Chapter 2

Hydrogen

2.1 Discovery of Hydrogen[1]

Hydrogen gas, H_2, was first artificially synthesized by Phillip von Hohenheim (known as Paracelsus, Figure 2.1) 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 2.2) 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 2.1: Renaissance physician, botanist, alchemist, and astrologer Paracelsus (1493 –1541).

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

Figure 2.2: Irish philosopher, chemist, physicist, and inventor Robert Boyle (1627 –1691).

In 1766, Henry Cavendish (Figure 2.3) 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 2.4) 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).

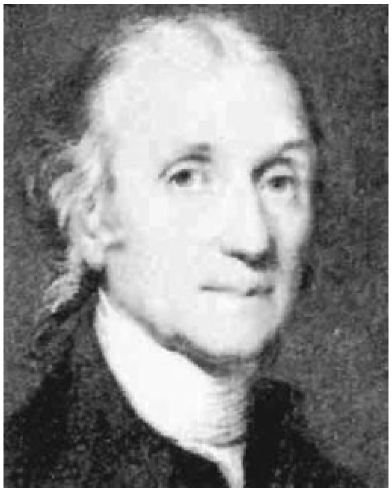

Figure 2.3: British scientist Henry Cavendish (1731 - 1810).

Figure 2.4: French chemist and biologist Antoine-Laurent de Lavoisier (1743 – 1794).

Using his invention, the vacuum flask, James Dewar (Figure 2.5) was the first to liquefy hydrogen in 1898. He produced solid hydrogen the next year.

Figure 2.5: Scottish chemist and physicist Sir James Dewar FRS (1842 –1923).

2.2 The Physical Properties of Hydrogen[2]

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.

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

2.3 Synthesis of Molecular Hydrogen[3]

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.

2.3.1 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).

$$C_{(s)} + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{(g)} \tag{2.1}$$

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).

$$CH_{4(g)} + H_2O_{(g)} \rightarrow 3\,H_{2(g)} + CO_{(g)} \tag{2.2}$$

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.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)} \tag{2.3}$$

This reaction is known as the water gas-shift reaction, and was discovered by Italian physicist Felice Fontana (Figure 2.6) in 1780.

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

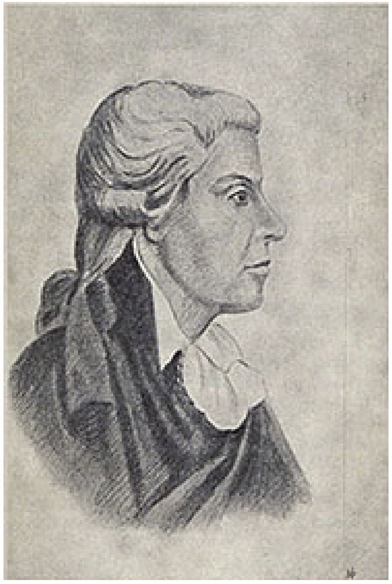

Figure 2.6: Italian physicist Felice Fontana (1730 - 1805).

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

$$C_3H_{8(g)} + 3\,H_2O_{(g)} \rightarrow 7\,H_{2(g)} + 3\,CO_{(g)} \qquad (2.4)$$

2.3.2 Electrolysis of water

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

$$2\,H_2O_{(l)} \rightarrow 2\,H_{2(g)} + O_{2(g)} \qquad (2.5)$$

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.

$$2\,NaCl_{(aq)} + 2\,Hg_{(l)} \rightarrow Cl_{2(g)} + 2\,NaHg_{(l)} \qquad (2.6)$$

The sodium mercury amalgam reacts with water to yield hydrogen.

$$2\,NaHg_{(l)} + 2\,H_2O_{(l)} \rightarrow H_{2(g)} + 2\,NaOH_{(aq)} + 2\,Hg_{(l)} \qquad (2.7)$$

Thus, the overall reaction can be written as:

$$2\,NaCl_{(aq)} + H_2O_{(l)} \rightarrow H_{2(g)} + 2\,NaOH_{(aq)} + Cl_{2(g)} \qquad (2.8)$$

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

2.3.3 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.,

$$Fe_{(s)} + 2\,H_3O^{+}{}_{(aq)} \rightarrow H_{2(g)} + 2\,H_2O_{(aq)} + Fe^{2+}{}_{(aq)} \qquad (2.9)$$

This method was originally used by Henry Cavendish (Figure 2.7) during his studies that led to the understanding of hydrogen as an element (Figure 2.8).

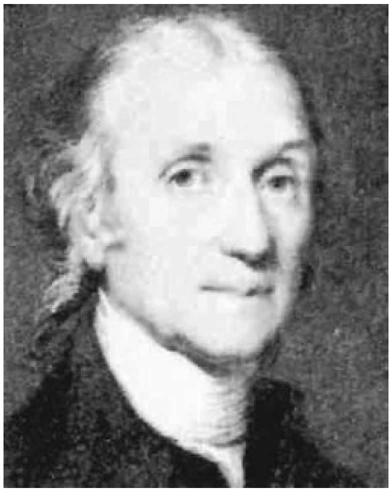

Figure 2.7: Henry Cavendish (1731 - 1810).

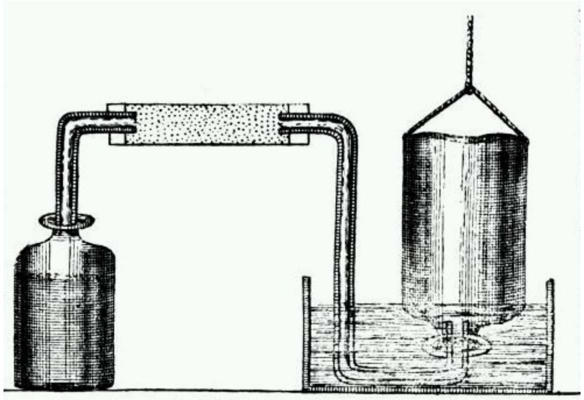

Figure 2.8: Cavendish's apparatus for making hydrogen in the left hand jar by the reaction of a strong acid with a metal and collecting the hydrogen gas above water in the right hand inverted jar.

The same method was employed by French inventor Jacques Charles (Figure 2.9) for the first flight of a hydrogen balloon on 27th August 1783. Unfortunately, terrified peasants destroyed his balloon when it landed outside of Paris.

Figure 2.9: Jacques Alexandre César Charles (1746 – 1823).

2.3.4 Hydrolysis of metal hydrides

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

$$CaH_{2(s)} + 2\,H_2O_{(l)} \rightarrow 2\,H_{2(g)} + 2\,OH^-_{(aq)} + Ca^{2+}_{(aq)} \tag{2.10}$$

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

2.4 Atomic Hydrogen[4]

Atomic hydrogen has the electron configuration of $1s^1$ and as such represents the simplest atomic configuration. However, as a consequence there is dispute as to its proper position within the Periodic Table. Its electron configuration is similar to the valence electron configuration of the alkali metals (ns^1) suggesting it be listed at the top of Group 1 (1A). However, its reaction chemistry is dissimilar to the alkali metals. Hydrogen is also one electron short of a Nobel gas configuration, and therefore it is possible to think of its relationship to the halogens.

2.4.1 Vapor phase

Atomic hydrogen ($H^\cdot$) is highly reactive and consequently has a short lifetime due to its reaction chemistry. Consequently, in order to generate and observe the reactivity they must be generate at low pressures.

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[4] This content is available online at <http://cnx.org/content/m16928/1.8/>.

Thermolysis of hydrogen compound (commonly halide) or photolysis at an energy above the bond dissociation energy results in the homoleptic cleavage of the H-X bond to generate the appropriate radical species.

$$\text{H-X} \xrightleftharpoons{\Delta \text{ or } h\nu} \text{H}^{\cdot} + \text{X}^{\cdot} \tag{2.11}$$

Alternatively, atomic hydrogen can be generated from elemental hydrogen.

$$\text{H-H} \xrightleftharpoons{\Delta \text{ or } h\nu} \text{H}^{\cdot} + \text{H}^{\cdot} \tag{2.12}$$

The reverse reaction (recombination of two hydrogen atoms) is highly exothermic (-434 kJ.mol^{-1}) and forms the basis of the heat generated in arc welding.

2.4.2 Solution

Atomic hydrogen may be generated in aqueous solution through the solvation of electrons.

$$\text{e}^{-}_{(aq)} + \text{H}_3\text{O}^{+} \rightleftharpoons \text{H}^{\cdot}_{(aq)} + \text{H}_2\text{O} \tag{2.13}$$

The formation equilibrium constant (K_{eq}) is very small resulting in very low concentrations being generated (10^{-5} M). As expected solvated atomic hydrogen is a strong reducing agent.

$$\text{Ag}^{+} + \text{H}^{\cdot} \rightarrow \text{Ag} + \text{H}^{+} \tag{2.14}$$

$$2\text{I}^{-} + 2\,\text{H}^{\cdot} \rightarrow 2\,\text{H}^{+} + \text{I}_2 \tag{2.15}$$

2.4.3 Solid state

Hydrogen atoms may be trapped in the solid state lattice upon generation by photolysis of HX. Observation by electron spin resonance (esr) of a signal split by $s = {}^{1}/_{2}$ nucleus (i.e., ^{1}H) results in a doublet with a coupling of 1428 MHz.

2.5 The Proton[5]

The proton, H^{+}, is the name given to hydrogen in the $+1$ oxidation state.

2.5.1 Gas phase

The proton can be formed from the photolysis of atomic hydrogen in the vapor phase at low pressure.

$$\text{H}^{\cdot}_{(g)} + h\nu \rightarrow \text{H}^{+}_{(g)} + \text{e}^{-}_{(g)} \tag{2.16}$$

The proton is more reactive than the hydrogen atom because of its high charge density. In addition, the proton's small ionic radius, 1.5 x 10^{-15} cm, means that it can get close to other atoms and hence form strong bonds.

$$\text{H}^{+}_{(g)} + \text{NR}_3 \rightarrow \text{HNR}_3{}^{+}_{(g)} \tag{2.17}$$

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[5] This content is available online at <http://cnx.org/content/m31441/1.2/>.

The strength of the bonding interaction is such that it is very hard to measure directly. Instead the relative bond strength between the proton and an appropriate base, B_1, is measured in the presence of a competing base, B_2.

$$B_1H^+_{(g)} + B_{2(g)} \rightleftharpoons B_2H^+_{(g)} + B_{1(g)} \qquad (2.18)$$

In measuring the exchange reaction, the *relative proton affinity* of B_1 and B_2 is measured. This is also known as the gas phase acidity, and as such it is a measure of the inherent acidity of a species X-H because it obviates any solvent effects.

2.5.2 Liquid and solution

The high reactivity of the proton means that it does not exist *free* in solution. There are however many H^+ containing species. These are generally classified as *acids*.

$$\underset{acid}{B_1H^+_{(sol)}} + \underset{base}{B_{2(sol)}} \rightleftharpoons \underset{acid}{B_2H^+_{(sol)}} + \underset{base}{B_{1(sol)}} \qquad (2.19)$$

The reaction between the acid and the base is a proton transfer reaction. While the proton travels from B_1 to B_2, it is never free in solution. Instead a bridged transition state or intermediate is formed, $B_1 \cdots H^+ \cdots B_2$.

2.5.2.1 Acidity and pH

The most common solvent for H^+ is water. The acid form is usually defined as the hydronium ion or H_3O^+, (2.20). The terms oxonium, hydroxonium and oxidanium are also used for the H_3O^+. Although we commonly use H_3O^+ it is known from spectroscopy that larger complexes are formed such as $H_9O_4{}^+$ (Figure 2.10).

$$H_2O + H^+ \rightarrow H_3O^+ \qquad (2.20)$$

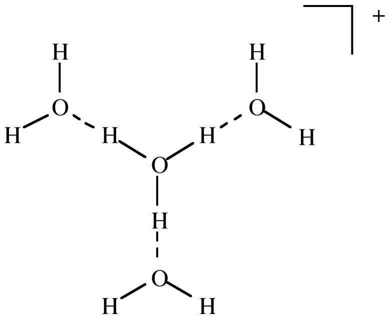

Figure 2.10: Structure of $H_9O_4{}^+$.

Acids and bases have been characterized in a number of different ways. In 1680 Robert Boyle (Figure 2.11) defined an acid as a compound that dissolved many other compounds, had a sour taste, and reacted with alkali (base).

Figure 2.11: Portrait of Robert Boyle (1627 – 1691).

Boyle's simple observational description was rationalized by Danish physical chemist Johannes Brønsted (Figure 2.12). Brønsted proposed that acids are *proton donors*, and bases are *proton acceptors*. An acid-base reaction is one in which a proton is transferred from a proton donor (acid) to a proton acceptor (base). Based upon Brønsted's proposal simple acids contain an ionizable proton. Examples of simple acids include neutral molecules (HCl, H_2SO_4), anions (HSO_4^-, $H_2PO_4^-$), and cations (NH_4^+). The most common Brønsted bases include metal hydroxides (MOH).

Figure 2.12: Johannes Nicolaus Brønsted (1879 –1947).

Brønsted noted that when an acid donates a proton it forms a conjugate base. The following are examples of an acid and its conjugate base.

$$\underset{\textit{acid}}{H_2O} \rightarrow H^+ + \underset{\textit{conjugate base}}{OH^-} \tag{2.21}$$

$$\underset{\textit{acid}}{H_2SO_4} \rightarrow H^+ + \underset{\textit{conjugate base}}{HSO_4^-} \tag{2.22}$$

$$\underset{\textit{acid}}{NH_4^+} \rightarrow H^+ + \underset{\textit{conjugate base}}{NH_3} \tag{2.23}$$

Exercise 2.5.1 ***(Solution on p. 104.)***

What is the conjugate base of HCl?

Exercise 2.5.2 ***(Solution on p. 104.)***

What is the conjugate base of HSO_4^-?

Exercise 2.5.3 ***(Solution on p. 104.)***

What is the conjugate base of $[Al(H_2O)_6]^{3+}$?

The same occurs when a base accepts a proton it forms a conjugate acid. The following are examples of a base and its conjugate acid.

$$\underset{\textit{base}}{H_2O} + H^+ \rightarrow \underset{\textit{conjugate acid}}{H_3O^+} \tag{2.24}$$

$$\underset{\textit{base}}{HCO_3^-} + H^+ \rightarrow \underset{\textit{conjugate acid}}{H_2CO_3} \tag{2.25}$$

$$\underset{\textit{base}}{F^-} + H^+ \rightarrow \underset{\textit{conjugate acid}}{HF} \tag{2.26}$$

Exercise 2.5.4 ***(Solution on p. 104.)***

What is the conjugate acid of NH_3?

Exercise 2.5.5 ***(Solution on p. 104.)***

What is the conjugate acid of S^{2-}?

Exercise 2.5.6 ***(Solution on p. 104.)***

What is the conjugate acid of CO_3^{2-}?

Thus, the reaction between an acid and a base results in the formation of the appropriate conjugate base and conjugate acid.

$$\text{acid}_1 + \text{base}_1 \rightleftharpoons \text{acid}_2 + \text{base}_2 \tag{2.27}$$

A specific example is as follows:

$$\underset{acid_1}{HNO_3} + \underset{base_1}{NH_3} \rightleftharpoons \underset{acid_2}{NH_4^+} + \underset{base_2}{NO_3^-} \qquad (2.28)$$

Exercise 2.5.7 ***(Solution on p. 104.)***

What is the conjugate acid and base formed from the reaction of NH_4^+ with S^{2-}?

In the equilibrium reactions shown in (2.27) and (2.28) there is a competition between the two bases for the proton. As would be expected the strongest base wins.

When a strong acid is added to (dissolved in) water it will react with the water as a base:

$$\underset{acid}{HCl} + \underset{base}{H_2O} \rightarrow \underset{acid}{H_3O^+} + \underset{base}{Cl^-} \qquad (2.29)$$

In contrast, when a strong base is added to (dissolved in) water it will react with the water as an acid:

$$\underset{acid}{H_2O} + \underset{base}{NH_3} \rightarrow \underset{acid}{NH_4^+} + \underset{base}{OH^-} \qquad (2.30)$$

2.5.2.2 pH a measure of acidity

The acidity of a water (aqueous) solution depends on the concentration of the hydronium ion, i.e., $[H_3O^+]$. The acidity of a solution is therefore the ability of the solution to donate a proton to a base. The acidity or pH of a solution is defined as:

$$pH = -\log [H_3O^+{}_a] \qquad (2.31)$$

It is important to note that the value is the *activity* of H_3O^+ and not the *concentration*.

> NOTE: Activity is a measure of the "effective concentration" of a species in a mixture. The difference between activity and other measures of composition such as concentration arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other.

The activity of the H_3O^+ ion can be measured by

(a) A glass electrode.
(b) Acid-base indicators.

2.5.2.3 Proton Transfer Reactions

The proton transfer reaction is one of the simplest reactions in chemistry. It involves no electrons and low mass transfer/change, giving it a low energy of activation. For proton transfer between O-H or N-H groups and their associated bases the reaction is very fast. The proton transfer occurs across a hydrogen-bonded pathway during which the proton is never free.

2.6 Hydrides[6]

The combination of hydrogen with another element produces a hydride, E_xH_y. The formal charge or oxidation state of the hydrogen in these compounds is dependant on the relative electronegativity of the element in question.

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[6] This content is available online at <http://cnx.org/content/m31549/1.3/>.

2.6.1 Ionic hydrides

Hydrogen compounds with highly electropositive metals, i.e., those in which the metal has an electronegativity of less than 1.2, are ionic with the hydrogen having a s^2 configuration (H^-). Typical ionic metal hydrides are those of the Group 1 (IA) metals and the heavier Group 2 (IIA) metals.

The ionic radius of the hydride ion is in between that of fluoride and chloride and the same as oxide (Table 2.2). As a consequence, in the solid state the hydride ion replicates that of a halide ion (e.g., Cl^-), and as such similar solid state structures are observed (Table 2.3).

Ion	**Ionic radius (Å)**
H^-	1.40
F^-	1.36
Cl^-	1.81
O^{2-}	1.40

Table 2.2: Selected ionic radii.

Metal	**Hydride**	**Fluoride**	**Chloride**
Li	4.085	4.0173	5.129
Na	4.880	4.620	5.640
K	5.700	5.347	6.292
Rb	6.037	5.640	6.581
Cs	6.376	6.008	7.020

Table 2.3: Lattice parameters (Å) for hydrides, and halides of the Group 1 metal salts with cubic rock salt structures.

Unlike the halide ions that are soluble in water, the hydride ion reacts with water, (2.32), and consequently NaH and CaH_2 are commonly used as drying agents. The liberation of hydrogen was used as a commercial source of hydrogen for small-scale applications.

$$H^- + H_2O \rightarrow OH^- + H_{2\,(g)} \qquad (2.32)$$

> WARNING: Group 1 and 2 metal hydrides can ignite in air, especially upon contact with water to release hydrogen, which is also flammable. Hydrolysis converts the hydride into the analogous hydroxide, which are caustic bases. In practice, most ionic hydrides are dispensed as a dispersion in oil, which can be safely handled in air.

2.6.2 Covalent hydrides

The most common binary compounds of hydrogen are those in which hydrogen bonds have covalent bond character. The E-H bond is usually polar ranging from those in which the hydrogen is polarized positively (e.g., those with non-metals such as F, O, S, and C) to where it is negative (e.g., those with metals and metalloids such as B, Al, etc). Magnesium hydride is intermediate between covalent and ionic since it has a polymeric solid similar to AlH_3, but reacts rapidly with water like ionic hydrides. Table 2.4 lists the important covalent hydrides of p-block elements. It should be noted that all organic hydrocarbons can be thought of as simply the hydrides of carbon!

Group 13	**Group 14**	**Group 15**	**Group 16**	**Group 17**
B_2H_6	C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}	NH_3, N_2H_4	H_2O, H_2O_2	HF
$(AlH_3)_n$	Si_nH_{2n+2}	PH_3, P_2H_4	H_2S, H_2S_n	HCl
Ga_2H_6	Ge_nH_{2n+2}	AsH_3	H_2Se	HBr
	SnH_4	SbH_3	H_2Te	HI

Table 2.4: Important covalent hydrides of the p-block elements.

The elements of Group 14 to 17 all form hydrides with normal covalent bonds in which the hydrogen is bonded by a single bond to the element in question. In contrast, the elements of Group 13 (as typified by boron) all exhibit a second type of covalent bond: the electron deficient hydrogen bridged bond. In this type of bond the hydrogen nucleus is embedded in a molecular orbital that covers more than two atoms to create a multi-center two-electron bond. Diborane (Figure 2.13) represents the archetypal compound containing the hydrogen bridge bond. Hydrides are not limited to terminal (E-H) or those bridging two atoms (E-H-E), but are also known where the hydrogen bridges (or caps) more than two atoms, i.e., Figure 2.14.

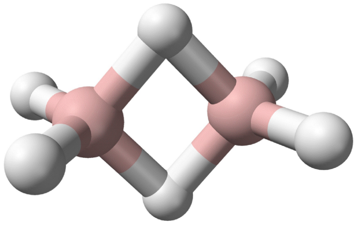

Figure 2.13: Structure of diborane (B_2H_6); where pink = boron; white = hydrogen.

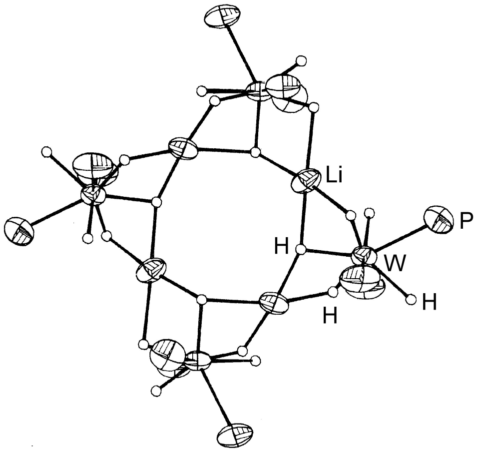

Figure 2.14: The structure of $\{[(Me_3P)_3WH_5]^{-}Li^{+}\}_4$ showing the presence of terminal, bridging, and trifurcated hydrides. The methyl groups have been omitted for clarity. Adapted from A. R. Barron, M. B. Hursthouse, M. Motevalli, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1986, 81.

2.6.2.1 Synthesis of covalent hydrides

Covalent hydrides can be made by a range of synthetic routes. The simplest is direct combination of the elements (in a similar manner to that used with ionic hydrides).

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \quad (2.33)$$

The use of a hydride as a reagent to reduce a halide or oxide of the desired element.

$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiAlCl_4 \quad (2.34)$$

Metal phosphides, carbides, silicides, and borides result in the formation of the hydride.

$$Ca_3P_2 + 6\,H_2O \rightarrow 2\,PH_3 + 3\,Ca(OH)_2 \quad (2.35)$$

Hydride compounds can be interconverted in the presence of a catalyst, heat, or an electrical discharge. This is the basis of catalytic cracking of petroleum mixtures.

2.6.3 Interstitial hydrides

Many transition metal, lanthanides and actinides absorb hydrogen to give a metallic hydride which retain the properties of a metal, although the presence of hydrogen does result in embrittlement of the metal. As such these hydrides are best considered as alloys since they do not have defined stoichiometries. For example, vanadium absorbs hydrogen to form an alloy with a maximum hydrogen content of $VH_{1.6}$. In a similar manner palladium forms $PdH_{0.6}$. The hydrogen atoms are present in interstitial sites in the metal's lattice; hence *interstitial hydride*. Interstitial hydrides show certain promise as a way for safe hydrogen storage.

2.6.4 Bibliography

- A. R. Barron, M. B. Hursthouse, M. Motevalli, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1986, 81.

2.7 The Hydrogen Bond[7]

Hydrogen bonds are formed between a species with a polar $X^{\delta-}$-$H^{\delta+}$ bond and a species with a lone pair ($Y^{\delta-}$), i.e., $X^{\delta-}$-$H^{\delta+}\cdots Y^{\delta-}$. The most common species for X are oxygen and nitrogen, and to a lesser extent carbon, fluorine, and sulfur. However, as long as the X-H bond is polar then hydrogen bonding is possible. Similarly, the most common Lewis bases that hydrogen bond involve oxygen, nitrogen, and fluorine as the donor atom. Again there are many examples of other atoms, but as long as the atom has a lone pair that is chemically active, hydrogen bonding can occur.

The majority of hydrogen bonds are asymmetrical, that is the hydrogen is closer to one atom than the other (Figure 2.15), even when X and Y are the same element, i.e., O-H···O. While the typical hydrogen bond involves one Lewis base (lone pair donor), there are many examples where the hydrogen interacts with two Lewis base lone pairs (Figure 2.16).

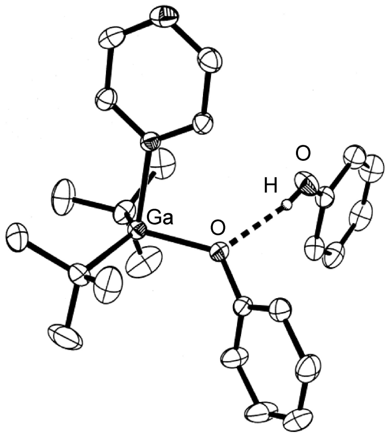

Figure 2.15: Structure of $(^tBu)_2Ga(OPh)(pyz).(PhOH)$ from X-ray crystallographic data showing the presence of an asymmetrical hydrogen bond. Hydrogen atoms attached to carbon are omitted for clarity. Adapted from L. H. van Poppel, S. G. Bott and A. R. Barron, *Polyhedron*, 2002, **21**, 1877.

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[7] This content is available online at <http://cnx.org/content/m31896/1.4/>.

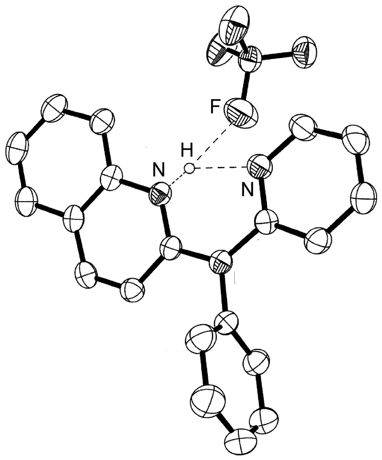

Figure 2.16: Structure of [H{PhN(py)(quin)}]BF_4 from X-ray crystallographic data showing the presence of a trifurcated asymmetrical hydrogen bond. Hydrogen atoms attached to carbon are omitted for clarity. Adapted from J. J. Allen, C. E. Hamilton, and A. R. Barron, *J. Chem. Cryst.*, 2009.

Hydrogen bonds are mostly electrostatic attractions, and as such they are weaker than covalent bonds, but stronger than van der Waal interactions. With bond strengths generally covering the range of 5 – 50 kJ/mol, the energy required to break a hydrogen bond is comparable to that of thermal motion within the temperature range of 0 – 200 °C. As a consequence the number of groups involved in hydrogen bonding decreases with increasing temperature, until few hydrogen bonds are observed in the vapor phase. One noted exception is the hydrogen bridged anion $[F\text{-}H\text{-}F]^-$, in which the strong interaction (243 kJ/mol) is covalent in character involving a three-center molecular orbital bond.

2.7.1 Classes of hydrogen bond

Although hydrogen bonds may be characterized with respect to the X and Y atom, it is more useful to classify them as either intramolecular or intermolecular hydrogen bonds. This is due to the difference in physical and chemical properties between these two classes.

2.7.1.1 Intramolecular

Intramolecular hydrogen bonds (X-H···Y) arise where the X and Y atoms are in the same molecule (Figure 2.17).

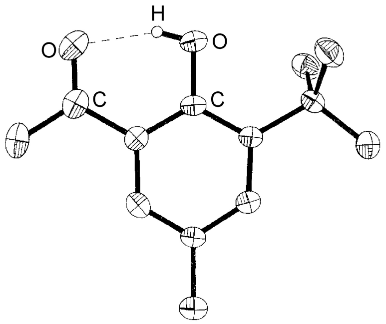

Figure 2.17: Structure of 3-*tert*-butyl-2-hydroxy-5-methylacetophenone showing the presence of an intramolecular hydrogen bond. Hydrogen atoms attached to carbon are omitted for clarity. Adapted from M. B. Power, A. R. Barron, S. G. Bott, E. J. Bishop, K. D. Tierce and J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, 1991, 241.

2.7.1.2 Intermolecular

If the hydrogen bond (X-H···Y) involves X and Y being from different molecules this is an intermolecular hydrogen bond. Within the range of intermolecular hydrogen bonded compounds there are two sub-categories: those involving discrete molecular species (oligomers) and those resulting in polymeric species.

Carboxylic acids are a typical example of a discrete oligomeric species that are held together by intermolecular hydrogen bonds (Figure 2.18a). A wide range of structurally analogous compounds also form head-to-tail hydrogen bonded dimers (e.g., Figure 2.19). In a polymeric hydrogen bonded species every molecule hydrogen bonds but in a random form. As an example, liquid primary alcohols form extended hydrogen networks (Figure 2.18b). Such an arrangement is labile and as such it is difficult to determine definitive speciation. Liquids that form this type of hydrogen-bonded network are known as *associated liquids*. In the solid state the networks generally adopt a more ordered structure. For example as is seen in the structure of ice.

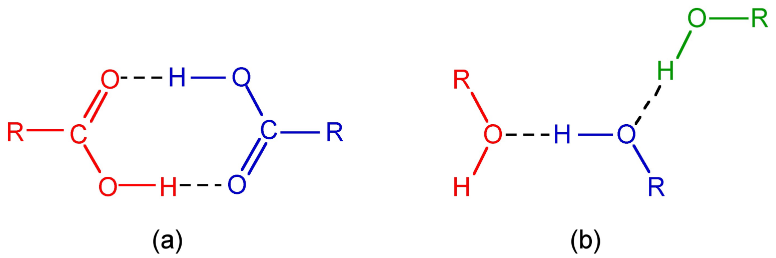

Figure 2.18: Structure of (a) the head-to-tail dimmer formed between two carboxylic acid molecules, and (b) a typical network of a primary alcohol in the liquid phase.

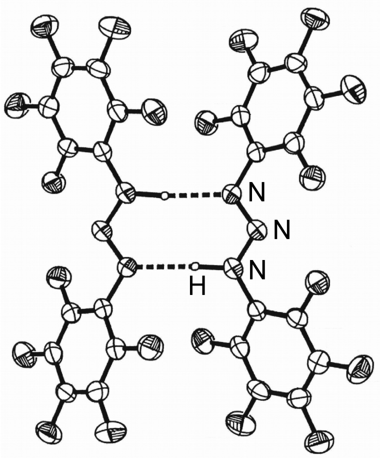

Figure 2.19: Structure of the hydrogen bonded diner of $(C_6H_5)NNN(H)(C_6F_5)$. Adapted from J. T. Leman, J. Braddock-Wilking, A. J. Coolong, and A. R. Barron, *Inorg. Chem.*, 1993, **32**, 4324.

2.7.2 Methods of study

The study of the structure arising from hydrogen bonding and the properties exhibited due to the presence of hydrogen bonds is very important.

2.7.2.1 Diffraction methods

X-ray diffraction of single crystals is the most common structural method employed to determine the presence, effect, and strength of a hydrogen bond. Unfortunately, in order for the location of the hydrogen to be determined with some degree of accuracy, diffraction data of a high quality is needed and/or low temperature (e.g., -196 °C) data collection is required. Neutron scattering can be used where very accurate data is required because hydrogen atoms scatter neutrons better than they do X-rays. Figure 2.20 summarizes the key parameters that are obtained from X-ray (and neutron) diffraction experiments.

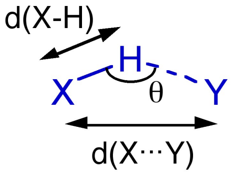

Figure 2.20: Structural parameters obtained from diffraction methods.

Given the electrostatic nature of a hydrogen bond between a polar X-H bond and a Lewis base it is reasonable that the X-H···Y angle (θ) is roughly linear (i.e., 180 °). However, it is not always so and non-linear interactions are known where steric or conformational restrictions limit the orientation of the X-H bond with respect to Y.

The distance between X and Y, d(X···Y), is less than the sum of the van der Waal radii of X and Y (Table 2.5). This is in line with the relative strength of these interactions. As would be expected the shorter the X···Y distance the stronger the hydrogen bond.

X	**Y**	**Sum of van der Waal radii (Å)**	**Typical X···Y distance (Å)**
O	O	2.8	2.50 – 2.69
O	N	2.9	2.75 - 2.85
N	N	3.0	2.69 – 2.98

Table 2.5: Comparison of the X···Y distance in hydrogen bonded species with the sum of the van der Waal radii.

The bond distance to hydrogen, d(X-H), is often longer in hydrogen bonded species. For example the O-H distance for an alcohol in the absence of hydrogen bonding is typically 0.97 Å. In contrast, the value typically seen for a hydrogen-bonded analog is 1.05 Å.

2.7.2.2 Spectroscopy

Spectroscopy is a simple method of comparing hydrogen-bonded systems in particular in the solution or liquid phase.

2.7.2.2.1 Infra red and Raman

The X-H stretching frequency in the IR (and Raman) spectrum is dependant on the identity of X, i.e., O-H = 3610 - 3640 cm^{-1} and N-H = 3400 - 3500 cm^{-1}. However, the ν(X-H) is shifted to lower energy (lower frequency) as a consequence of hydrogen bonding. In addition, while non-hydrogen bonded X-H stretches are sharp, the presence of hydrogen bonding results in the peak being broadened. Figure X demonstrates both these effects. The O-H stretch for dilute ^{n}BuOH in CCl_4 is a sharp peak at 3650 cm^{-1} due to the lack of hydrogen bonding between the two components (Figure 2.21a), and the presence of hydrogen bonding between ^{n}BuOH and ^{n}BuOH is limited by the dilution. By contrast, a dilute solution of ^{n}BuOH in Et_2O results in a shift to lower frequency and a significant increase of peak width (Figure 2.21b) as a result of fairly strong O-H···O bonds. Finally, a dilute solution of ^{n}BuOH in NMe_3 results in a further shift to 3250 cm^{-1} and a very broad peak (Figure 2.21c). The broadening of the peaks is due to the distribution of X-H distances within a X-H···Y hydrogen bond.

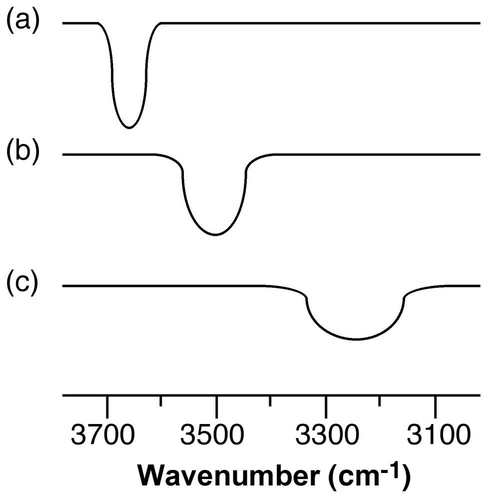

Figure 2.21: Schematic representation of the O-H stretch region in the IR spectra of a dilute solution of ^{n}BuOH in (a) CCl_4, (b) Et_2O, and (c) NEt_3.

2.7.2.2.2 NMR

The presence of hydrogen bonding results the shift to higher ppm (lower frequency) of the ^{1}H NMR resonance for the proton. This shift is due to the decrease in shielding of the proton. A dilute solution of ^{n}BuOH in CCl_4 shows a resonance typical of a non-hydrogen bonded compound (Figure 2.22a), while that for ^{n}BuOH in NMe_3 (Figure 2.22b) shows a significant low field shift. Very strong intra or intermolecular hydrogen bonded species show a very large ^{1}H NMR shift (e.g., Figure 2.22c).

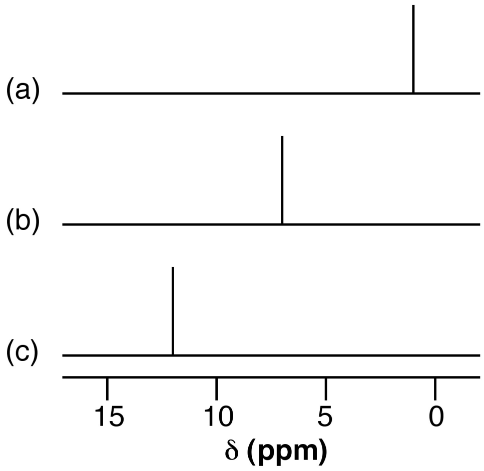

Figure 2.22: Schematic representation of the relative shift of the O*H* resonance for (a) ^{n}BuOH in CCl_4, (b) ^{n}BuOH in NEt_3, and (c) concentrated acetic acid.

2.7.3 Effects of hydrogen bonding

2.7.3.1 Physical effects

The presence of intermolecular hydrogen bonding provides additional attractive forces between molecules. Thus, properties that depend on intramolecular forces are affected.

Liquids with significant hydrogen bonding exhibit higher boiling points, higher viscosity, and higher heat of vaporization (ΔH_v) as compared to analogous compounds without extensive hydrogen bonding. For solids the presence of hydrogen bonding results in an increase in the melting point of the solid and an increase in the associated heat of fusion (ΔH_f).

The archetypal case for the effect of hydrogen bonding is the melting and boiling points of the hydrides of the Group 16 elements, i.e., H_2E. For a series of analogous compounds with the same molecular structure it would be expected that the boiling points would be related to the molecular mass. However, as can be seen from Table 2.6, the melting and boiling points of water are anomalously higher than those of its heavier analogs. In fact from Figure 2.23 it is clear that just considering H_2S, H_2Se, and H_2Te, the expected trend is observed, and it is similar to that for the Group 14 hydrides (CH_4, SiH_4, etc). Therefore, water must have additional intermolecular forces as compared to its heavier homologs. This observation is consistent with the strong hydrogen bonding in water, and the very weak if nonexistent hydrogen bonding in the sulfur, selenium, and tellurium analogs.

Compound	**Molecular weight (g/mol)**	**Mpt (°C)**	**Bpt (°C)**
H_2O	18.01	0	100
H_2S	34.08	-85.5	-60.7
H_2Se	80.98	-60.4	-41.5
H_2Te	129.62	-49	-2

Table 2.6: Summary of physical properties for the hydrides of the Group 16 elements.

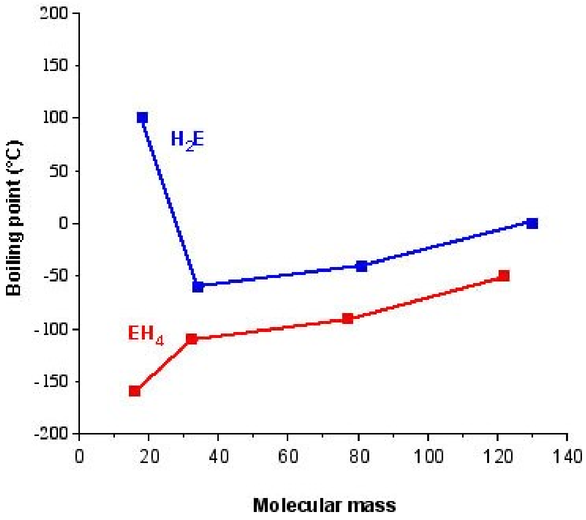

Figure 2.23: Plot of boiling point as a function of molecular weight for the hydrides of the Group 14 (EH_4) and 16 (H_2E) elements.

A similar but not as pronounced trend is observed for the Group 15 hydrides, where ammonia's higher values are associated with the presence of significant hydrogen bonding (Table 2.7).

Compound	Molecular weight (g/mol)	Mpt (°C)	Bpt (°C)
NH_3	17.03	-77.7	-33.35
PH_3	34.00	-133.5	-87.4
AsH_3	77.95	-113.5	-55
SbH_3	124.77	-88.5	-17

Table 2.7: Summary of physical properties for the hydrides of the Group 15 elements.

Exercise 2.7.1 ***(Solution on p. 104.)***

Would you expect H_2S_2 to have a higher or lower boiling point that H_2O_2? Why?

The types of hydrogen bond can also have a significant effect on the physical properties of a compound. For example, the *cis* isomer of hydroxybenzaldehyde melts at 1 °C, while the *trans* isomer has melting and boiling points of 112 °C. Both compounds exhibit strong hydrogen bonding in the solid state, however, as may be seen from Figure 2.24a, *cis*-hydroxybenzaldehyde (salicylaldehyde) has a configuration that allows strong intramolecular hydrogen bonding, which precludes any intermolecular hydrogen bonding. The melting point of *cis*-hydroxybenzaldehyde is going to be controlled by the van der Waal forces between adjacent molecules. In contrast, since intramolecular hydrogen bonding is precluded in the *trans* isomer (Figure 2.24b) it can form strong intermolecular hydrogen bonds in the solid state, and thus, it is these that define the melting point. The boiling points are controlled in a similar manner.

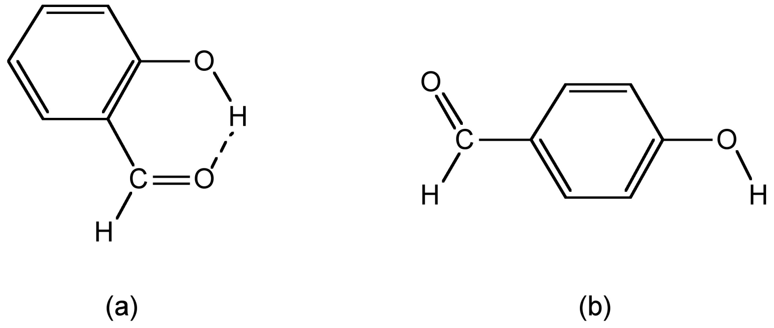

Figure 2.24: Structures of (a) salicylaldehyde and (b) *trans*-hydroxybenzaldehyde.

Exercise 2.7.2 ***(Solution on p. 104.)***

4-Hydroxybenzoic acid melts at 213 °C, while 2-hydroxybenzoic acid melts at 158 °C. Explain this observation.

Melting and boiling are not the only physical properties that are affected by hydrogen bonding. Solubility can also be affected. Consider two isomers of $C_4H_{10}O$: ^nBuOH and Et_2O. The n-butanol is much more soluble in water than diethyl ether. The reason for this is that while both compounds can hydrogen bond to water, those between ^nBuOH and water are much stronger than those between Et_2O and water, and thus, dissolution of ^nBuOH in water does not disrupt the very strong hydrogen bonding in water as much as Et_2O does.

2.7.3.2 Acid strength

The acidity of a protic species can be affected by the presence of hydrogen bonding. For example, consider the di-carboxylic acid derivatives of ethylene (fumaric acid). Each of the carboxylic acid groups has sequential equilibria that may be defined by the pK values, (2.36). Table 2.8 lists the pK values for the *cis* and *trans* isomers. The acidity of the first and second carboxylic group for the *trans* isomer is similar, the difference being due to the increased charge on the molecule. In contrast, the second proton in the *cis* isomer is much less acidic than the first proton: why? A consideration of the structure of the mono anion of the *cis* isomer (Figure 2.25) shows that a very strong intramolecular hydrogen bond is formed once the first proton is removed. This hydrogen bond makes the second acidic proton much more difficult to remove and thus lowers the acidity of the proton.

$$HO_2C\text{-}HC{=}CH\text{-}CO_2H \xrightleftharpoons{pK_1} {}^-O_2C\text{-}HC{=}CH\text{-}CO_2H \xrightleftharpoons{pK_2} {}^-O_2C\text{-}HC{=}CH\text{-}CO_2^- \qquad (2.36)$$

Isomer	**pK$_1$**	**pK$_2$**	**Ratio**
Trans	3	4.5	25:1
Cis	1.9	6.2	10,000:1

Table 2.8: Acidity equilibrium constants for *cis* and *trans* isomers of fumaric acid.

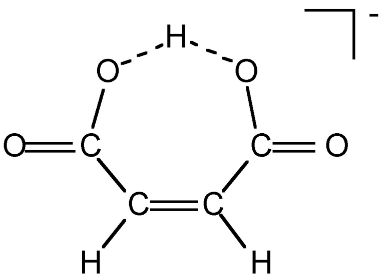

Figure 2.25: Structure of *cis*-[O_2C-HC=CH-CO_2H]$^-$.

2.7.3.3 Solid state structure

In the solid state, molecules that can form hydrogen bonds will tend to arrange themselves so as to maximize the formation of linear hydrogen bonds. The structure of ice is a typical example, where each water molecule's hydrogen bonds to four other molecules creating a diamond-like lattice (Figure 2.26). However, ice isn't the only compound whose solid state structure is defined by its hydrogen bonding. Cyanuric acid forms six strong intermolecular hydrogen bonds to three other molecules in the plane of the heterocyclic ring and thus creates a graphite-like structure (Figure 2.27).

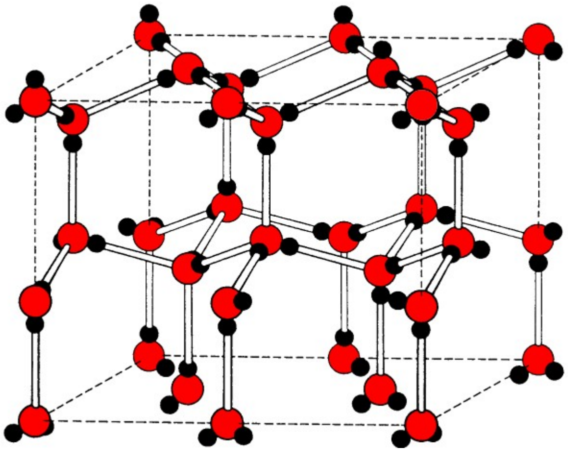

Figure 2.26: The diamond-like structure formed in ice by hydrogen bonding.

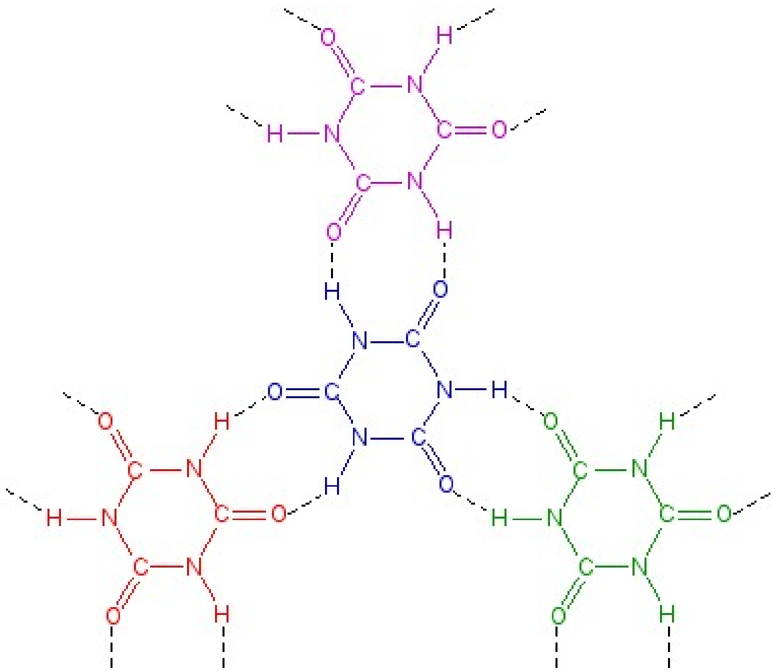

Figure 2.27: The hydrogen bonding of cyanuric acid.

2.7.3.4 Conformational stabilization

The presence of hydrogen bonding can stabilize certain conformations over others that in the absence of hydrogen bonding would be more favored. For example, based on steric considerations $H_2NCH_2CH_2C(O)H$ would be expected to adopt a staggered conformation as is typical for compounds with free rotation about a C-C bond. However, due to the presence of a strong intramolecular hydrogen bond it adopts a sterically disfavored eclipsed conformation (Figure 2.28).

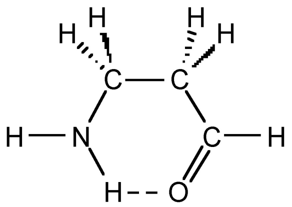

Figure 2.28: Stable conformation of $H_2NCH_2CH_2C(O)H$.

This conformational stabilization is even more important in biopolymers such as peptides. If we assume that a peptide chain (Figure 2.29) made from a sequence of amino acids would not adopt any eclipsed conformations on steric grounds, and that the amide group (H-N-C=O) is near planar due to delocalization, then there will be 3^2 possible conformations per nitrogen in the peptide chain, i.e., three each for the C-C and C-N bonds (Figure 2.29). Assuming a modest peptide has 50 amino acids, there will be 3^{2x50} potential conformations of the polymer chain, i.e., over 5 x 10^{47} conformations. However, in reality there are limits to the number of conformations observed since particular ones are stabilized by intramolecular hydrogen bonds. The most important of these are the α-helix (Figure 2.30) and β-sheet structures.

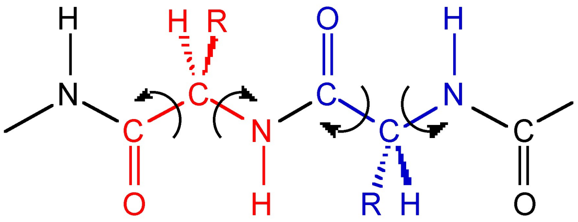

Figure 2.29: A section of a peptide polymer chain showing the possible rotational freedom of the C-C and C-N bonds.

Figure 2.30: A representation of a peptide α-helix structure showing the stabilizing hydrogen bonds.

2.7.4 Bibliography

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- R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320.

2.8 Isotopes of Hydrogen[8]

Hydrogen has three isotopes (Table 2.9) and unlike other elements these are given special names to differentiate then from the most abundant isotope. Tritium is radioactive with a half life of about 10 years.

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[8] This content is available online at <http://cnx.org/content/m31520/1.3/>.

Isotope	**Hydrogen-1**	**Hydrogen-2**	**Hydrogen-3**
Special name	Hydrogen	Deuterium	Tritium
Symbol	H	D	T
Atomic number	1	1	1
Number of neutrons	0	1	2
Mass number	1	2	3
Natural abundance	99.9844%	0.0156%	very small

Table 2.9: Summary of isotopes of hydrogen.

2.8.1 Synthesis of deuterium compounds

2.8.1.1 Electrolysis of water

The electrolysis of hydrogen-1 water (H_2O) in the presence of an alkali results in the formation of hydrogen and oxygen.

$$2\ H_2O_{(l)} \rightarrow 2\ H_{2(g)} + O_{2(g)} \tag{2.37}$$

In a similar manner the hydrolysis of deuterated water (D_2O) yields deuterium and oxygen.

$$2\ D_2O_{(l)} \rightarrow 2\ D_{2(g)} + O_{2(g)} \tag{2.38}$$

However, the rate of electrolysis of D_2O is slightly slower than that of H_2O. Thus, the partial hydrolysis of water with a mixture of natural isotopes results in the slight enrichment of the water with D_2O. The level of enrichment in one step is less than 1%. In order to obtain high levels of D_2O (e.g., ca. 30%) it is necessary to reduce the original volume of water by 1/100,000th.

2.8.1.2 Chemical equilibrium

Proton exchange reactions can be used to enrich compounds in deuterium. For example, the reaction of HSD with water shown in (2.39) has a slight preference for the formation of H_2S, i.e., $K_{eq} = 1.012$. Thus, bubbling HSD through water results in the enrichment of the water in HOD. However, about 30% enrichment is about the best that can be achieved by this method.

$$H_2O_{(l)} + HSD_{(g)} \rightleftharpoons HOD_{(l)} + H_2S_{(g)} \tag{2.39}$$

2.8.1.3 Fractional distillation

The boiling point of H_2O is (by definition) 100 °C, in contrast the boiling point of D_2O is 101.4 °C. Thus, it is possible to separate H_2O from D_2O by fractional distillation. This method provides the most suitable route to high isotopic enrichment and D_2O of 99.8% can be produced this way.

NOTE: The term *heavy water* is used for D_2O of greater than 99.8% enrichment.

2.8.2 Uses of deuterium compounds

2.8.2.1 Possible nuclear fusion

The largest use of D_2O is as a moderator and heat exchanger for fission nuclear reactors, however, the biggest potential application will be if nuclear fusion is realized as a commercial process.

The fusion of two deuterium atoms to form a helium atom and energy would be one source of energy, (2.40), however, deuterium-tritium fusion is the most promising, (2.41).

$$ {}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \text{energy} \tag{2.40}$$

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \text{energy} \tag{2.41}$$

The deuterium part of the fuel does not pose a great problem because about 1 part in 5000 of the hydrogen in seawater is deuterium. This amounts to an estimate that there is over 10^{15} tons of deuterium in the oceans. The tritium part of the fuel is more problematic since there is no significant natural source (Table 2.9), and the tritium would have to be obtained by breeding the tritium from lithium.

$$ {}^{6}_{3}\mathrm{Li} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H} \tag{2.42}$$

Since a gallon of seawater could produce as much energy as 300 gallons of gasoline, there is clearly a large amount of energy that can potentially be realized through nuclear fusion. Unfortunately, this advantage is also a disadvantage since the temperatures attained are similar to the surface of the sun, which would vaporize any conventional container. Fusion experiments therefore use a magnetic field to contain the reaction. The shape of the field is like a bottle, hence the term “magnetic bottle”.

One demonstrated fusion process is the so-called hydrogen bomb or thermonuclear bomb in which a fission atom bomb is used to initiate a fusion reaction. The atomic bomb is surrounded by a layer of lithium deuteride. Neutrons from the atomic explosion (fission) cause the lithium to be converted into helium, tritium, and energy, (2.42). The atomic explosion also supplies the 50,000,000 °C temperature needed for the subsequent fusion of deuterium with tritium, (2.41). So in-fact the hydrogen bomb is misnamed and it should be called a deuterium bomb.

> NOTE: The original calculations to model the hydrogen bomb were performed using ENIAC (short for Electronic Numerical Integrator And Computer) that was originally designed to generate tables of trajectories of shells fired from large artillery. The artillery firing tables were made by women mathematicians who were called “calculators” – hence the name used today. Built in 1946 ENIAC is often assumed to be the first programmable electronic computer, however, it was predated by the six Colossus machines that were used to successfully crack the German Enigma code as early as 1944. However, the existence of the Colossus machines was kept secret until 1975.

2.8.2.2 Spectroscopy

In the chemical laboratory deuterium compounds are commonly used in spectroscopy for:

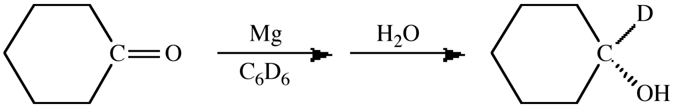
a) The assignment of resonances in IR, Raman, and NMR spectroscopy.
b) As a non-proton containing solvent in ^{1}H NMR spectroscopy.

A description of these applications is given below.

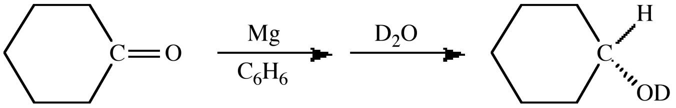
2.8.2.3 Reaction mechanism and rate determination

Given the larger mass of deuterium over hydrogen there is an associated difference in the rate of reactions (see below) and therefore investigations using hydrogen and deuterium analogs can provide information as to reaction mechanisms.

The spectroscopic differences between hydrogen and deuterium can also be used as a tracer to uniquely determine the source of particular substituents. For example, the magnesium (or Grignard) reduction of a ketone yields upon hydrolysis the secondary alcohol. If the reaction is carried out in a deuterated solvent and H_2O used for hydrolysis then the secondary carbon is deuterated, (2.43). In contrast, if the reaction is carried out in a non-deuterated solvent and hydrolysis is accomplished with D_2O then the deuterated alcohol is formed, (2.44). These experiments define that the initial reduction occurs at the ketone's α-carbon.



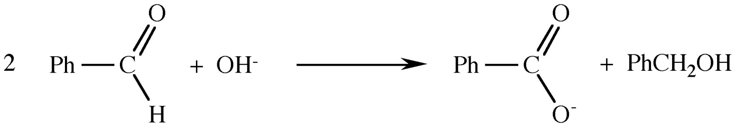
(2.43)

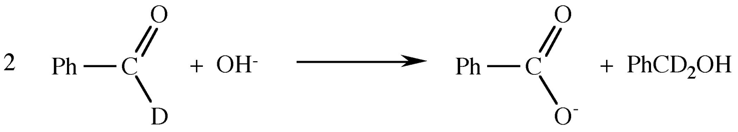


(2.44)

Exercise 2.8.1 ***(Solution on p. 104.)***

Given the following reactions and the isotope distribution of the products suggest the reaction mechanism.





2.8.3 Differences between hydrogen and deuterium

2.8.3.1 Properties that depend on nuclei properties

The nuclear magnetic moment of an atomic nucleus arises from the spins of the protons and neutrons within the nucleus. As a consequence the magnetic moment for hydrogen and deuterium are very different and hence the conditions for detection by NMR are very different. Thus, in observing the ^1H NMR spectrum of a compound not only are the deuterium atoms not observed, but the coupling is now H-D rather than H-H (Figure 2.31).

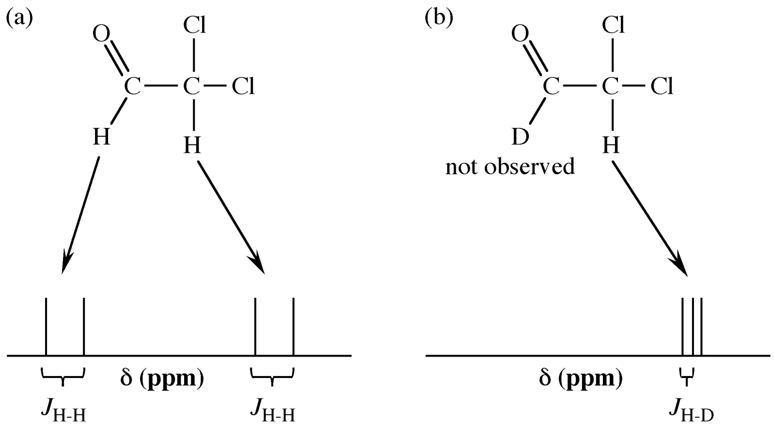


Figure 2.31: An example of the differences in the ^{1}H NMR spectrum upon deuterium substitution.

Deuterium is better at scattering neutrons than hydrogen. The H and D cross sections are very distinct and different in sign, which allows contrast variation in such experiments. Hydrogen's low electron density makes it difficult to determine its position by X-ray diffraction methods, neutron diffraction methods allow for highly accurate structure determination. Hydrogen can be seen by neutron diffraction and scattering, however, it has a large incoherent neutron cross-section. This is nil for deuterium and thus delivers much clearer signals may be obtained for deuterated samples. Neutron scattering of deuterated samples is indispensable for many studies of macromolecules in biology.

2.8.3.2 Properties that depend on mass

The difference in mass between hydrogen and deuterium obviously results in a difference in molecular mass of their analogous compounds. This difference can be used for analysis by mass spectrometry, but it also results in different densities of compounds. For example, the density of H_2O at 25 °C is 0.997 g/cm^3, while the density of D_2O at 25 °C is 1.104 g/cm^3.

The vibrational frequency for a diatomic molecule, H-X, can be defined by the equation:

$$\nu_{\text{H-X}} = \frac{1}{2\pi}\sqrt{\frac{f_{\text{H-X}}}{\mu_{\text{H-X}}}} \tag{2.45}$$

where $f_{\text{H-X}}$ is the H-X bond force constant, and $\mu_{\text{H-X}}$ is the reduced mass.

$$\mu_{\text{H-X}} = \frac{m_H \cdot m_X}{m_H + m_X} \tag{2.46}$$

If substitute H for D the D-X force constant is the same as the H-X force constant, but the reduced mass is twice the value for the H-X bond. As a result the ratio of the vibrational frequency of an H-X bond to that of the analogous D-X bond is given by the following equation.

$$\frac{\mu_{\text{D-X}}}{\mu_{\text{H-X}}} = \left(\frac{\mu_{\text{H-X}}}{\mu_{\text{D-X}}}\right)^{1/2} = \frac{1}{\sqrt{2}} \tag{2.47}$$

With the change in vibrational energy there is concomitant change in the bond strength.

$$E_{D\text{-}X} > E_{H\text{-}X} \tag{2.48}$$

Thus, the rate of reactions will be faster for hydrogen derivative than the deuterium analog. The ratio of the rate constants will be dependant on the involvement of H-X bond breaking or forming in the rate limiting step (the slowest reaction step within the overall reaction mechanism). When an H-X bond is made or broken in the rate limiting step, then the ratio of the rate constants upon deuterium substitution will be:

$$\frac{k_{H\text{-}X}}{k_{D\text{-}X}} \approx 7 \tag{2.49}$$

This is known as the *primary isotope effect*. In this case where H-X bond breaking or forming is not part of the rate limiting step, then the isotope effect will be much smaller and is known as a *secondary isotope effect*.

The position of equilibrium reactions that involve hydrogen exchange, (2.50), will be effected by the presence of deuterium to favor the deuterium being concentrated in the more stable bond. This is the basis of the concentration of HOD from HSD and water, (2.39).

$$\text{X-H} + \text{Y-D} \rightleftharpoons \text{X-D} + \text{Y-H} \tag{2.50}$$

2.8.4 Bibliography

- M. B. Power, S. G. Bott, J. L. Atwood, and A. R. Barron. *J. Am. Chem. Soc.*, 1990, **112**, 3446.
- A. S. Borovik and A. R. Barron, *Main Group Chem.* 2005, **4**, 135.

2.9 Nuclear Fusion[9]

The process of nuclear fission and radioactive decay are both associated with the conversion of an atom with a large nucleus to an atom (or atoms) with a smaller nucleus. In the process, mass is lost and energy is produced. However, what happens if two atoms with small nuclei are combined to give a single atom with a larger nucleus? In such a process the nuclei would be fused together, and this process is called nuclear fusion.

One of the simplest fusion processes involves the fusing of two hydrogen-2 (deuterium) atoms:

$${}^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} \tag{2.51}$$

The mass of each deuterium atom is 2.0140 amu, while the mass of the resulting helium is 4.0026 amu. The mass defect of the reaction is 0.0254 amu or 0.63% of the original mass. While this percentage of the original mass may not seem much, it should be noted that the mass defect for the conversion of uranium-238 to lead-206 is only 0.026%, and that for splitting uranium-235 is 0.056%. Based upon these comparisons it is clear that fusion of hydrogen produces 24x the energy kg/kg than natural radioactivity and 11x that of nuclear fission.

In addition to being a plentiful source of energy, fusion is actually the most important process in the universe. Since the statement in 1847 of the Law of conservation of energy (the total amount of energy in an isolated system remains constant) scientists had wondered how the sun works. No source of energy was known in the 19th century that could explain the sun. Based upon the age of the earth it is known that the sun is 4,550,000,000 years old, and it was marveled at the continued source of energy over that span of time. By the 1920s nuclear energy was defined as being the most powerful source of energy, and

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[9] This content is available online at <http://cnx.org/content/m31443/1.3/>.

British astrophysicist Arthur Eddington (Figure 2.32) suggested that the sun's energy arises from the fusion of hydrogen into helium.

Figure 2.32: Arthur Stanley Eddington (1882 –1944).

In 1929 American Henry Norris Russell (Figure 2.33) studied the spectrum of the sun. Based upon his studies he calculated the composition of the sun to be 90% hydrogen, 9% helium, and 1% of all other elements up to iron (but nothing of higher atomic number). Given the composition it became clear that the only reaction possible to account for the sun's energy was the fusion of hydrogen. In 1938 Hans Bethe (Figure 2.34) demonstrated a model for how the sun worked. The energy source is the fusion of hydrogen to give helium (Figure 2.35), while in massive starts the presence of heavier elements such as carbon, oxygen, nitrogen, neon, silicon, and iron are the result of the fusion of helium.

Figure 2.33: Henry Norris Russell (1877 - 1957).

Figure 2.34: Hans Albrecht Bethe (1906 - 2005).

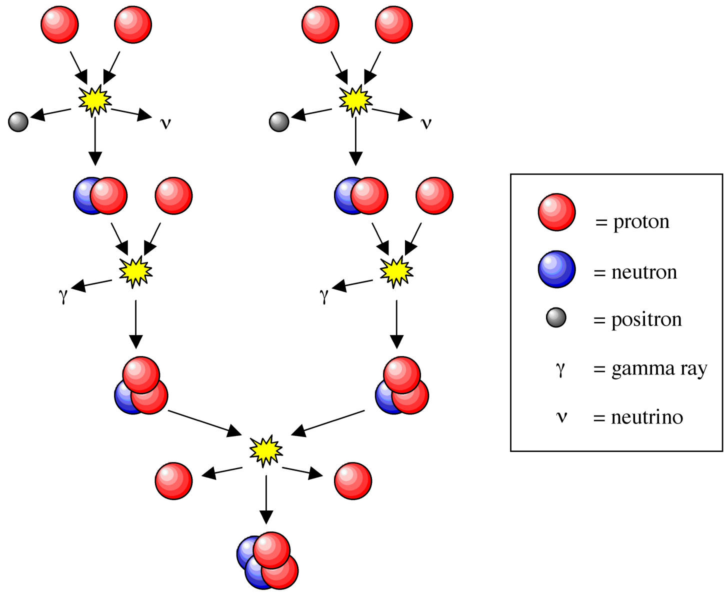

Figure 2.35: The proton-proton chain dominates in stars the size of the Sun or smaller.

Why is it that uranium, thorium and other radioactive elements undergo radioactive decay, but hydrogen does not undergo spontaneous fusion? The reason for this difference is that any change that uranium undergoes occurs inside a nucleus that is already formed, while fusion requires that two nuclei must come together. This process results in extremely large repulsive forces. So why does it happen in a star? The temperatures inside a star approach 15,000,000 °C, while the high pressure results in a density of approximately 160 g/cm^3 which for comparison is 8x that of gold. Under these conditions the nuclei are free to move in a sea of electrons. Nuclear fusion takes place in the core of the sun where the density is at the highest but an explosion does not result due to the extreme gravity of the sun: 333,000x that of Earth.

Research into controlled fusion, with the aim of producing fusion power for the production of electricity, has been conducted for over 50 years. It has been accompanied by extreme scientific and technological difficulties, but has resulted in progress. At present, break-even (self-sustaining) controlled fusion reactions have not been demonstrated, however, work continues since the fuel for such a fusion reaction is hydrogen (in its compounds including water) is the 3rd most abundant element on the Earth.

2.10 Storage of Hydrogen for Use as a Fuel[10]

NOTE: This module is based upon the Connexions course *Methods of Hydrogen Storage for Use as a Fuel Case Study* by Christian Cioce.

2.10.1 Introduction

Dihydrogen is a colorless and odorless gas at room temperature which is highly flammable, releasing a large amount of energy when combusted. As compared with combustion of the current fuels which operate

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[10] This content is available online at <http://cnx.org/content/m32176/1.1/>.

automobiles, for example petrol or diesel, the energy released when hydrogen is combusted is more than three times greater. The heat of combustion for hydrogen is 141.9 kJ/mol as compared to 47.0 kJ/mol and 45.0 kJ/mol for gasoline and diesel, respectively.

Furthermore, the combustion of hydrocarbons releases the greenhouse gas carbon dioxide (CO_2) into the atmosphere, and is therefore not a "clean" fuel. When hydrogen is combusted in the presence of oxygen (from air) the only product is water, (2.52). Both its clean reactivity and the large chemical energy make H_2 extremely appealing for use as a fuel in automobiles.

$$2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(g)} \tag{2.52}$$

If hydrogen has such a potential as a fuel why has it not been widely implemented? Dihydrogen is a gas at room temperature. Gases, compared to the other states of matter (liquid and solid), occupy the most volume of space, for a given number of molecules. Octane and the other hydrocarbons found in gasoline are liquids at room temperature, demanding relatively small fuel tanks. Liquids are therefore easier to store than compressed gases.

Hydrogen has a high energy content per weight (more than three times as much as gasoline), but the energy density per volume is rather low at standard temperature and pressure. Volumetric energy density can be increased by storing the gaseous hydrogen under increased pressure or storing it at extremely low temperatures as a liquid. Hydrogen can also be adsorbed into metal hydrides and highly porous materials (Table 2.10). The current available methods of storing hydrogen include compressed hydrogen and liquefied hydrogen, however many promising methods exist, namely metal organic materials (MOMs), metal hydrides and carbon nanostructures.

Material	**H-atoms per cm^3 (x 10^{22})**	**% of weight that is H_2**
H_2 gas, 200 bar (2850 psi)	0.99	100
H_2 liquid, 20 K (-253 °C)	4.2	100
H_2 solid, 4.2 K (-269 °C)	5.3	100
MgH_2	6.5	7.6
Mg_2NiH_4	5.9	3.6
$FeTiH_2$	6.0	1.89
$LaNi_5H_6$	5.5	1.37

Table 2.10: Comparison of hydrogen storage ability of metal hydrides.

2.10.2 Liquid hydrogen

Liquid hydrogen is made possible by cryogenically cooling it to below its boiling point, -253 °C. As a liquid, the same amount of gaseous hydrogen will require much less volume, and therefore is feasible to individual automobile use. A refrigeration system is required to keep the liquid cooled, for if the system temperature rises above hydrogen's critical point (-241 °C), the liquid will become a gas. There must exist a vacuum insulation between the inner and outer walls of liquid hydrogen tank system, for heat cannot travel through a vacuum. There is a tradeoff, however, because the tank must be an open system to prevent overpressure. This will lead directly to heat loss, though minimal.

The relative tank size has a broad range, with small tanks having a volume of 100 L, and large spherical tanks sizing all the way up to 2000 m^3. Refrigeration systems are not a likely feature for every automobile, and open systems may pose a hazard should an accident occur. Cooling hydrogen down to a liquid is a convenient method of storage, however, and its implementation most likely will be limited to large stationary tanks as well as mobile multi-axle trucks.

2.10.3 Compressed hydrogen

Compressing gas is the process of applying an external force which minimizes the distance between gas particles, therefore forcing the system to occupy less volume. This is attractive since many particles can exist in a reasonably sized tank. At room temperature and atmospheric pressure, 4 kg of hydrogen occupies a volume of 45 m^3, which corresponds to a balloon with a diameter of 5 m. Clearly compression is required to store and transport the gas. When it comes to individual mobility however, these tanks are still far too large for the average sized automobile.

Compressed tanks are regularly filled to 200 atmospheres in most countries. Storing 4 kg of hydrogen still requires an internal volume of 225 L (about 60 gallons). This amount can be divided into 5 tanks with 45 L internal volume.

2.10.4 Metal hydrides for storage

Metal hydrides are coordinated complexes and/or crystal systems which reversibly bind hydrogen. The hydrogen is favorably incorporated into the complex and may be released by applying heat to the system. A major method to determine a particular complex's effectiveness is to measure the amount of hydrogen that can be released from the complex, rather than the amount it can store (Table 2.10).

Some issues with metal hydrides are low hydrogen capacity, slow uptake and release kinetics, as well as cost. The rate at which the complex accepts the hydrogen is a factor, since the time to fuel a car should ideally be minimal. Even more importantly, at the current stage of research, the rate at which hydrogen is released from the complex is too slow for automobile requirements. This technology is still a very promising method, and further research allows for the possibility of highly binding and rapid reversal rates of hydrogen gas.

Solutions to Exercises in Chapter 2

Solution to Exercise 2.5.1 (p. 76)
Cl^-

Solution to Exercise 2.5.2 (p. 76)
SO_4^{2-}

Solution to Exercise 2.5.3 (p. 76)
$[Al(H_2O)_5(OH)]^{2+}$

Solution to Exercise 2.5.4 (p. 76)
NH_4^+

Solution to Exercise 2.5.5 (p. 76)
HS^-

Solution to Exercise 2.5.6 (p. 76)
HCO_3^-

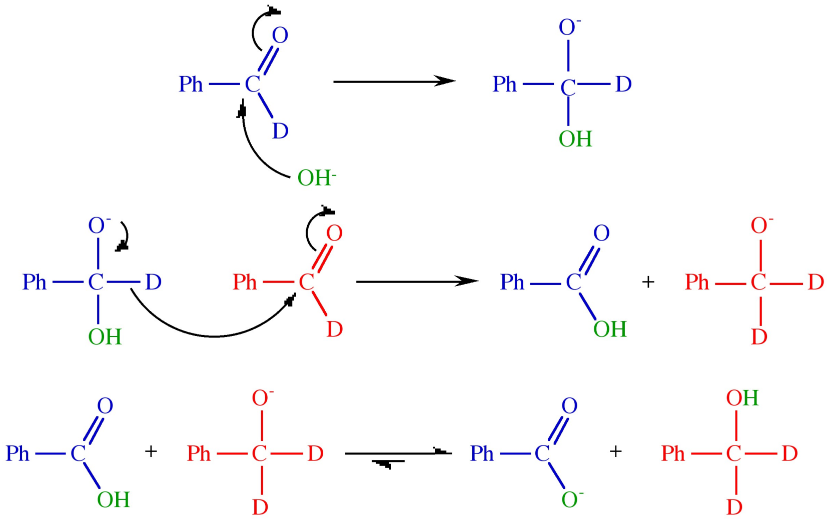
Solution to Exercise 2.5.7 (p. 77)

$$\underset{acid_1}{NH_4^+} + \underset{base_1}{S^{2-}} \rightleftharpoons \underset{acid_2}{HS^-} + \underset{base_2}{NH_3}$$

Solution to Exercise 2.7.1 (p. 88)
The boiling point for H_2O_2 is 150.2 °C, while that of 70.7 °C. The difference in boiling point is due to the stronger intermolecular hydrogen bonding in H_2O_2 than in H_2S_2.

Solution to Exercise 2.7.2 (p. 89)
2-Hydroxybenzoic acid exhibits strong intramolecular hydrogen bonding while 4-hydroxybenzoic acid has strong intermolecular hydrogen bonding.

Solution to Exercise 2.8.1 (p. 96)



Step 1.

Step 2.

Step 3.