considered different methods for concentrating deuterium, he included the electrolytic method, and discussed it with Victor LaMer, a colleague at Columbia, and a world authority on electrochemistry. LaMer was so discouraging about success in separating hydrogen isotopes by electrolysis that Urey abandoned the electrolytic method and adopted the distillation method. LaMer reasoned that the differences in equilibrium concentrations of isotopes at the electrodes of a cell at room temperature would be very small and hence a fractionation of the isotopes would be negligible. Washburn viewed the situation differently. He pointed to the large relative difference in atomic weights of the hydrogen isotopes—a relative difference that is much larger for the hydrogen isotopes than for the isotopes of any other element. Hence, thought Washburn, the hydrogen isotopes might behave differently from the isotopes of other elements.

Washburn, the empiricist, was right; the isotopes of hydrogen are separated relatively easily by electrolysis, but this was not realized until after the discovery of deuterium.

The hydrogen we liquefied and distilled for Urey was generated electrolytically. Before preparing the first sample for Urey, the electrolytic generator was completely dismantled, cleaned and filled with a freshly prepared solution of sodium hydroxide. Because deuterium becomes concentrated in the electrolyte in the generator, the first gaseous hydrogen to be discharged was deficient in deuterium. The concentration of deuterium in the hydrogen evolved was about one sixth the concentration of deuterium in the electrolyte, and hence about one sixth the concentration of deuterium in normal hydrogen. Distillation of the deuterium-deficient liquid hydrogen increased the concentration of D relative to H and restored in the first sample approximately the original concentration of deuterium in normal hydrogen.

As electrolysis progressed, water was added to replace that which was consumed. The concentration of deuterium in the electrolyte increased to the point where the rate at which deuterium left the generator balanced the rate at which it arrived in the added water. Hence, after the electrolytic generator had been in use for some time, there was a dynamic equilibrium; so the hydrogen evolved from the generator for our second and third samples for Urey had approximately the normal concentration of deuterium.

When we liquefied this hydrogen and evaporated 5 or 6 liters down to 2 cm³, the concentration of deuterium in the residue was increased by a factor of about six. Here we lower the curtain on a 'comedy of errors'—LaMer's error of not understanding better the principles that govern isotopic fractionation during electrolysis, and my error of attributing to sloppy technique our failure to effect an increase of deuterium concentration in the first sample we sent to Urey. Had I analyzed our part of the process, I think we might have discovered the electrolytic concentration of deuterium. Had LaMer been more knowledgeable, Urey would have made his own concentration of deuterium electrolytically and I should have had no part in the discovery of deuterium.

**Calculated Balmer series wavelengths**

<table>
<thead>
<tr>
<th>Line</th>
<th>(\lambda(H^+)^{-1}) ((\AA))</th>
<th>(\lambda(D)^{-1}) ((\AA))</th>
<th>(\Delta\lambda(H^+ - D)) calculated ((\AA))</th>
<th>(\Delta\lambda(H^+ - D)) observed ((\AA))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>6564.686</td>
<td>6562.869</td>
<td>1.787</td>
<td>1.79</td>
</tr>
<tr>
<td>(\beta)</td>
<td>4862.730</td>
<td>4861.407</td>
<td>1.323</td>
<td>1.33</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>4341.723</td>
<td>4340.541</td>
<td>1.182</td>
<td>1.19</td>
</tr>
<tr>
<td>(\delta)</td>
<td>4102.929</td>
<td>4101.812</td>
<td>1.117</td>
<td>1.12</td>
</tr>
</tbody>
</table>

These values were calculated using equation 1 with \(M_H = 1.00775\) g, \(M_D = 2.01363\) g and \(R_o = 109677.759\) cm⁻¹.
research in that period was done with string and sealing wax; it was in fact done mostly with homemade apparatus. The US government policy of grants in support of research dates from a later time—from World War II. Before the War it was a problem to find funds for travel to scientific meetings. I received a telephone call from Urey, telling me that it appeared he was not going to get funds to travel to the December 1931 American Physical Society meeting at Tulane University, where he planned to present a paper reporting the discovery of deuterium. He asked me if I could get travel funds and present the paper. For this I had to see Lyman J. Briggs, assistant director of research and testing at the Bureau of Standards. Briggs, soon to be named NBS director, was an understanding and considerate physicist who, on learning of the work to be reported, made funds available for my travel. In the meantime, Bergen Davis, a prominent physicist at Columbia, heard of Urey's problem and went to see Columbia president Nicholas Murray Butler, who made funds available for Urey's travel. So we both went to Tulane for the APS meeting, and Urey presented the ten-minute paper. Over the next few months we published more detail in a letter to the editor and a full-length paper in Physical Review.

I remember asking Birge at a later APS meeting why he and Giauque had not followed up on his prediction of the existence of heavy hydrogen. They might have demonstrated the existence of deuterium by concentrating the heavy isotope through distillation of a large quantity of liquid hydrogen as Urey and I had done. Giauque had a very fine, large-capacity hydrogen liquefier suitable for this. Birge's reply was that he was busily engaged on other important work that demanded his attention. When I told Urey of this discussion, his comment was: "What in the world could Birge have been working on that was so important?"

Apropos of the above, I quote here from a letter of 6 May 1981 from Robert W. Birge, son of Raymond T. Birge, and also a physicist:

After reading some more about my father's life, I think I know why he didn't try to concentrate deuterium. I believe he was an analyst more than a hardware builder and it probably never occurred to him to do it that way. He said that at the time several people were trying to see the deuterium lines in spectra, but they [Urey, Brickwedde and Murphy] did it first. But as you know, the important point was that Urey realized that the concentration of deuterium could be enhanced.

The two men remained friends throughout their lifetime.

Frederick Soddy, the English chemist who received the 1921 Nobel Prize in Chemistry for discovering the phenomenon of isotropy, did not accept the notion that deuterium was an isotope of hydrogen. Soddy worked with isotopes of the naturally radioactive elements, whose atomic weights are large and whose isotopic relative mass differences are small. These isotopes showed no observable differences in chemical properties and were inseparable chemically. When Soddy coined the word isotope he gave it a definition that included chemical inseparability of isotopic species of the same element. This was generally accepted before the discovery of the neutron in 1932.

After the discovery of the neutron, isotopes were defined as atomic species having the same number of protons in their nuclei but different numbers of neutrons. But Soddy stuck to chemical inseparability as a criterion for isotopes and therefore refused to recognize deuterium as an isotope of hydrogen. For Soddy, deuterium was a species of hydrogen, with different atomic weight, but not an isotope of hydrogen.

A fortunate mistake

Four years after the discovery of deuterium, Aston reported an error in his earlier mass-spectrographic value of 1.00778 for the atomic weight of hydrogen-1 on the physical scale—the value used by Birge and Menzel in their 1931 letter. The revised value on the physical scale was 1.00813, which corresponds to 1.0078 on the chemical scale, in agreement with the then current value for the atomic weight of hydrogen (1.00777) on the chemical scale. There was then no need or place for a heavy isotope of hydrogen. The conclusion of Birge and Menzel was thus rendered invalid. Indeed, on the basis of Aston's revised value, Birge and Menzel would have been obliged to conclude that, if anything, there was a lighter—not a heavier—isotope of hydrogen.

The prediction of Birge and Menzel of a heavy isotope of hydrogen was based on two incorrect values for the atomic weight of hydrogen, namely Aston's mass-spectrographic value and the chemical value, which also should have been greater. We are obliged to conclude that the experimental error in the determination of the atomic weights exceeded the difference in the atomic weights on the two scales.

Urey was not aware of this when he planned his experiment. It was not until 1935 when Urey's Nobel lecture was in proof that Aston published his revised value. Urey added the follow-
ing to the printed Nobel lecture:  

Addendum

Since this [Nobel lecture] was written, Aston has revised his mass-spectrographic atomic weight of hydrogen (H) to 1.0081 instead of 1.0078. With this mass for hydrogen, the argument by Birge and Menzel is invalid. However, I prefer to allow the argument of this paragraph [the third paragraph of Urey’s Nobel lecture] to stand, even though it now appears incorrect, because this prediction was of importance in the discovery of deuterium. Without it, it is probable we would not have made a search for it and the discovery of deuterium might have been delayed for some time.

Needless to say, Urey and his colleagues were very glad that an error of this kind had been made. Aston said that he did not know what the moral of it all was. He would hardly advise people to make mistakes intentionally, and he thought perhaps the only thing to do was to keep on working.

Impact of the discovery

It has been said that Nobel prizes in physics and chemistry are awarded for work, experimental or theoretical, that has made a significant change in ongoing work and thinking in the sciences. The announcement that Urey was chosen as the 1934 laureate in chemistry came less than three years after that ten-minute paper in New Orleans announcing the discovery of deuterium. This uncommonly early award followed a spectacular display in deuterium-related research. In the first two-year period following the discovery, more than 100 research papers were published on or related to deuterium and its chemical compounds, including heavy water. And there were more than a hundred more in the next year, 1934.

The use of deuterium as a tracer made it possible to follow the course of chemical reactions involving hydrogen. This was especially fruitful in investigations of complex physiological processes and in medical chemistry, as in the breakdown of fatty tissue and in cholesterol metabolism. Also, the discovery of heavy hydrogen provided a new projectile, the deuteron, for nuclear bombardment experiments. The deuteron proved markedly efficient in disintegrating a number of light nuclei in novel ways. As the deuteron, with one proton and one neutron, is the simplest compound nucleus, studies of its structure and of its proton-neutron interaction took on fundamental importance for nuclear physics.

Many of the early research papers dealt with isotopic differences in physical and chemical properties. Theories developed for the atomic mass dependence of physical and chemical properties were tested experimentally. These investigations were especially interesting because, before the discovery of deuterium, chemical properties were generally supposed to be determined by the number and configuration of the extranuclear electrons, quantities that are identical for isotopes of the same element. It had not been realized that chemical properties are also affected—but to a lesser degree—by the mass of the nucleus.

In thinking about Urey’s search for deuterium, beginning with his early diagram of the isotopes, I am reminded of the Greek inscription on the façade of the National Academy of Sciences building in Washington, taken from Aristotle:

The search for truth is in one way hard and in another easy, for it is evident that no one can master it fully or miss it wholly. But each adds a little to our knowledge of nature, and from all the facts assembled there arises a certain grandeur.

I wish to acknowledge the valuable assistance of my wife, Langhorne Howard Brickwedde, especially for her help in recalling incidents of the early thirties connected with the discovery of deuterium. This article is based on a paper I presented 22 April 1981 in Baltimore, Maryland, at the inaugural session of the American Physical Society’s Division of History of Physics.

References

4. For an interesting account of the discovery of deuterium, see G. M. Murphy, “The discovery of deuterium,” in Isotopic and Cosmic Chemistry, H. Craig, S. L. Miller, G. J. Wasserburg, eds., North-Holland, Amsterdam 1964 (Dedicated to Urey on his seventieth birthday.)