Hydrogen

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C O N N E X I O N S

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Chapter 1

Discovery of Hydrogen[1]

Hydrogen gas, H_2, was first artificially synthesized by Phillip von Hohenheim (known as Paracelsus, Figure 1.1) by mixing metals with strong acids. He was unaware that the flammable gas produced by this chemical reaction was a new chemical element. In 1671, Robert Boyle (Figure 1.2) rediscovered the reaction between iron filings and dilute acids, which results in the production of hydrogen gas. He noted that these fumes were highly flammable and that the flame gave off a lot of heat but not much light.

Figure 1.1: Renaissance physician, botanist, alchemist, and astrologer Paracelsus (1493 –1541).

[1] This content is available online at <http://cnx.org/content/m31897/1.2/>.

Figure 1.2: Irish philosopher, chemist, physicist, and inventor Robert Boyle (1627 –1691).

In 1766, Henry Cavendish (Figure 1.3) was the first to recognize hydrogen gas as a discrete substance, by identifying the gas from a metal-acid reaction as *flammable air*. One of the richest men in Britain at the time, he lived in London and spent his time in his private laboratory at his home. In 1781 he was the first person to find that the gas produces water when burned. This was a key experiment in disproving the Aristotelian theory of the four elements. As a consequence of his work he is usually given credit for its discovery as an element. However, it was Antoine Lavoisier (Figure 1.4) who in 1783 named the element *hydrogen* (from the Greek *hydro* meaning water and *genes* meaning creator) after he reproduced Cavendish's findings.

> NOTE: The four Aristotalian elements were *Earth*, *Fire*, *Air* and *Water*. A fifth element, *Aether*, was ascribed as a divine substance that made up the heavenly spheres and heavenly bodies (stars and planets).

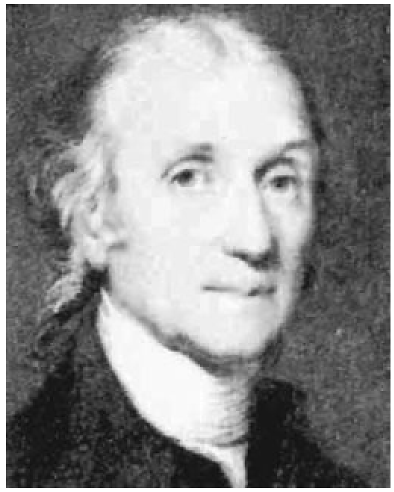

Figure 1.3: British scientist Henry Cavendish (1731 - 1810).

Figure 1.4: French chemist and biologist Antoine-Laurent de Lavoisier (1743 – 1794).

Using his invention, the vacuum flask, James Dewar (Figure 1.5) was the first to liquefy hydrogen in 1898. He produced solid hydrogen the next year.

Figure 1.5: Scottish chemist and physicist Sir James Dewar FRS (1842 –1923).

Chapter 2

The Physical Properties of Hydrogen[1]

Chemical symbol	H
Atomic number	1
Electron configuration	$1s^1$
Atomic weight	1.00794
Melting point	-259 °C
Boiling point	-253 °C
Density (gas)	0.090 g/L
Density (liquid)	0.070 g/L
Ionization potential	13.598 eV
Pauling electronegativity	2.1
Ionic radius (H^-)	1.54 Å
van der Waal radius	1.2 Å
Explosive limit	4 - 75%
Ignition temperature	585 °C

Table 2.1: Physical properties of hydrogen.

[1] This content is available online at <http://cnx.org/content/m31908/1.2/>.

Chapter 3

Synthesis of Molecular Hydrogen[1]

Although hydrogen is the most abundant element in the universe, its reactivity means that it exists as compounds with other elements. Thus, molecular hydrogen, H_2, must be prepared from other compounds. The following outlines a selection of synthetic methods.

3.1 Steam reforming of carbon and hydrocarbons

Many reactions are available for the production of hydrogen from the reaction of steam with a carbon source. The choice of reaction is guided by the availability of raw materials and the desired purity of the hydrogen. The simplest reaction involves passing steam over coke at high temperatures (1000 °C).

$$C_{(s)} + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{(g)} \quad (3.1)$$

Coke is a grey, hard, and porous carbonaceous material derived from destructive distillation of low-ash, low-sulfur bituminous coal. As an alternative to coke, methane may be used at a slightly higher temperature (1100 °C).

$$CH_{4(g)} + H_2O_{(g)} \rightarrow 3\,H_{2(g)} + CO_{(g)} \quad (3.2)$$

In each case the carbon monoxide formed in the reaction can react further with steam in the presence of a suitable catalyst (usually iron or cobalt oxide) to generate further hydrogen.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)} \quad (3.3)$$

This reaction is known as the water gas-shift reaction, and was discovered by Italian physicist Felice Fontana (Figure 3.1) in 1780.

[1] This content is available online at <http://cnx.org/content/m31442/1.3/>.

Figure 3.1: Italian physicist Felice Fontana (1730 - 1805).

The dominant industrial process for hydrogen production uses natural gas or oil refinery feedstock in the presence of a nickel catalyst at 900 °C.

$$C_3H_{8(g)} + 3\,H_2O_{(g)} \rightarrow 7\,H_{2(g)} + 3\,CO_{(g)} \tag{3.4}$$

3.2 Electrolysis of water

Electrolysis of acidified water in with platinum electrodes is a simple (although energy intensive) route to hydrogen.

$$2\,H_2O_{(l)} \rightarrow 2\,H_{2(g)} + O_{2(g)} \tag{3.5}$$

On a larger scale hydrolysis of warm aqueous solutions of barium hydroxide can yield hydrogen of purity greater than 99.95%. Hydrogen is also formed as a side product in the production of chlorine from electrolysis of brine (NaCl) solutions in the presence of a mercury electrode.

$$2\,NaCl_{(aq)} + 2\,Hg_{(l)} \rightarrow Cl_{2(g)} + 2\,NaHg_{(l)} \tag{3.6}$$

The sodium mercury amalgam reacts with water to yield hydrogen.

$$2\,NaHg_{(l)} + 2\,H_2O_{(l)} \rightarrow H_{2(g)} + 2\,NaOH_{(aq)} + 2\,Hg_{(l)} \tag{3.7}$$

Thus, the overall reaction can be written as:

$$2\,NaCl_{(aq)} + H_2O_{(l)} \rightarrow H_{2(g)} + 2\,NaOH_{(aq)} + Cl_{2(g)} \tag{3.8}$$

However, this method is being phased out for environmental reasons.

3.3 Reaction of metal with acid

Hydrogen is produced by the reaction of highly electropositive metals with water, and less reactive metals with acids, e.g.,

$$Fe_{(s)} + 2\ H_3O^+_{(aq)} \rightarrow H_{2(g)} + 2\ H_2O_{(aq)} + Fe^{2+}_{(aq)} \tag{3.9}$$

This method was originally used by Henry Cavendish (Figure 3.2) during his studies that led to the understanding of hydrogen as an element (Figure 3.3).

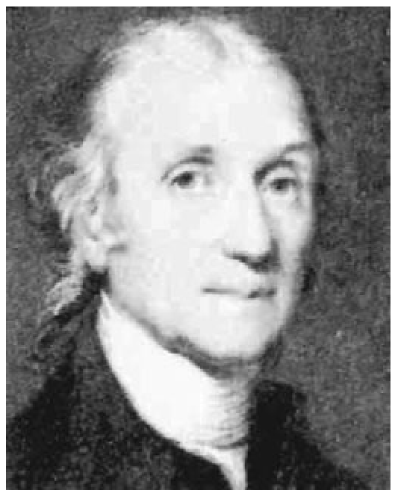

Figure 3.2: Henry Cavendish (1731 - 1810).

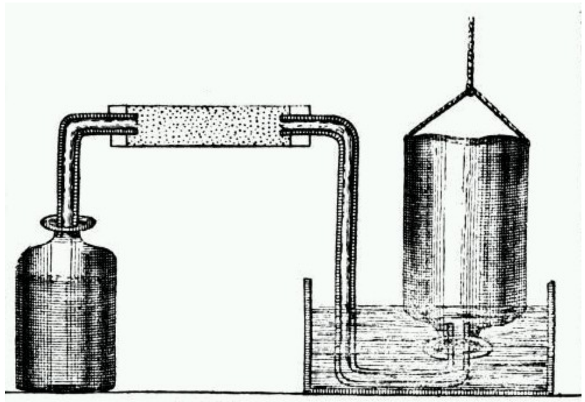

Figure 3.3: Cavendish's apparatus for making hydrogen in the left hand jar by the reaction of a strong acid with a metal and collecting the hydrogen gas above water in the right hand inverted jar.

The same method was employed by French inventor Jacques Charles (Figure 3.4) for the first flight of a hydrogen balloon on 27$^{\text{th}}$ August 1783. Unfortunately, terrified peasants destroyed his balloon when it landed outside of Paris.

Figure 3.4: Jacques Alexandre César Charles (1746 – 1823).

3.4 Hydrolysis of metal hydrides

Reactive metal hydrides such as calcium hydride (CaH_2) undergo rapid hydrolysis to liberate hydrogen.

$$CaH_{2(s)} + 2\,H_2O_{(l)} \rightarrow 2\,H_{2(g)} + 2\,OH^-_{(aq)} + Ca^{2+}_{(aq)} \tag{3.10}$$

This reaction is sometimes used to inflate life rafts and weather balloons where a simple, compact means of generating H_2 is desired.