Hydrogen: It's compounds and Selected Uses

Hydrogen is a very important element. Not only does it combine with carbon to give numerous organic compounds, but also serves as a fuel and as a reducing agent for both metal-oxides and non-metals. Hydrogen forms more compounds than any other element, including carbon!

Some Physical Properties

Hydrogen is the lightest element. It boils at -225.8˚C. The bond dissociation energy H-H → H + H is 104.4 kcal/mole. The molecule is thus very thermally stable. At a temperature of 1727˚C only 1% of H_2 molecules in a sample of the gas will be dissociated to atoms.

Isotopes of Hydrogen

Hydrogen has three isotopes: **hydrogen (^{1}H)**; **deuterium (^{2}H or D)** and **tritium (^{3}H or T)**. Deuterium, a natural isotope of hydrogen sometimes labeled D, has one neutron in addition to the one electron and one proton present in "normal" hydrogen.

It is present in seawater, for example, as D_2O or HDO; the ratio of D:H being 1:5000.
The other isotope of hydrogen, tritium, is sometimes depicted as T. It has two neutrons in addition to the one electron and one proton. Tritium is radioactive and does not exist in nature. The diatomics that are possible are H_2, D_2, T_2, HD, HT, DT.

The two hydrogen isotopes play a very important role in nuclear fusion reactions which release a very large amount of energy, which if harnessed, can replace conventional fuels.

In nuclear reactions the energy released is given per atom rather than per mole as in chemical reactions. One ev/atom is equal to 23.06 kcal/mole. The fusion reaction between D and T is the basis for the hydrogen bomb. It produces ^4He and a neutron along with the 17.6 Mev of energy. This weapon requires the use of an atomic bomb (fission reaction) as a detonator to establish momentary temperatures of up to one million degrees to get the fusion reaction going.

Presently, attempts are being made to fuse two deuterium atoms (obtained from seawater) to yield useful energy. It is doubtful that such energy will become available for everyday use in this century, but the available fuel supplies of oil and coal can be expected to be exhausted sometime in the future if other energy substitutes are not found. Note that the population of this Earth was 2.4 billion in 1944 and is presently >5 billion. The necessity for alternate sources of energy is thus obvious. The possibility for obtaining energy from fusion reactions appears to be good even though it may turn out to be expensive. It should be realized that if it can be harnessed by fusion, the energy contained in one cubic kilometer of seawater is equivalent to the world's total supply of petroleum!!

Preparation of Hydrogen

Hydrogen is expensive to prepare. It is prepared by **electrolysis of water**, a process that requires the use of expensive electricity. Research has been going on for many years to develop methods of obtaining hydrogen by the splitting of water using light energy, but the long term practicality of this procedure has yet to be established.

<u>Electrolysis</u>. For electrolysis to occur, an electrolyte (i.e., ions) must be present in the water. Sulfuric acid can be used for this purpose. Illustrative reactions are shown below.

1. **Electrolysis of Water:**

$$2\ H_2O \xrightarrow[\text{electrolysis}]{H_2SO_4} 2\ H_2 + O_2$$

The half reactions are:

(reduction) cathode: $4\ H^+ + 4e^- \rightarrow 2\ H_2$
(oxidation) anode: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e^-$

2. **Electrolysis of Brine (an aqueous NaCl Solution):**

$$2\ Na^+ + 2\ Cl^- + 2\ H_2O \xrightarrow{\text{electrolysis}} 2\ Na^+ + 2\ OH^- + H_2 + Cl_2$$

Sodium metal is not deposited from aqueous solution; hydrogen is evolved instead.

3. **Steam Reforming of Hydrocarbons:**

$$C_nH_{2n+2} + n\ H_2O \xrightarrow[600\ ^oC]{\text{Ni catalyst}} n\ CO + (2n+1)\ H_2$$

The CO thus produced can be further converted to hydrogen by the **water-gas shift reaction**:

$$n\ CO + n\ H_2O \xrightarrow[250\ ^oC]{\text{catalyst}} n\ CO_2 + H_2$$

The CO_2/H_2 product is bubbled through water leaving hydrogen behind. (The CO_2 is soluble in H_2O). Any untreated CO cannot be allowed to escape in the atmosphere as it is very toxic, so the water-gas shift reaction must be made to go to completion.
The hydrocarbons used for steam reforming are CH_4 (methane) and C_2H_6 (ethane).

Reactions of Hydrogen

Some important reactions that involve hydrogen and illustrate its reactivity are:

1. **Preparation of HBr**

$$H_2 + Br_2 \xrightarrow[350\ ^{o}C]{\text{catalyst}} 2\ HBr_{(g)}$$

2. **Preparation of Ammonia (Haber Process)**

$$N_2 + 3\ H_2 \xrightarrow[\text{pressure}]{\text{Fe catalyst}} 2\ NH_3$$

The conversion of N_2 per pass is only 17%. The unreacted gases are recirculated. It is noteworthy that the conversion per pass was 15% when this process was

first invented in 1915. Evidently not much has changed since then.
Ammonia and ammonium salts are used in fertilizer.

3. **Formation of Hydrides**

$$H_2 + 2\ Li \xrightarrow[700\ ^oC]{} 2\ Li^+H^-$$

LiH is a white crystalline solid that melts at 680˚C.

4. **Isolation of Pure Metals from Ores by Reduction with H_2**

(a) $Cu_2S + 2\ O_2 \rightarrow 2\ CuO + SO_2$
(b) $MoS_2 + 7/2\ O_2 \rightarrow MoO_3 + 2\ SO_2$
(c) $CuO + H_2 \rightarrow Cu + H_2O$
(d) $MoO_3 + 3\ H_2 \rightarrow Mo + 3\ H_2O$

Molybdenum (Mo) is used in special steels where strength and corrosion resistance are required.

5. **Hydrogenation Reactions**

1. R-HC=CHR + $H_2 \rightarrow RCH_2\text{-}CH_2R$
(saturated hydrocarbons)

The hydrogenation of double bonds, which occur in vegetable oils, yields solid fats (i.e. Crisco).

2. $$\text{Coal} + H_2 \xrightarrow[\text{Co, Mo}]{\text{catalyst}} \text{oils}$$

6. **CO + H_2 Synthesis Reactions**

Synthesis gas which is a mixture of CO and H_2 is obtained from coal and can be converted to organic compounds.
Exemplary reactions are:

$$CO + 2\ H_2 \xrightarrow[400\ ^{o}C]{\text{Cu, Zn catalyst}} CH_3OH\ \text{(methanol)}$$

Methanol added to gasoline increases its octane value

7. **Fischer-Tropsch (FT) Synthesis**

$$CO + H_2 \xrightarrow{\text{catalyst}} \text{Mixture of hydrocarbons}$$

Catalysts: Co, Fe, Mo

This process was used by Germany during World War II to manufacture gasoline from coal.

Compounds of Hydrogen that contain one other element (compounds with only two element types are called Binary Compounds)

1. **Ionic or salt-like hydrides**
   Na^+H^- contains the hydride ion H^-

2. **Molecular or Covalent hydrides**
   SbH_3, SiH_4, H_2O, NH_3

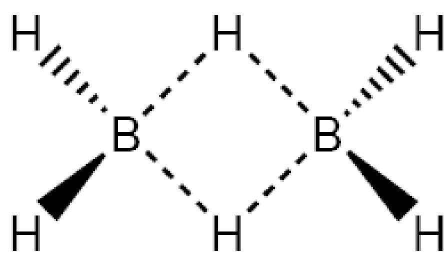
3. **Interstitial Hydrides**

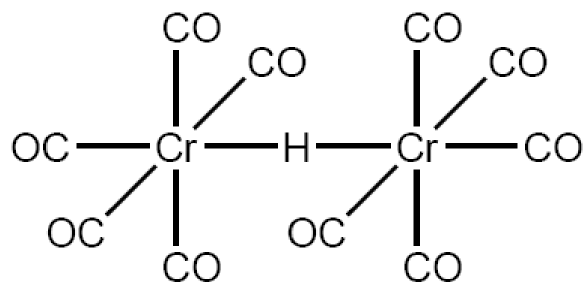
Interstitial hydrides are compounds prepared by absorption of H_2 into transition element metals or alloys. The hydrogen is usually present in the atomic form as H_2. These hydrides can be used for the storage of hydrogen (fuel storage) because the H_2 can be easily liberated by heat. Typical examples are $TiH_{1.7}$ and $LaNi_5H_6$.
It turns out that more hydrogen can be stored in such hydrides on a volume basis than by liquefying hydrogen.

Bonding features of Hydrogen

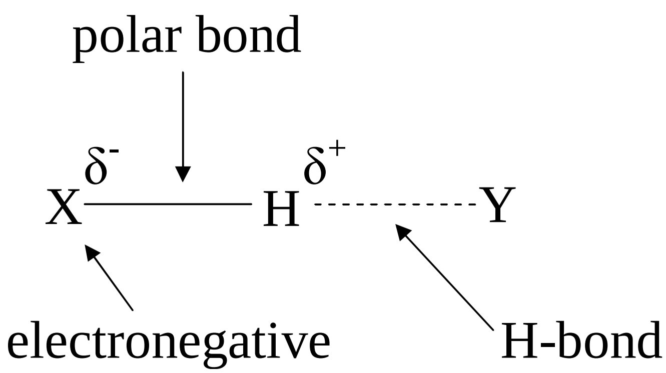
(1) Numerous M_xH_y hydride materials are known that are often non-stoichiometric

(2) Formation of 3-center bonds via H-bridges





(3) The Hydrogen Bond



Largely Electrostatic between Y and H

Bottom Line:
Main chemistry is loss of an electron to give H^+ and gain of an electron to give H^-

(b) Water of Crystallization – Hydrates. In some compounds water is an integral part of the crystalline material as indicated below.

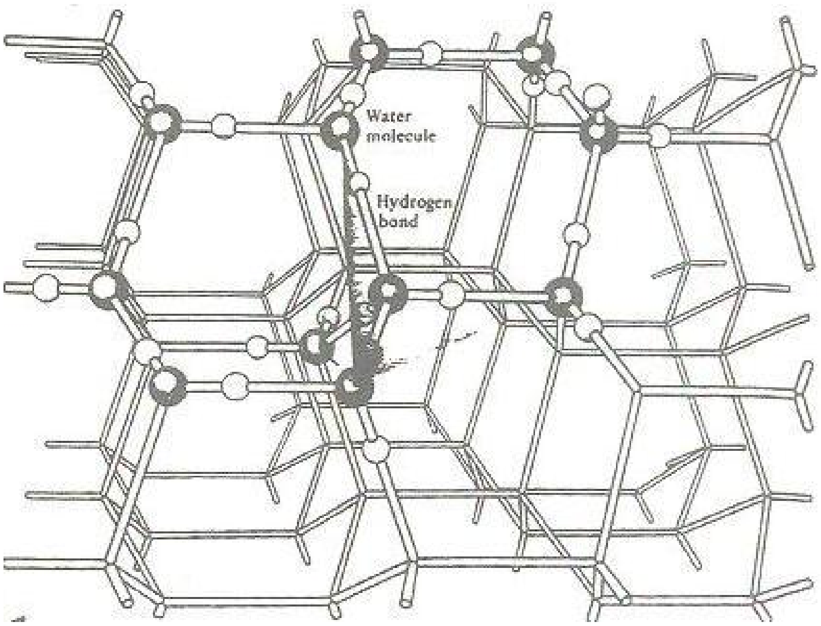
$$Na_2SO_4 \cdot 10\ H_2O \underset{}{\overset{34\ ^{o}C}{\rightleftharpoons}} Na_2SO_4 + 10\ H_2O$$

This reversible adsorption accounts for the desiccant (dehydrating) action of anhydrous sodium sulfate. The interaction between water and the Na^+ or $[SO_4]^{2-}$ ion within the crystal is weak, thus water evolution can occur at a low temperature.

(c) Coordinate Covalent Bonding. Water can form coordinate covalent bonds in a number of metal salts, such as $CuSO_4{\cdot}5H_2O$. Anhydrous copper sulfate is white but the penthydrate is blue due to the coordination of water molecules about the copper atom. In $CuSo_4{\cdot}5H_2O$, four water molecules are bonded with the water coordinated onto the cupric ion. It is thus properly formulated as $[Cu(H_2O)_4]SO_4{\cdot}H_2O$. Copper sulfate pentahydrate becomes anhydrous (loses all its water) at temperatures obove 250 ºC. (as opposed to 34 ºC above more difficult to release H_2O coordinated to a metal!)

The acidic behavior in water solutions of some metal salts can be explained by the strong coordination of water to the metal atom. For example, aluminum nitrate hexadrate, $Al(NO_3)_3 \cdot 6H_2O$, is best represented by the formula $[Al(H_2O)_6](NO_3)_3$. The six water molecules form six strong Al-O bonds. The acidic behavior of this compound results from the hydrolysis of the hydrated aluminum ion:

Hydrolysis:
$[Al(H_2O)_6]^{+3} \rightarrow [Al(H_2O)_6(OH)]^{+3} + H^+$ etc.,



Ice I
Tetrahedral
O atom
arrangements

Hydrogen Bonding in Ice

There are nine known crystal structures of ice

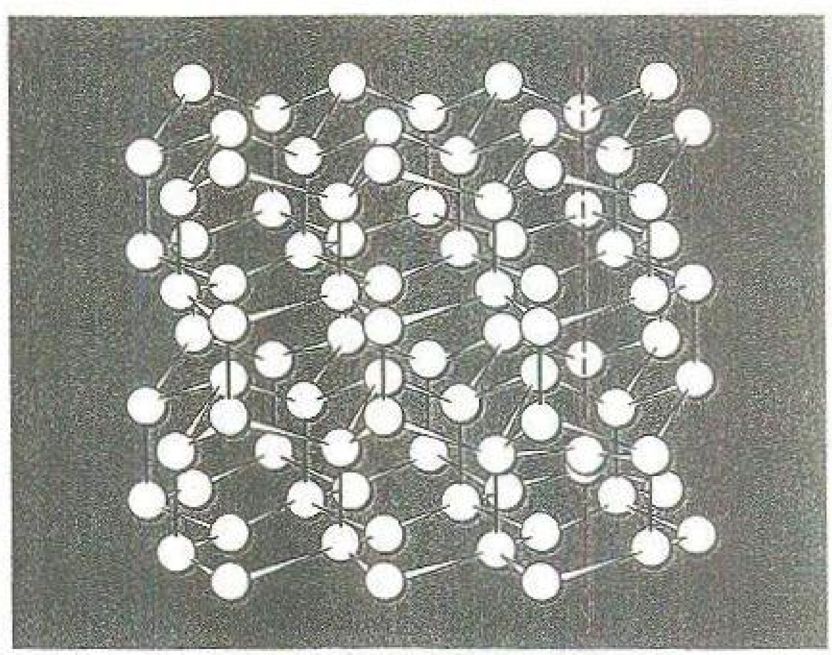


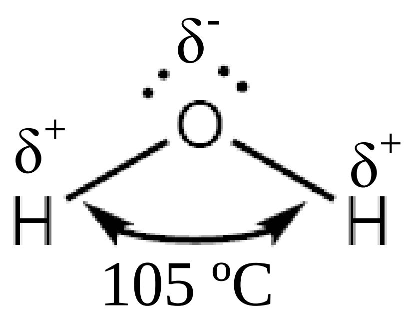
Figure 9-2 The structure of ice I. Only the oxygen atoms are shown. The O···O distances are 2.75 Å

O-O distances are 2.75A˚

Water

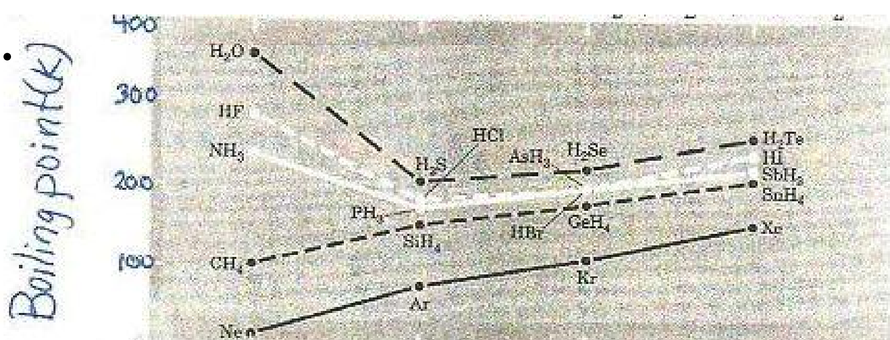
Water is a most abundant and interesting compound. This supplement to the notes emphasizes some of its important properties.

Bonding Aspects. Because of the electronegativity difference between hydrogen and oxygen, the O-H bonds in water are highly polar. The δ in the diagram below indicates a partial charge.



The H-O-H angle is 105˚. We can think of water as having two lone pairs of electrons on the oxygen atom. The resulting repulsion between these electron pairs and the two O-H bond electron pairs would then cause the H-O-H angle to be less than tetrahedral (109.5˚).

Hydrogen Bonding. Several of the properties of water can be attributed to its ability to form extensive hydrogen bonding in the solid and liquid phases. Only the gaseous phase can exist as discrete molecules. In the solid and liquid phases, aggregates are held together in the three-dimensional network by 1.77A. Hydrogen bonds are weak in comparison to normal covalent bonds (8-34 kJ/mole), and vary in strength from molecule to molecule. The H-bond in water is 21 kJ/mole and is directional; that is, it is usually between a lone pair of electrons on an atom of one molecule and the positive pole of another molecule. Hydrogen Bonding plays a vital role in biological processes, especially in holding protein structures intact, and it is responsible for the high boiling point of water. We can obtain the boiling point of water as a function of molecular weight in the <u>absence</u> of hydrogen bonding from a plot of the boiling points of its congeners, H_2S, H_2Se, and H_2Te.



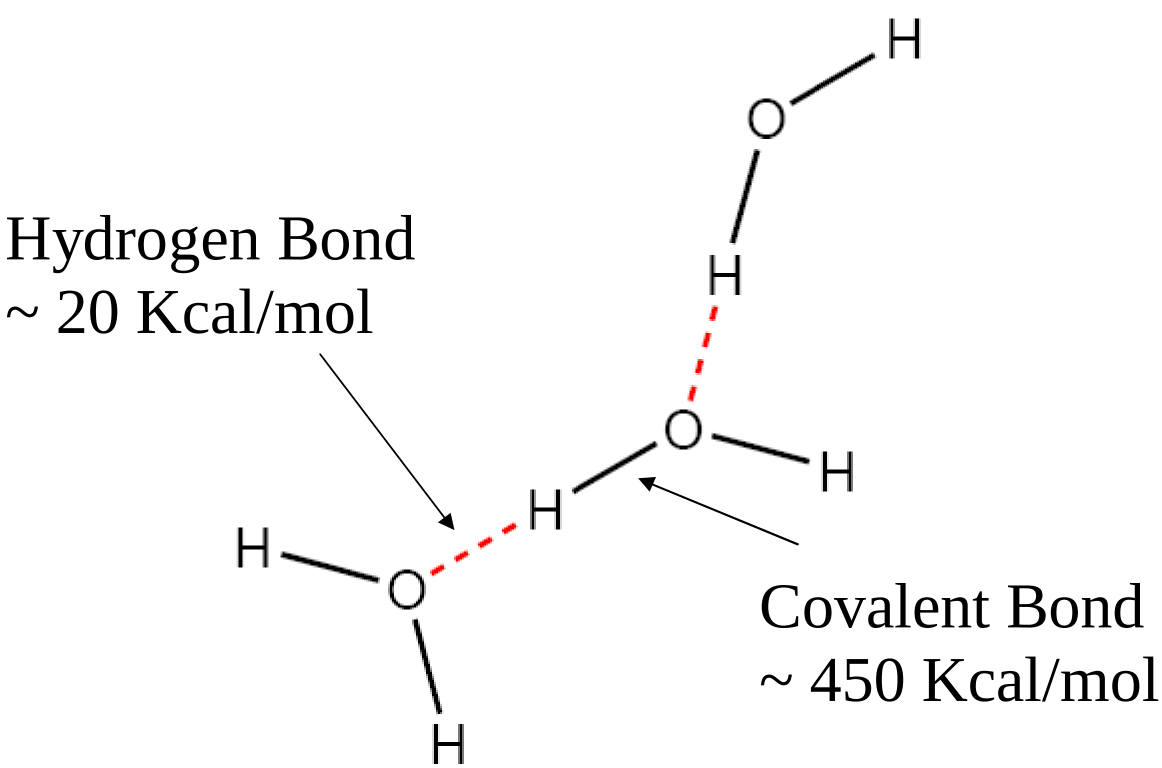
Appropriate data for such a plot are:

Mol. Wt.	Compound	b.p.(°C)
18	H_2O	100
34	H_2S	-60.3
81	[illegible]	[illegible]

The boiling points of H_2S, H_2Se, and H_2Te increase with increasing molecular weight, but the b.p. of water is some 200˚C higher than that expected (-90˚C) by extrapolation. Hydrogen bonding is almost negligible in H_2S, H_2Se, and H_2Te, mostly because of the large size of the central atom.

Hydrogen Bonding in water gives it <u>very special properties</u>

1. Very high boiling point
2. VERY LOW DENSITY OF SOLID FORM (ICE)
3. “Glue” for proteins and DNA



Bottom Line: LIFE AS WE KNOW IT WOULD NOT EXIST WITHOUT HYDROGEN BONDING!

WHY?

H_2O would be a gas at room temperature (we would not be here!)

H_2O solid (ice) would not float – lakes would freeze from the bottom up and aquatic life would not be capable of existing.

Water-Containing Compounds. Water is known to form hydrates and compounds called clathrates with various elements.

(a) Clathrate Compounds. Clathrates are cage-like compounds of water in which other molecules or atoms can be trapped. For example,. Xenon forms compounds of the composition $Xe \cdot 7.3\ H_2O$, and chlorine $Cl_2 \cdot 8H_2O$. Water in the solid state forms pockets or cage-like holes where the Xe atoms and Cl_2 molecules fit. Hydrocarbons like methane, CH_4, and butane, C_4H_{10}, also form clathrate compounds with water. It is presently believed that xenon and chloroform ($CHCl_3$) act as anesthetics by forming clathrate compounds with water within connecting parts of the nervous system, thus clocking the transmission of pain. It is also believed that methane gas is trapped under the sea by forming clathrate compounds with water.

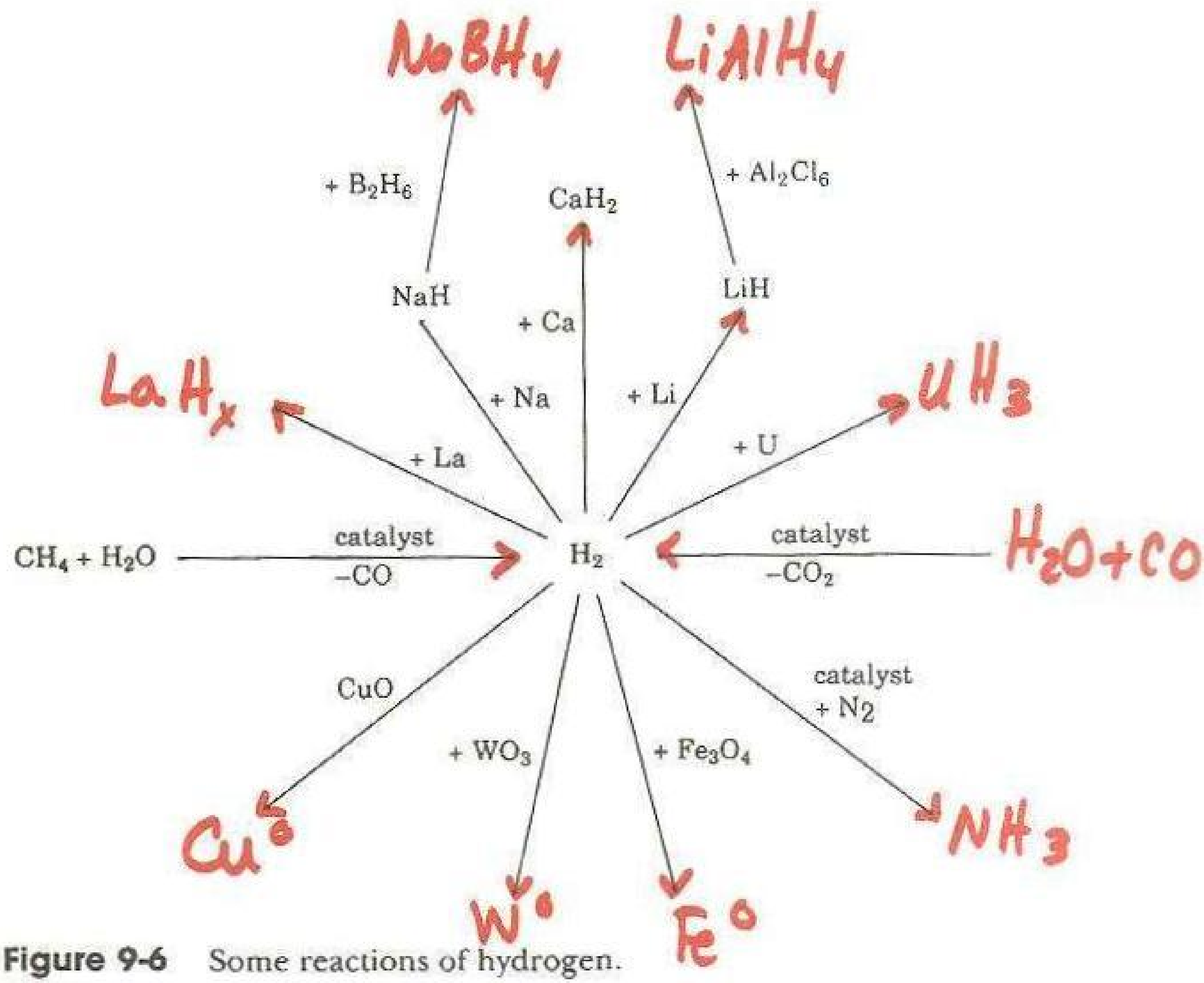


Figure 9-6 Some reactions of hydrogen.