

## 4.1: Hydrogen and hydrides

### (a) Hydrogen

Hydrogen is the simplest element consisting of a proton and an electron, and the most abundant element in the universe. It is next to oxygen and silicon, and about 1 wt% of all the elements on the Earth. Needless to say, most hydrogen exists as water on the Earth. Since its polarity may change freely between hydride ( $\text{H}^-$ ), atom ( $\text{H}$ ), and proton ( $\text{H}^+$ ), hydrogen also forms various compounds with many elements including oxygen and carbon. Therefore, hydrogen is highly important in chemistry.

Of the three kinds of isotopes of hydrogen, deuterium, D, was discovered by H. C. Urey and others in 1932, and subsequently tritium, T, was prepared from deuterium in 1934. About 0.015% of hydrogen is present as deuterium, and this can be enriched by electrolysis of water. Tritium is a radioactive isotope emitting  $\beta$ -particles with a half-life of 12.33 years. Since the mass of deuterium and tritium is about twice and three times that of hydrogen, respectively, the physical properties of the isotopes, and compounds containing them, differ considerably. Some properties of the isotopes and water are listed in Table 4.1.1. When the E-H bond in a hydrogen compound is converted into the E-D by deuterium substitution, the E-H stretching frequency in an infrared spectrum is reduced to about  $\frac{1}{\sqrt{2}}$ , which is useful for determining the position of the hydrogen atom. It is sometimes possible to conclude that scission of the bond with a hydrogen is the rate-determining step when the deuterium substitution shows a marked effect on the rate of reaction of a hydrogen-containing compound.

Since the nuclear spin of hydrogen is  $1/2$  and given its abundance, it is the most important nuclide for NMR spectroscopy. NMR is widely used not only for identification of organic compounds, but also for medical diagnostic purposes using MRI (magnetic resonance imaging) of water in living bodies. Human organs can now be observed with this non-invasive method.

Table 4.1.1 Properties of isotopic hydrogen and water

Properties	$\text{H}_2$	$\text{D}_2$	$\text{T}_2$	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$	$\text{T}_2\text{O}$
Melting point*	13.957	18.73	20.62	0.00	3.81	4.48
Boiling point	20.39	23.67	25.04	100.00	101.42	101.51
Density ( $\text{g cm}^{-3}$ , $25^\circ\text{C}$ )				0.9970	1.1044	1.2138
Temp. of maximum density ( $^\circ\text{C}$ )				3.98	11.23	13.4

\* hydrogen (K), water ( $^\circ\text{C}$ )

There are nuclear-spin isomers in diatomic molecules of the nuclides whose spin is not zero. Especially in the case of a hydrogen molecule, the difference of properties is significant. Spins of **para-hydrogen** are anti-parallel and the sum is 0 leading to a **singlet state**. Spins of **ortho-hydrogen** are parallel and the sum is 1 resulting in a **triplet state**. Since *para*-hydrogen is in a lower energy state, it is the stabler form at low temperatures. The theoretical ratio of *para*-hydrogen is 100% at 0 K, but it decreases to about 25% at room temperature, since the ratio of *ortho*-hydrogen increases at higher temperatures. Gas chromatography and rotational lines in the electronic band spectrum of  $\text{H}_2$  can distinguish two hydrogen isomers.

### (b) Hydride

Binary hydrides can be classified according to the position of the element in the periodic table, and by the bond characters. The hydrides of alkali and alkaline earth metals among s-block elements are ionic compounds structurally analogous to halides and are called saline hydrides. The Group 13-17 p-block elements form covalent molecular hydrides. No hydride of rare gas elements has been reported. Some of the d-block and f-block transition metals form metal hydrides exhibiting metallic properties. Transition metals which do not give binary hydrides form many molecular hydride complexes coordinated by stabilization ligands, such as carbonyl (CO), tertiaryphosphines ( $\text{PR}_3$ ), or cyclopentadienyl ( $\text{C}_5\text{H}_5$ ) (refer to Section 6.1). Typical hydrides of each class are given below.

## Saline hydrides

**Lithium hydride**, LiH, is a colorless crystalline compound (mp (melting point) 680 °C). Li<sup>+</sup> and H<sup>-</sup> form a lattice with a rock salt type structure. Quantitative evolution of hydrogen gas at the anode during the electrolysis of the fused salt suggests the existence of H<sup>-</sup>. Water reacts vigorously with lithium hydride evolving hydrogen gas. Since it dissolves in ethers slightly, the hydride is used as a reducing agent in organic chemistry.

**Calcium hydride**, CaH<sub>2</sub>, is a colorless crystalline compound (mp 816 °C), and reacts mildly with water evolving hydrogen gas. This hydride is used as a hydrogen gas generator, or a dehydrating agent for organic solvents. It is used also as a reducing agent.

**Lithium tetrahydridoaluminate**, LiAlH<sub>4</sub>, is a colorless crystalline compound (decomposes above 125 °C) usually called lithium aluminum hydride. The hydride dissolves in ethers, and reacts violently with water. It is used as a reducing and hydrogenating agent and for dehydrating organic solvents.

**Sodium tetrahydroborate**, NaBH<sub>4</sub>, is a white crystalline compound (decomposes at 400 °C) usually called sodium borohydride. It is soluble in water and decomposes at high temperatures evolving hydrogen gas. It is used as a reducing agent for inorganic and organic compounds, for preparation of hydride complexes, etc.

## Molecular hydrides

All hydrides other than those of carbon (methane) and oxygen (water) are poisonous gases with very high reactivity and should be handled very carefully. Although there are methods of generating the gases in laboratories, recently many are also available in cylinders.

**Diborane**, B<sub>2</sub>H<sub>6</sub>, is a colorless and poisonous gas (mp -164.9 °C and bp -92.6 °C) with a characteristic irritating odor. This hydride is a powerful reducing agent of inorganic and organic compounds. It is also useful in organic synthesis as a hydroboration agent that introduces functional groups to olefins, after addition of an olefin followed by reactions with suitable reagents.

**Silane**, SiH<sub>4</sub>, is a colorless and deadly poisonous gas (mp -185 °C and bp -111.9 °C) with a pungent smell, and is called also monosilane.

**Ammonia**, NH<sub>3</sub>, is a colorless and poisonous gas (mp -77.7 °C and bp -33.4 °C) with a characteristic irritating odor. Although it is used in many cases as aqueous ammonia since it dissolves well in water, liquid ammonia is also used as a nonaqueous solvent for special reactions. Since the Harber-Bosch process of ammonia synthesis was developed in 1913, it has been one of the most important compounds in chemical industries and is used as a starting chemical for many nitrogenous compounds. It is used also as a refrigerant.

**Phosphine**, PH<sub>3</sub>, is a colorless and deadly poisonous gas (mp -133 °C and bp -87.7 °C) with a bad smell, and is called also phosphorus hydride. It burns spontaneously in air. It is used in vapor phase epitaxial growth, in transition metal coordination chemistry, etc.

**Hydrogen sulfide**, H<sub>2</sub>S, is a colorless and deadly poisonous gas (mp -85.5 °C and bp -60.7 °C) with a rotten egg odor. Although often used with insufficient care, it is very dangerous and should be handled only in an environment with good ventilation. It is used in chemical analysis for the precipitation of metal ions, preparation of sulfur compounds, etc.

**Hydrogen fluoride**, HF, is a colorless, fuming, and low boiling point liquid (mp -83 °C and bp 19.5 °C), with an irritating odor. It is used for preparing inorganic and organic fluorine compounds. Because of its high permittivity, it can be used as a special nonaqueous solvent. The aqueous solution is called fluoric acid and is stored in polyethylene containers since the acid corrodes glass.

## Metallic hydrides

The hydrides MH<sub>x</sub> which show metallic properties are nonstoichiometric interstitial-type solids in which hydrogen occupies a part of the cavities of the metal lattice. Usually x is not an integer in these compounds. There are Group 3 (Sc, Y), Group 4 (Ti, Zr, Hf), Group 5 (V, Nb, Ta), Cr, Ni, Pd, and Cu metallic hydrides among the d block elements, but the hydrides of other metals in Group 6 to 11 are not known. Palladium Pd reacts with hydrogen gas at ambient temperatures, and forms hydrides that have the composition PdH<sub>x</sub> (x < 1). Many metallic hydrides show metallic conductivity. LaNi<sub>5</sub> is an intermetallic compound of lanthanum and nickel. It occludes nearly 6 hydrogen atoms per unit lattice and is converted to LaNi<sub>5</sub>H<sub>6</sub>. It is one of the candidates for use as a hydrogen storage material with the development of hydrogen-fueled cars.

### ? Exercise 4.1.1

Write the oxidation number of the hydrogen atom in  $\text{H}_2$ ,  $\text{NaH}$ ,  $\text{NH}_3$ , and  $\text{HCl}$ .

#### Answer

- $\text{H}_2$  (0)
- $\text{NaH}$  (-1)
- $\text{NH}_3$  (+1)
- and  $\text{HCl}$  (+1).

## Hydride complexes

Complexes coordinated by hydride ligands are called **hydride complexes**. The Group 6 to 10 transition metals that do not form binary hydrides give many hydride complexes with auxiliary ligands such as carbonyl and tertiaryphosphines. Although it was only at the end of the 1950s that hydride was accepted as a ligand, thousands of hydride complexes are known at present. Furthermore, with the synthesis in the 1980's of molecular hydrogen complexes, the chemistry of transition metal hydrogen compounds took a new turn. Research on the homogeneous catalysis of hydrocarbons in which hydride or dihydrogen complexes participate is also progressing.

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