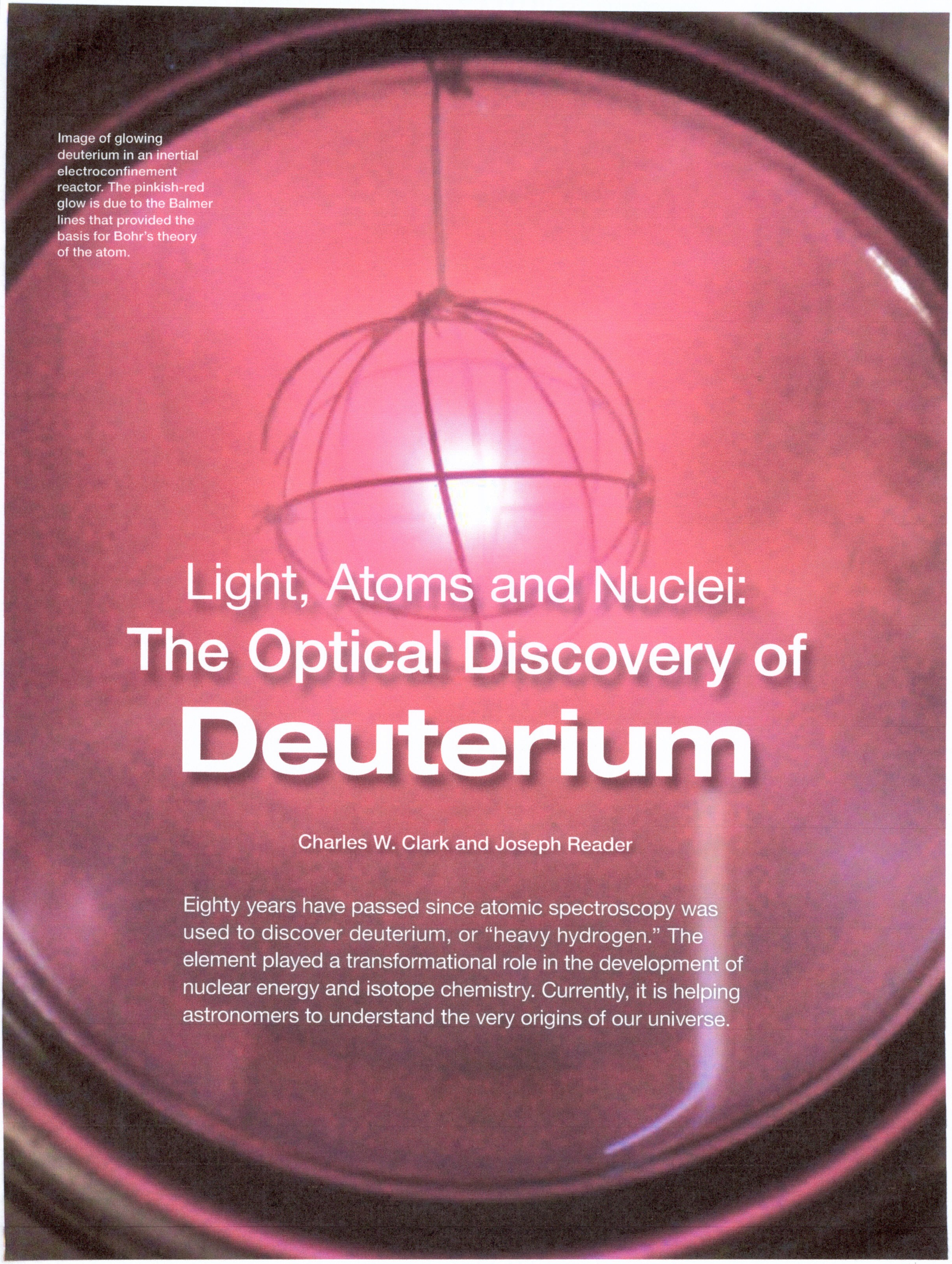


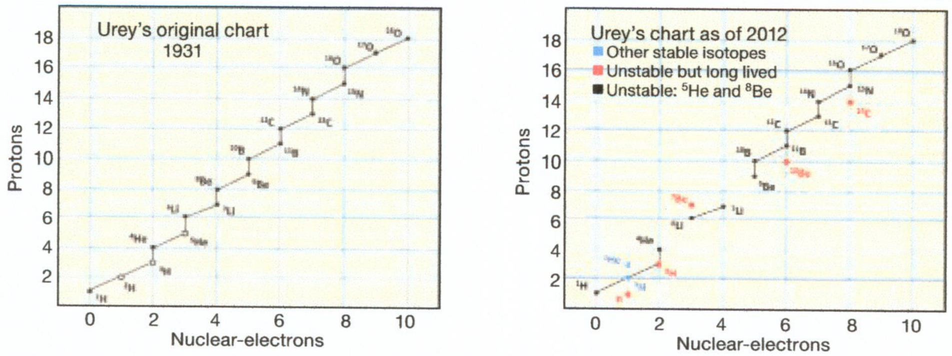
Image of glowing deuterium in an inertial electroconfinement reactor. The pinkish-red glow is due to the Balmer lines that provided the basis for Bohr's theory of the atom.

Light, Atoms and Nuclei: The Optical Discovery of Deuterium

Charles W. Clark and Joseph Reader

Eighty years have passed since atomic spectroscopy was used to discover deuterium, or "heavy hydrogen." The element played a transformational role in the development of nuclear energy and isotope chemistry. Currently, it is helping astronomers to understand the very origins of our universe.

[Isotope "road maps," then and now]



(Left) Isotope chart constructed by Harold C. Urey in 1931 in his search for deuterium. The labels demonstrate the conception of nuclear structure at the time: The nucleus was thought to consist exclusively of protons and tightly bound "nuclear-electrons." The neutron was unknown. Filled circles indicate known isotopes; open ones show those that might be expected to be found by following an obvious trend. Urey saw this as a "road map" to the likely existence of deuterium. (Right) Today's road map, showing the stable isotopes known to Urey (black); stable isotopes discovered since—just ^{2}H and ^{3}He (blue); and long-lived but unstable isotopes of practical importance, including the neutron (red). Two isotopes indicated in the chart on the left have since been found to be unstable, ^{5}He and ^{8}Be.

At dawn on Thanksgiving Day, 1931, no one in the world had an accurate idea of the nature of the atomic nucleus. That day, at Columbia University in New York, Harold C. Urey and George M. Murphy measured the optical emission spectra of samples of hydrogen gas received by railway express shipment from the National Bureau of Standards in Washington, D.C., U.S.A. Urey arrived home late for Thanksgiving dinner, but with the news that he had discovered the mass 2 isotope of hydrogen. He later remarked, "I thought maybe my discovery might have the practical value of, say, neon in neon signs. My colleagues felt I was exaggerating [its] importance."

As it happens, the discovery by optical spectroscopy of that isotope, which Urey and his collaborators subsequently named "deuterium," transformed our understanding of nuclear structure. It made possible the first thermonuclear explosion 21 years later, and, just this past December, it provided perhaps the first direct glimpse of primordial gas created in the Big Bang.

A history of isotope chemistry

In the early 20th century, chemists were puzzled by the existence of isotopes: atoms of the same chemical element with different weights. These atoms had been discovered in 1912 by Soddy in his study of the decay of uranium to radon. He realized that there could be versions of an element whose masses were different, even though their chemical properties were the same. He named this concept an isotope, which is Latin for "same place." In other words, atoms of differing weight could occupy the same place in the periodic table as the original element. In 1913, J.J. Thomson succeeded in separating isotopes of neon by passing a beam of neon ions through a magnetic field, which deflects an ion in proportion to the ratio of its electric charge and mass.

Aston's construction of a mass spectrograph in 1919 made possible the discovery of many other isotopes of stable elements. By Thanksgiving Day 1931, almost all of the stable isotopes of light atoms that are known today had been found, mostly via mass spectroscopy.

Everything changed within a few months. Deuterium, the heavy stable isotope of hydrogen, was discovered Thanksgiving afternoon in the optical spectrum of the hydrogen atom. The neutron was discovered in February 1932. Shortly thereafter, Werner Heisenberg's suggestion that neutrons and protons were alternative quantum states of the same particle deepened physicists' understanding of the structure of the nucleus, and the electrolysis of water proved to be an efficient means for producing deuterium.

Wikipedia

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Few substances have had such rapid development from basic discovery to transformational applications. Industrial-scale production began in 1934. The 21st birthday of the discovery was marked by the ignition of the first nuclear fusion bomb, which was fueled by liquid deuterium.

Deuterium is now widely used in a variety of scientific and industrial tasks. The atomic spectroscopy used to find it is now a standard experiment in undergraduate physics laboratory courses. And new applications keep cropping up. For example, scientists recently conducted a more elaborate version of the same experiment to confirm the validity of the standard cosmological model of nucleosynthesis at the dawn of the universe.

Chemists noticed that the atomic weight of hydrogen as measured by chemical methods differed slightly from the physical value found in Aston's mass spectrograph. This discrepancy could be explained by the existence of a heavy isotope of hydrogen.

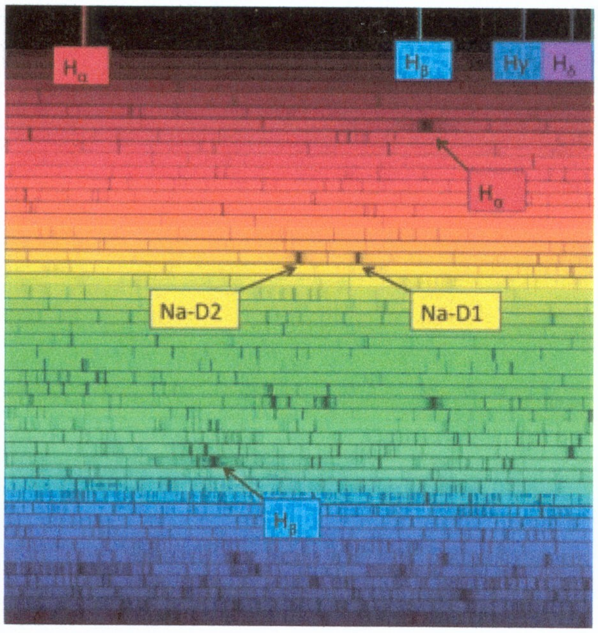
As of Thanksgiving 1931, researchers had accumulated much empirical knowledge on the nature of isotopes. The masses of isotopes had all been found to be close to integer multiples of the mass of atomic hydrogen, and the charges of all ions had been revealed to be multiples of the elementary charge of the hydrogen nucleus. That nucleus consists of one proton with a radius of about 10^{-15} m. According to Bohr's 1913 theory of the hydrogen atom, an electron moves around the proton in an orbit with a radius of about 5×10^{-11} m.

The mass of the proton is about 1,800 times that of the electron, and the proton and electron charges are opposite and equal to a high degree of accuracy. Thus, a reasonably accurate description of the masses of the isotopes came from supposing that their nuclei consisted entirely of protons plus some "nuclear-electrons" as needed to balance the nuclear charge. For example, the nucleus of helium-4 (^{4}He), which has the charge of two protons and the mass of about four protons, should consist of four protons plus two nuclear-electrons.

It was not known how nuclear-electrons could be confined to a volume that is 100 trillion times smaller than that of the atom, nor was there any understanding of which isotopes actually existed, as shown in the figure on p. 37. The pattern of isotopes shown suggests some obvious "missing links"—most notably, a hydrogen isotope of mass 2 (in units of the proton mass), which would arguably be the simplest example of an isotope. That isotope, subsequently named deuterium, had never been identified in mass spectroscopy.

One might think that it would be easy to find there, since its relative mass difference is greater than that for any other element in the periodic table. In fact, mass spectroscopy of hydrogen almost always displays a huge peak in the mass 2 channel, but this is due to the presence of the molecular ion H_2^+, an example of the phenomenon of "isobaric interference" that is pervasive in mass spectroscopy. Deuterium was hiding in plain sight!

[Solar spectrum of hydrogen absorption lines]



Spectrum of the Sun showing the absorption lines of H_α at 656 nm and H_β at 486 nm, as well as the famous D lines of sodium, D1 at 589 nm and D2 at 596 nm. This image was created from a Fourier transform spectrum at Kitt Peak National Observatory. The spectrum was chopped into 50 slices, each covering 6 nm and pasted together to simulate an echelle spectrogram, typical of what is often used with astronomical telescopes. Above the Sun's absorption spectrum is an emission spectrum showing H_α and H_β as well H_γ at 434 nm and H_δ at 410 nm.

The hunt for heavy hydrogen

In early 1931, chemists noticed that the atomic weight of hydrogen as measured by chemical methods differed slightly from the physical value found in Aston's mass spectrograph. This discrepancy could be explained by the existence of a heavy isotope of hydrogen in nature.

Harold C. Urey, then an associate professor of chemistry at Columbia University, spearheaded the search. Fixed to the wall of his laboratory was a chart similar to the one on the left side of the figure on p. 37, which served as a constant reminder to Urey of the likely existence of a heavy isotope of hydrogen. At some point Urey realized, as he wrote in his Nobel Prize lecture in 1934, that "Bohr's theory, given some 20 years ago, permits the calculation of the Balmer spectrum of the heavier isotopes of hydrogen from [the] spectrum of hydrogen."

The Balmer spectrum is the portion of the spectrum of atomic hydrogen that has emission and absorption lines visible to the eye. The Bohr theory depicts a nucleus of mass M and electron of mass m in motion about their common center of mass, which is always much closer to the nucleus than the electron. In the center-of-mass frame, a nucleus of mass M executes a small orbital motion, with a radius of (m/M) times the atomic radius, and the kinetic energy of that minor orbital motion adds directly to the energy of the atom. For hydrogen, $m/M = 1/1{,}836$, so this is quite a small effect, even less for possible heavier isotopes of hydrogen.

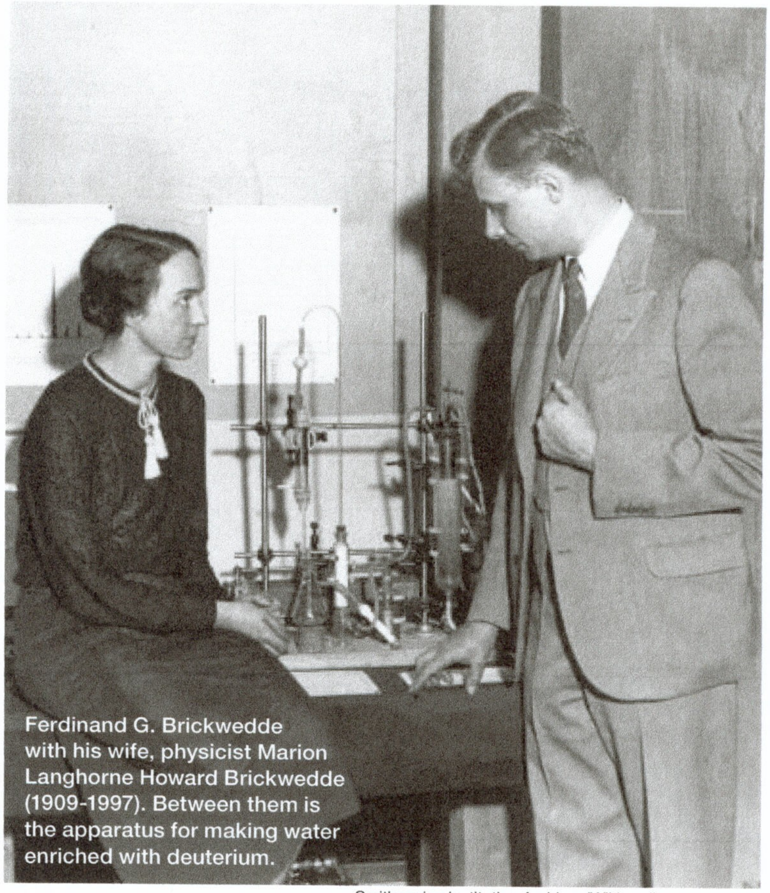
Low-temperature physics joins atomic spectroscopy

The energy of nuclear motion introduces a shift of about 0.1 nm between the wavelengths of the Balmer lines of hydrogen and a hypothetical isotope of mass 2, an effect that was well within the resolving power of the diffraction grating spectrometer that Urey had built at Columbia. He and his associate George M. Murphy evidently saw the lines of the mass 2 isotope soon after they started looking for them. However, due to the low natural abundance of the heavy isotope, these lines were weak features that were comparable to some known artifacts in the spectrum.

Urey decided to try to make samples of hydrogen in which the concentration of heavy isotopes would be enriched. He settled on the idea of creating liquid hydrogen and evaporating it near its triple point. This distillation should leave behind a liquid in which heavier isotopes are concentrated, since heavier molecules have lower speeds of thermal motion, and should be less likely to evaporate from the liquid. To pursue this approach, Urey enlisted the help of Ferdinand G. Brickwedde, chief of the Low Temperature Laboratory of the National Bureau of Standards (NBS) in in the autumn of 1931 in Washington, D.C. NBS is now the National Institute of Standards and Technology, or NIST.

Then only 28 years old, Brickwedde had already developed a reputation in low-temperature physics. Earlier that year, he led an NBS team that produced the first liquid helium made in the United States (which, by the way, made NBS only the fourth laboratory in the world to liquefy helium in the 23 years since its first production by Heike Kamerlingh Onnes in Leiden, Holland). His laboratory was then one of only two in the United States that could produce liquid hydrogen on a regular basis, the other being that at the University of California, Berkeley, directed by William F. Giauque (subsequently Nobel Laureate in chemistry, 1949).

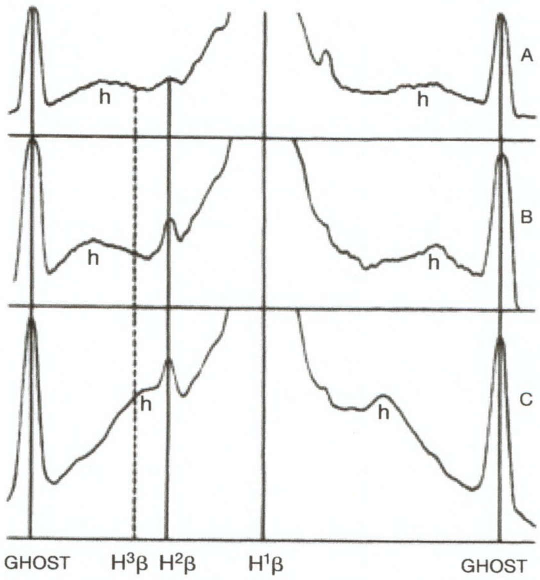
In the hunt for a heavy isotope of hydrogen, Brickwedde prepared several samples of liquid hydrogen at different levels of distillation. The most enriched was a sample that started with 4,000 cm^3 of liquid hydrogen and had all but 1 cm^3 evaporated off. The samples were sent by railway express from NBS to Columbia University, where their emission spectra were recorded with Urey's high-resolution spectrometer. The



Ferdinand G. Brickwedde with his wife, physicist Marion Langhorne Howard Brickwedde (1909-1997). Between them is the apparatus for making water enriched with deuterium.

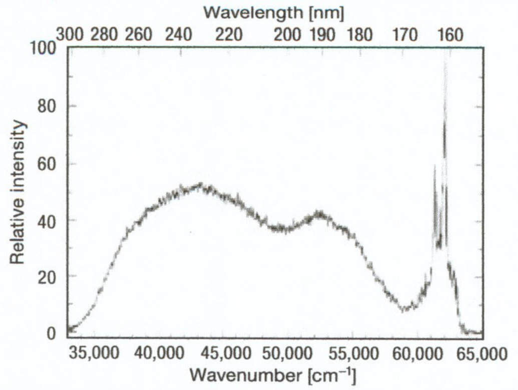
Smithsonian Institution Archives/Wikimedia

[Balmer emission spectra of three samples]



Ferdinand Brickwedde prepared three samples to increasingly concentrate any heavy isotopes of hydrogen. $H^1\beta$ is the ordinary Balmer line of atomic hydrogen at 486.1 nm, in the blue-green. $H^2\beta$ and $H^3\beta$ mark the lines predicted by the Bohr theory for emissions by isotopes of mass 2 and 3, respectively. The "ghost" and "halation" features are instrumental artifacts; their prominence with respect to the obvious $H^2\beta$ feature motivated Urey to show that that feature was enhanced by distilling liquid hydrogen, resulting in a relative increase of the mass 2 isotope (deuterium). No evidence for mass 3 (tritium) is seen.

[Continuous emission from a deuterium lamp]



Continuous emission from a deuterium lamp observed with a Fourier transform spectrometer at the National Institute of Standards and Technology. In the 160 nm region are emission lines of molecular hydrogen. The long wavelength cutoff near 286 nm is due to the falloff in the detector response in this region.

results showed that, at the wavelength that Bohr's theory predicted for the mass 2 isotope of hydrogen, there was a line that grew in strength with the expected concentration of the sample. There was no evidence for an isotope of mass 3. It seems fitting that the discovery of deuterium took place using the very same Balmer spectral lines of hydrogen that provided key evidence for Bohr's atomic theory.

Brickwedde's samples were subsequently sent by Urey to Walker Bleakney, an eminent mass spectroscopist at Princeton University. Bleakney sought deuterium not in the mass 2 channel, which was notorious for isobaric interference, but in the mass 3 channel where the molecular ion HD^+ might be seen. This was successful.

Consequences of the discovery

The discovery of deuterium was published in *The Physical Review* on New Year's Day, 1932. Just seven weeks later, James Chadwick announced his discovery of the neutron: a neutral particle with a mass very nearly equal to that of the proton. In early June, Werner Heisenberg suggested that the neutron and proton should be regarded as two alternative states of a two-level quantum particle, which we now call the "nucleon." All nuclei would be made up only of these nucleons. If the coordinates (particle identity, spatial coordinates, spin) of any two particles in the nucleus would be interchanged, the wave function of the nucleus would change sign—that is, the nuclear wave function would be antisymmetric with respect to the interchange of any two nucleons. We now call particles that produce antisymmetric wave functions "fermions." Fermions are particles (electrons, protons, neutrons) or composite bodies (atoms or molecules) with half-integral spin. They obey the Pauli exclusion principle.

This instantly solved several outstanding problems with the previous nuclear-electron model. For example, the nucleus of lithium-6 (^{6}Li) was then known from molecular spectroscopy to be what we now call a boson, for which the wave function is invariant under the interchange of particles. Bosons are particles or composite bodies with integral spin. Since the nuclear charge of Li is $Z = 3$, in the old nuclear-electron model, the nucleus of ^{6}Li would have to contain six protons plus three nuclear electrons, or a total of nine fermions. But the composite particle of an odd number of fermions must be a fermion, not a boson. So the old model had to be discarded.

Randy Hulet's group at Rice University made a dramatic demonstration of the boson-fermion difference in the isotopes ^{6}Li and ^{7}Li in 2001. Their research involved creating a Bose-Einstein condensate of lithium atoms. It is not possible to create a Bose-Einstein condensate with fermions because of their adherence to the exclusion principle. Indeed, all Bose-Einstein condensates of atoms are done with bosons. Since the ^{6}Li atom has six fermions in its nucleus (three protons and three neutrons) and three electrons in Bohr orbits, the ^{6}Li atom constitutes a fermion. By the same token, the ^{7}Li atom constitutes a boson. When Hulet's group cooled atoms of these isotopes in the same magnetic trap, ^{7}Li underwent Bose-Einstein condensation, while ^{6}Li did not.

The nucleon idea resolved all of the outstanding problems in molecular spectroscopy, and the nucleon symmetrization principle made possible a systematic classification of states of nuclei which is valid to this day. It is a precursor to the standard model of particle physics.

Discovery to application

In 1934, Urey was awarded the Nobel Prize in chemistry for discovering deuterium, and Chadwick received the Nobel Prize in physics in 1935 for uncovering the neutron. Both discoveries were rapidly put to use. We now know that deuterium is found in sea water at a level of about 1 atom of deuterium (D) to 6,400 atoms of hydrogen (H). Working with Urey during 1932, Edward Washburn of NBS found efficient methods for separating the deuterated ("heavy") water from normal water by electrolysis, thereby eliminating the need to pursue the complex low-temperature road to obtaining deuterium.

Electrolysis techniques for deuterium separation were implemented on an industrial basis in 1934 at the Norsk Hydro hydroelectric plant in Rjukan, Norway. By 1935, Norsk Hydro was shipping 99 percent pure heavy water at a cost of \$0.50/g. The easy availability of deuterium spurred the growth of isotope chemistry, in which deuterium was substituted for hydrogen in molecules to elucidate molecular structure and biological function.

Deuterium also turned out to have unique value for the development of nuclear energy and weapons. It played a key role in the Nazi nuclear program in World War II. The Norsk Hydro plant in occupied Norway was the scene of protracted struggle, as dramatized in the 1965 film *The Heroes of Telemark.* When the United States decided to build a thermonuclear weapon (the "hydrogen bomb"), its resident center of expertise in low-temperature physics, NBS, was charged with producing large quantities of liquid deuterium to fuel the first test explosion, at Enewetak Atoll on 1 November 1952. Ferdinand Brickwedde led the NBS team that produced this fuel, and thus, within 21 years, he was instrumental both in the basic discovery of deuterium and its most spectacular application.

> The discovery of deuterium was published in *The Physical Review* on New Year's Day, 1932. Just seven weeks later, James Chadwick announced his discovery of the neutron.

Today, deuterium is at the heart of thermonuclear research through its fusion reaction with tritium to produce helium, thus releasing copious quantities of energy, both in hydrogen bombs and in the magnetically confined plasmas of tokamak reactors, such as the international ITER machine under construction in France. (Tritium is a radioactive isotope with a half-life of about 12 years. Produced by cosmic rays and nuclear fission, it has a relative abundance with respect to hydrogen of about 1 part in 10^{16}. There are only about 7 kg of tritium in Earth's environment at any given time.) Deuterium provides the moderator in heavy-water fission reactors to slow down the neutrons produced in the fission, so as to produce a chain reaction. The nucleus of deuterium, which consists of a single proton and neutron, is called the deuteron. It is used extensively in nuclear physics research.

In optics, deuterium is used to produce lamps that provide continua in the ultraviolet as background for absorption spectroscopy as well as for radiometric calibration of UV spectrometers. The spectrum is not a confluence of close lines. It is a pure continuum formed by the decay of an upper, bound, molecular state to an unbound lower state that dissociates. The continuum is a superposition of the continua formed by the decay of each of the vibrational levels in the upper state to the dissociating lower state. For deuterium, which is heavier than hydrogen, both the vibrational and rotational levels in the bound states are much more closely spaced than in hydrogen, and the continuum is thus much stronger. Hence, deuterium is preferred to hydrogen for use in commercial continuum lamps.

Deuterium and the origin of the universe

The abundance of deuterium in the cosmos is currently a subject of great interest. Its concentration in astronomical objects varies greatly from that on Earth. For example, the deuterium abundance on Jupiter has been measured at only 26 atoms of D per million atoms of H, compared to 156 atoms of D per million atoms of H on Earth. Because deuterium is destroyed in the interiors of stars faster than it is produced, and because other natural processes can only produce insignificant amounts of deuterium, nearly all deuterium found in nature is believed to have been produced in the Big Bang, 13.7 billion years ago!

Astronomers believe that the D/H ratio found in giant gas planets such as Jupiter represents something close to the true primordial ratio. The ratio measured in comets is similar to that on Earth—which leads to the speculation that the Earth's surface water may have originated in comets.

The question of measuring the true primordial D/H ratio is closely related to current questions regarding dark matter and dark energy. It is known from the cosmic microwave background that the fraction of all matter and energy in the universe that can be attributed to ordinary baryonic matter (protons and neutrons) is only about 4.5 percent. The other 95.5 percent is dark matter or dark energy. According to the Big Bang theory, this percentage predicts a cosmic ratio of 25 atoms of D per million atoms of H. The problem is to find an astronomical object that can be considered to be pristine—that is, not contaminated by heavy elements created by nucleosynthesis long after the Big Bang.

Recently astronomers M. Fumagalli, J.M. O'Meara and J.X. Prochaska used the 10-m Keck I telescope to observe light absorption from a quasar by an intergalactic cloud. Those observations have shown that this cloud contains almost no elements heavier than lithium, and can thus be considered to be uncontaminated. From the intensities of absorption line of D in this cloud, the D/H abundance ratio is determined as 20±5 atoms of D per million atoms of H. According to the authors, "The detection of deuterium in one system at the level predicted by primordial nucleosynthesis provides a direct confirmation of the standard cosmological model."

There will no doubt be much more science news regarding the applications of deuterium. It is a pleasure for us to note that both its initial discovery and its contributions to cosmology reported 80 years hence are both the results of atomic spectroscopy. Better living through … optics!

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