• Hydrogen (not carbon) forms more compounds than any other element! The isotopes are:

  ◦ $^1\text{H}$
  ◦ $^2\text{D}$ (0.0156%)
  ◦ $^3\text{T}$ (Formation: $^{14}\text{N}(p,n)^{14}\text{O}$ and then (using the neutron) $^{14}\text{N}(n,^3\text{H})^{12}\text{C}$
     Abundance: $10^{-15} - 10^{-16}$ %, Decay: $^3\text{H}(\beta)^3\text{He}$ $t_{1/2} = 12.35$ y.

• The different name arise because isotope effects, which affect kinetics and equilibria, are especially marked for hydrogen.

• Deuterium is obtained by fractional distillation of water (or hydrogen sulphide?) or electrolysis of water. D$_2$O is used as a moderator in nuclear reactors and as a source of D for chemical studies of all sorts.

• Made in the lab from the action of acid on Zn or Fe and industrially by the catalysed reaction of steam with hydrocarbons, coal and other organic materials to give "synthesis gas, "syngas":

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \\
\text{CO} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{CO} \\
\text{CO} + \text{H}_2 & \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

H$_2$ can also be made by the "water-gas reaction" and the catalysed "water-gas shift reaction":

\[
\begin{align*}
\text{H}_2\text{O} + \text{CO} & \rightarrow \text{CO} + \text{H}_2 \\
\text{CO} + \text{H}_2 & \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

The hydrogen can be isolated by absorption of the carbon dioxide, and removal of residual CO and CO$_2$. (The "syngas" is an important industrial raw material itself.)

• It, and "syngas" are used in the production of organics via alcohols:

\[
2\text{CO} + 4\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}
\]

and the production of ammonia via the Haber process:

\[
\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3
\]

• Hydrogen has a bond energy of 434.1 kJ mol$^{-1}$. It will burn in air but reacts explosively with oxygen and some halogens via chain reactions:
Br₂ + light

2Br chain initiation

Br + H₂

HBr + H chain propagation

H + Br₂

HBr + Br

H + HBr

H₂ + Br

2Br

Br₂ chain termination

Notice there is no direct H-H bond fission in this processs.

The Bonding of Hydrogen

As mentioned before, hydrogen is found bonded in two covalent situations:

1. The complexed proton, e.g. H₃O⁺ or NH₄⁺, and "conventional" covalent situations, e.g. CH₄. The distinction between these two is rather artificial, except that the cations would have a rather more polarized and labile X-H bond, and are prone to transferring the proton to another molecule, i.e. behaviour as an acid.

2. Hydrides such as KH, which contain the H⁻ ion.

It has some special ways of bonding as well:

1. The formation of metallic hydrides, that is, hydrides which have metallic properties as apposed to ionic H⁻ containing materials, for example PdH₀.₄₋₀.₇.

   Note that the density of Pd is = 11.99 g cm⁻³ or 11.99/106.42 = 0.113 mol cm⁻³

   so in PdH₀.₇ the density of hydrogen is 0.113 x 0.7 = 0.0789 mol cm⁻³ or 0.0789 x 1.008 = 0.0790 g cm⁻³

   i.e. more than liquid hydrogen where the density (at -252.78 °C) is 0.07099 g cm⁻³!

The form of the hydrogen in metals is ambiguous: it tends to migrate towards the negative end of a potential gradient in wires, so it seems proton-like. On the other hand, salt like properties and M-H bond distances in some metal hydrides are more suggestive of H⁺ compounds. (Perhaps only a small part of the hydrogen is cationic in nature.)
2. The formation of covalent hydrogen bridges for example in $\text{B}_2\text{H}_6$ and $(\text{CO})_5\text{CrHCr(CO)}_5$. These are prototypes for $2e^-$ - 3-centre bonding.

3. A newish class of hydrogen bonds called "agostic" have been identified in certain transition metal compounds which seem to be a sort of frozen intermediate in the catalytic activation of C—H bonds. They come as "open" and "closed":

4. So called "hydrogen bonding" described in the following section.

---

**The Hydrogen Bond**

- When hydrogen is bonded to an electronegative element, $X$, usually $\text{F}$, $\text{O}$, $\text{N}$ or $\text{Cl}$, and there is another molecule around with a Lewis base donor atom, $Y$, a very strong largely electrostatic bond can form: $X^\text{d-} - H^\text{d+} \cdots \cdots Y$

  The $X—H$ bond is slightly longer than it would be without the proximity of the $Y$, and the $H \cdots \cdots Y$ "bond" is much longer than a $H—Y$ bond would be. Usually, hydrogen bonding is identified if this distance appreciably less than the sum of the van der Waals' radii for $H$ and $Y$ (e.g. $<(1.30 + 1.40) = 2.70 \text{ Å}$ for $H \cdots \cdots O$. In many cases the position of the hydrogen must be inferred: in this case $O—H$ should be about $0.37 + 0.70 = 1.07 \text{ Å}$ so an $O$ to $O$ distance less than about $2.70 + 1.07 = 3.75 \text{ Å}$ would imply a hydrogen bond is present.)

- The text refers to the case of crystalline $\text{NaHCO}_3$ where there are 4 $O$ to $O$ distances: 3.12, 3.15 and 3.19 Å which are well over the van der Waals' contact distance, and 2.55 Å which is somewhat less, and tells us where the $H$ is to be found.

- The hydrogen bond can also be identified by a shift in the infra-red stretching frequency to lower wavelengths. It is also broadened and made more intense. For example, free $O—H$ comes at 3500 cm$^{-1}$ but can be lowered several hundred wave-numbers by H-bonding.

- The table below gives some approximate hydrogen bond enthalpies:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F—H—F}$</td>
<td>30</td>
</tr>
<tr>
<td>$\text{N—H—N}$</td>
<td>25</td>
</tr>
<tr>
<td>$\text{O—H—O}$</td>
<td>25</td>
</tr>
<tr>
<td>$\text{N—H—F}$</td>
<td>21</td>
</tr>
</tbody>
</table>
Hydrogen bonding affects boiling points (and heats of vaporization) producing some anomalies. See text Figure 9-1.

There are specially strong hydrogen bonds that are 4e$^-$-3-centre bonds. Examples include [FHF]$^-$ with a centered proton and F to F distance of 2.26 Å.

Ice and Water

- There are 9 forms of ice which exist at high pressure, except the normal ice I.
- The normal hexagonal ice structure is depicted in Fig 9-2.
- In liquid water, an ice-like structure persists, but there are additional "interstitial" water molecules, and the whole system is "fluxional". The density of liquid water is greater than that of ice. The density is maximum at 4 °C.

Hydrates and Water Clathrates

Most hydrates are salts containing water in addition to the cations and anions. The water is sometimes in the first coordination sphere of the cations and is sometimes rather more loosely held:

CuSO$_4$.5H$_2$O

CuSO$_4$.3H$_2$O

CuSO$_4$.H$_2$O

CuSO$_4$ anhydrous

The water molecules are successively more difficult to remove, as the sulphate takes their place in the Cu$^{2+}$ coordination sphere.

Sometimes the water is so tightly bound, a decomposition occurs on heating:

ScCl$_3$.6H$_2$O

ScOCl + 2HCl + 5H$_2$O

"Gas hydrates" are an example of a class of "clathrate" compounds:
1. There is a cubic symmetry form that features a 46-water molecule unit cell including six medium sized and two small cages. With the medium-sized cages trapping a "guest" molecule each the formula would be $X_8(7.67)H_2O$. All eight cages filled would give $X_8(5.76)H_2O$. Clathrates of the first type are known for Ar, Kr, Xe, Cl$_2$, SO$_2$ and CH$_3$Cl (among others).

2. Another geometry, also cubic has 136 H$_2$O's in the unit cell and features 8 larger cages and 16 smaller ones. Molecules such as CHCl$_3$ and CH$_3$CH$_2$Cl can be trapped.

3. One other class made with the salts of R$_4$N$^+$ or R$_3$S$^+$ have the anions acting as part of the "host" structure. Examples are: [(C$_4$H$_9$)$_4$N][C$_6$H$_5$CO$_2$].(39.5)H$_2$O or [(C$_4$H$_9$)$_3$S]F.(20)H$_2$O.

### Hydrides

Many hydrogen compounds are collectively called hydrides, including many cases where the hydrogen is actually less electronegative than the atom to which it is bound, and which are not individually named hydrides, in addition to those where it is more electronegative, up to the saline hydrides containing $H^-$. In addition, there is the class of metallic hydrides, See Figure 9-4:

#### Covalent

1. Neutral - Group IVB (14) CH$_4$ (methane), SiH$_4$ (silane) etc
2. Somewhat basic - Group VB (15) NH$_3$, PH$_3$ (phosphine) etc
3. Weakly acidic - Group VIB (16) H$_2$O, H$_2$S (hydrogen sulphide) etc
4. Strongly acidic - Group VIIB (17) HCl, HI (hydrogen halides) etc
5. The boron hydrides (B$_n$H$_m$)
6. Hydride anions eg LiAlH$_4$ (alanate), LiBH$_4$ (borohydride or boranate)

**Preparation:**

$$(8LiH + Al_2Cl_6)$$

$$2LiAlH_4 + 6LiCl)$$

$$(2NaH + B_2H_6)$$

$$2NaBH_4)$$

**Typical Reactions:**

$$2LiAlH_4 + 2SiCl_4$$

$$2SiH_4 + 2LiCl + Al_2Cl_6$$

$$I_2 + LiBH_4$$

$$B_2H_6 + 2NaI + H_2$$
**Saline**

Some are made by direct reaction: \( M + H_2 \)

\[
\text{MH (Li - Cs)}
\]

or \( \text{MH}_2 \) (Mg - Ba)

The hydrides of Li and Be have covalent character, especially BeH\(_2\) which is really a polymer. Most saline hydrides react violently with water to give \( H_2 \)

They are also powerful hydride transfer reagents, sometimes useful for making other hydrides:

\[
\text{B(OR)}_3 + \text{NaH}
\]

\[
\text{Na[BH(OR)}_3]
\]

\[
4\text{NaH} + \text{TiCl}_4
\]

\[
\text{Ti}^0 + 4\text{NaCl} + 2\text{H}_2
\]

\[
\text{NaH} + \text{ROH}
\]

\[
\text{NaOR} + \text{H}_2
\]

**Transition metal**

These include the stoichiometric hydrides, for example UH\(_3\) and HCo(CO)\(_4\) and hydride anions, for example \([\text{ReH}_9]^{2-}\).

There are also the non-stoichiometric (interstitial) ones including PdH\(_{0.7}\) and ZrH\(_{1.9}\).

**Dihydrogen as a Ligand**

Dihydrogen complexes, where the hydrogen molecule is bonded sideways on to the metal, but the H-H bond is largely intact have been discovered only recently. The metal accepts electrons from the H-H s-orbital, and donates electrons back to the H-H s*-orbital. Both types of bonding should lead to weakening and ultimate cleavage of the H-H bond to give normal hydrides, and only very a few special cases short of this. An example is:

\[
\text{W(CO)}_3\text{P(Pr}^3\text{)}_2 + \text{H}_2
\]

\[
\text{W(CO)}_3\text{P(Pr}^3\text{)}_2(\text{H}_2)
\]

H-H by neutron diffraction = 0.75 Å, by X-ray diffraction = 0.84 Å and in H\(_2\) = 0.74 Å
Contributors

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