Hydrogen – an element for the Space Age!

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Abstract

Hydrogen, the simplest and most common element in the Universe, is often overlooked when considering the elements. This article investigates the element's discovery and early uses along with more recent discoveries including the unusual species H_3^+. It is aimed both as a resource and as a source of inspiration for teachers and students interested in the more unusual aspects of the elements. Concepts such as catalytic water splitting are discussed in the context of generating hydrogen and oxygen from ice reserves on the moon to initiate discussion of where such technologies could be at the forefront of future space exploration.

On the 50th anniversary of the first moon landings in 1969 it seems fitting to examine the importance of the simplest element, hydrogen, both in space and in space exploration. Hydrogen is the most abundant element in the universe where it is found in stars and some planets such as the "gas giant" Jupiter. Its flammability, low density and ability to expand rapidly from the liquid to gas state make it an excellent fuel for both terrestrial transport and the rockets used by space agencies the world over.

Origins

Hydrogen is found everywhere, in stars such as our sun, around planets and in interstellar space, and forms 75% of the mass of the universe. Once formed on Earth, through biological or geological activity, it is quickly lost from the atmosphere due to its volatile nature. Three isotopes are known to occur naturally; the simplest of which constitutes over 99% of the element on Earth.

RAM 1.008	**Flammability** Very high
Melting point -259 °C	**1st IE** 1312 kJmol^{-1}
Boiling point -253 °C	**Key bond enthalpies** H-H 436 kJmol^{-1} C-H 413 kJmol^{-1} O-H 463 kJmol^{-1} N-H 391 kJmol^{-1} H-Cl 434 kJmol^{-1}
State gas (25 °C)	
Electronegativity 2.200	
Radius 1.10 Å (vdW) 0.32 Å (cov)	

Table 1. Some properties of hydrogen

Discovery

It has been suggested that elemental hydrogen was first observed by Paracelsus but his *Opera Omnia* of 1658 does not mention the experiments later attributed to him. Instead, it is generally agreed that hydrogen was discovered by Robert Boyle in 1671 who treated iron with dilute sulfuric acid to generate a flammable gas. Later experiments by Henry Cavendish between 1766 and 1783 demonstrated that the same gas could be formed quantitatively through the action of several acids on a range of metals. In 1784 he reported his *Experiments on Air* to the Royal Society where he asserted that water was a compound of his "inflammable air" and a gas known as "dephlogisticated air". Dephlogisticated air had been isolated independently by Priestley and Scheele in the 1770s and is now known as oxygen. In 1783, and aware of Cavendish's experiments, Antoine Lavoisier proposed the name 'hydrogen' – Greek for 'water-former' – for this gas.

Figure 1. Henry Cavendish.

Hydrogen and the development of quantum mechanics

When heated in a vacuum hydrogen emits a distinctive line spectrum rather than the rainbow of colours seen in white light. This discovery by Johann Balmer in 1885 led him to develop a simple formula which, when solved, predicted the wavelength of these lines. Soon afterwards Johannes Rydberg revised the formula into its current form:

Name	**Symbols**	**Protons**	**Electrons**	**Neutrons**	**Abundance**	**Stable?**
Hydrogen	^{1}H (H)	1	1	0	99.98%	Yes
Deuterium	^{2}H (D)	1	1	1	< 0.02%	Yes
Tritium	^{3}H (T)	1	1	2	trace	No (β-decay)

Table 2. Isotopes of hydrogen

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

where λ is the line's wavelength, R_H is the Rydberg constant for hydrogen (1.0968 x 10^7 m^{-1}) and n is a whole number that is larger than 2. Solving the equation when n is 3, 4, 5 and 6 gives the first four emission lines at 410 nm, 434 nm, 486 nm and 656 nm. This appearance of integral values led Ernest Rutherford and Niels Bohr to develop models for the hydrogen atom which had concentric electronic orbits of increasing energies. This, in turn, led to Max Plank, Albert Einstein, Erwin Schrödinger, Paul Dirac and others to formulate the wave and quantum mechanics we now use to understand atomic behaviour.

Figure 2. The Balmer series for hydrogen.

Synthesis

In Nature hydrogen gas is formed during photosynthesis in photosystem II and in a range of hydrogenase enzymes. In addition to high temperature catalysis of organic compounds, hydrogen can also be generated from water through electrochemical or photocatalytic methods. As these result in the formation of a fuel and oxygen for respiration, water splitting has been identified as having applications in any future lunar and Martian exploration.

The proton

Hydrogen can lose its electron to form a proton (H^+) which is the active species in acids and highly reactive. It is most often encountered in the context of aqueous acids e.g. $HCl_{(aq)}$ in which it is more correctly described as H_3O^+, the hydronium (or oxonium) ion. The proton's small size and +1 charge give it a high charge density but by reacting with water it can reduce this property. In this form it is easy to isolate (e.g. complexed by 18-crown-6). Other forms of 'protonated water' have also been isolated including $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. This extended network of water molecules form through hydrogen bonding (see below) and helps to give an insight into the mechanisms by which protons move in aqueous solution.

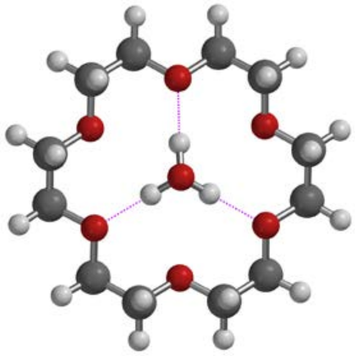

Figure 3. A computer model of H_3O^+ captured by 18-crown-6 showing hydrogen bonds in purple

Hydrides

Hydride species are found in three types of compounds:

Hydrogen can share its electron to form a covalent bond with a large number of elements. It often completes the valence of carbon or more polar elements such as nitrogen, to form amines, or oxygen to form alcohols. Other examples include H_2O, PH_3 or the metallic hydride BeH_2.

When combined with more electropositive elements hydrogen can gain an electron to form the very reactive hydride anion (H^-) which is isoelectronic with helium. Anionic hydrides can form when hydrogen reacts with any of the group 1 metals or with some inorganic reducing agents such as lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$). Compounds with the formula MH (where M is an alkali metal) are highly reactive and decompose in water sometimes igniting the H_2 that is produced.

Interstitial hydride compounds where hydrogen atoms absorbed into metallic lattices to fill interstitial sites – the tiny gaps between the metal atoms.

Hydrogen bonding

One of the most important aspects of hydrogen's chemistry is its ability to become positively polarised when bonded to a significantly more electronegative atom such as O, N or a halide. Electronegative atoms or negatively polarised molecules are in turn attracted to the hydrogen. This sets up a weak form of intermolecular interaction (5 - 50 $kJmol^{-1}$ *cf*. covalent bonds 150 - 1100 $kJmol^{-1}$) known as hydrogen bonding.

It is impossible to understate the importance of this interaction. It allows proteins to fold, DNA to bind complementary bases and replicate, and ensures that water is a liquid at room temperature. Indeed, life only exists on Earth because the planet is in the "Goldilocks zone" where water is normally in its liquid form and it is only liquid due to hydrogen bonding! Figure 4 shows the trends in boiling points for elemental hydrides in groups 14, 15 and 16 (data from Lide, 2005). Note that both oxygen and nitrogen induce hydrogen bonding whereas carbon does not and if the boiling point of water was extrapolated from those of H_2S, H_2Se and H_2Te it would be expected to boil at -100 °C – far too low for the biochemistry of life to occur. Hydrogen bonding is also responsible for the surface tension that allows insects to skate across ponds and lakes.

Figure 4. Boiling points for hydrides of group 14, 15 and 16 elements.

Hydrophobic interactions

When an organic molecule contains a large number of covalently bound hydrogens, as in an oil, it becomes hydrophobic and will not easily interact with water. While this may not seem very important, it has significant implications for chemical structures and properties. For example, if two hydrophobic molecules approach each other in water they will attempt to squeeze out any water molecules that are between them as this reduces the energy of the system. Such hydrophobic interactions are essential for many proteins and biomolecules to stick together – from the formation of cell membranes from phospholipids to the aggregation of proteins which allows active sites of enzymes to work together in complex biochemical pathways.

Applications

Use in air travel

The potential for hydrogen to fill a balloon and lift objects was noted by both the Scottish chemist Joseph Black and the French chemist Jacques Charles. The latter designed the first hydrogen balloon to fly, in August 1783 in Paris, for which the gas was generated by the action of sulfuric acid on iron. The experiment, observed by the American scientist, and later statesman, Benjamin Franklin, was a success and the unmanned balloon travelled for several miles. The first manned flight using hydrogen occurred in December 1783, also in Paris, with Charles piloting the balloon and a co-pilot in attendance. Later that day Charles, alone, took the balloon up 3 km into the air. He survived the flight but never ascended in a balloon again.

Despite the dangers of working with hydrogen, lighter-than-air-craft were famously developed by Ferdinand von Zeppelin. His original design dated to 1874 but the first airship, *Lufftschiff Zeppelin 1* (*LZ 1*), was not built until 1899 with its first flight in 1900. Von Zeppelin was unable to secure further funding until 1906 and, although several accidents and fires would dog the early models, over 10,000 people flew in his zeppelins up to the outbreak of World War I. The large size of these airships would require far greater quantities of hydrogen than could be generated quickly and safely from mineral acids and metals; the *Hindenburg* could hold 140,000 m^3 of hydrogen in its 16 gas bags. Fortunately a process using carbon monoxide and water, heated to over 500 °C in the presence of iron, had been invented in 1903 by Howard Lane (equations 1 to 3). The Lane hydrogen producer was able to provide the volumes of hydrogen gas needed for the airships.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (1)$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \quad (2)$$

Overall: $$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

During the war the zeppelins were used mainly for land and sea reconnaissance. Bombing raids, mainly over England and France, were largely unsuccessful due to difficulties manoeuvring the slow moving zeppelins and the ease with which they could be hit by enemy fire. After the war the remaining zeppelins were either destroyed or handed over to the Allied Powers.

The pre-war commercial success of the zeppelins resulted in a resurgence in airship manufacture from the 1920s. In Britain the *R100* and *R101* were built in 1929 but their success was short-lived. The *R101* caught fire and crashed near Beauvais in northern France on its first international flight in 1930, killing 48 of the 54 passengers and crew. The German *LZ 126 Graf Zeppelin* flew around the world in under 22 days in 1929 before it was joined on the transatlantic route by *LZ 129 Hindenburg* in 1936. The next year, while landing at Lakehurst in the USA, the

Hindenburg caught fire and crashed killing 35 of the 97 passengers and crew together with one person on the ground. Although it was not as deadly as the *R101* disaster, the *Hindenburg*'s destruction effectively ended airship travel. The crash was filmed and photographed by reporters on the scene and the live radio commentary by Herbert Morrison became instantly famous.

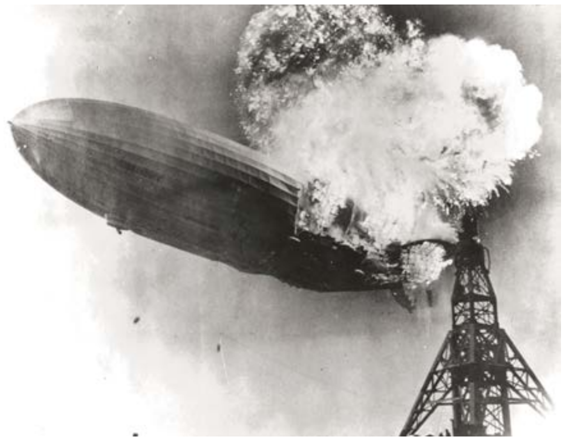

Figure 5. The ill-fated *Hindenburg*.

Use in terrestrial transport

Hydrogen has been seen as the ultimate 'green fuel' as its reaction with oxygen generates nothing but energy and pure water. The first experiments with hydrogen-powered cars date back to the *Hippomobile* designed by Étienne Lenoir in 1863 and used his internal combustion engine. Current examples store compressed hydrogen in tanks which is later combined with oxygen in a fuel cell stack, however, these cars are predominantly electric hybrid vehicles with hydrogen taking the place of petrol or diesel to generate 'zero emission' energy.

Use as rocket fuel

Saturn I, used in early NASA launces, and *Saturn V* rockets, that propelled NASA astronauts to the moon, incorporated three stages of engines. The first used a mixture of refined petroleum (RP-1) and liquid oxygen (LOX) to generate the energy required for lift off. Stages two and three used LOX and liquid hydrogen (LH2). By contrast the *Vostok* rockets, used by the Soviet Union in its space programme, had three stages powered by LOX/kerosene mixtures.

Figure 6. A *Saturn 1* rocket at the US Space & Rocket Center, Huntsville, Alabama, USA.

Hydrogen in space

In space hydrogen is found mainly as H atoms, plasma and a surprisingly large number of organic compounds. One very unusual form is the triangular molecule trihydrogen. This was first observed, as the charged species H_3^+, by J. J. Thomson in 1911. By 1989 it had been observed in Jupiter's atmosphere and it has since been found wherever astronomers have trained their infrared telescopes. In fact, the presence of H_3^+ has become an excellent method by which the temperatures of stars and planets can be measured as it absorbs sunlight and re-emits it at wavelengths which correlate to the molecule's temperature. H_3 can also exchange a hydrogen with a deuterium cation to give H_2D^+. In this species the ratio of the two hydrogen atoms' spin states can be used to estimate the age of the molecule and therefore the age of the star, dust cloud or planet in which the H_2D^+ is found (Pelley, 2019).

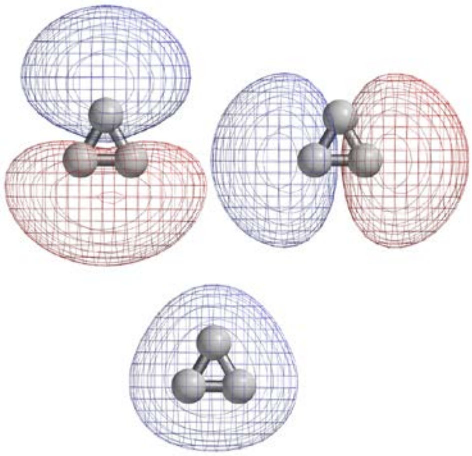

Figure 7. A computer model of H_3^+ showing its bonding (bottom) and antibonding (top) orbitals.

Could hydrogen from the moon or Mars help future space exploration?

In 2008 the Indian spacecraft Chandrayaan-1 dropped the Moon Impact Probe at the moon's South Pole and analysed the ejected debris. Mass spectrometric evidence was found for water and chemical species with the O-H absorption pattern were detected by infrared spectroscopy (Neish *et al.*, 2011). In 2010 instruments on board detected over 40 craters that were permanently frozen; estimates suggest that this could amount to 600 million tonnes of water. Analysis of data from NASA's Moon Mineralogy Mapper (M3) in 2018 supported these findings (Li *et al.*, 2018). These discoveries mean that astronauts landing at the poles would not only have access to drinking water but also a source of hydrogen and oxygen. Equipment designed to generate liquid water in low gravity environments and split it into its constituent elements could be trialled on the moon should humans return there.

It has long been established that Mars has had surface water in the past but in 2015 images from NASA's Mars Reconnaissance Rover showed changing surface features consistent with the release of salty water during seasonal warming. It is also likely that deep craters or caves in the walls of canyons contain mixtures of frozen carbon dioxide and water ice. If so, then a future mission to Mars could also be supported by technology developed on the moon.

Figure 8. The first astronauts on Mars could split water to generate hydrogen for fuel and oxygen to breathe.

References

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Useful online resources

The Royal Society of Chemistry has links to the properties of hydrogen and other interesting facts at http://www.rsc.org/periodic-table/element/1/hydrogen

Prof. Sir Martyn Poliakoff has an excellent video on YouTube at https://www.youtube.com/watch?v=6rdmpx39PRk

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