Chapter 9

HYDROGEN

9-1 Introduction

Hydrogen (not carbon) forms more compounds than any other element. For this and other reasons, many aspects of hydrogen chemistry are treated elsewhere in this book. Protonic acids and the aqueous hydrogen ion have already been discussed in Chapter 7. This chapter examines certain topics that most logically should be considered at this point.

Three isotopes of hydrogen are known: ^1H, ^2H (deuterium or D), and ^3H (tritium or T). Although isotope effects are greatest for hydrogen, justifying the use of distinctive names for the two heavier isotopes, the chemical properties of H, D, and T are essentially identical, except in matters such as rates and equilibrium constants of reactions. The normal form of the element is the diatomic molecule; the various possibilities are H_2, D_2, T_2, HD, HT, DT.

Naturally occurring hydrogen contains 0.0156% deuterium, while tritium (formed continuously in the upper atmosphere in nuclear reactions induced by cosmic rays) occurs naturally in only minute amounts that are believed to be of the order of 1 in 10^{17} and is radioactive (β^-, 12.4 years).

Deuterium, as D_2O, is separated from water by fractional distillation or electrolysis and is available in ton quantities for use as a moderator in nuclear reactors. Deuterium oxide is also useful as a source of deuterium in deuterium-labeled compounds.

Molecular hydrogen is a colorless, odorless gas (fp 20.28 K) virtually insoluble in water. It is most easily prepared by the action of dilute acids on metals such as Zn or Fe, and by electrolysis of water.

Industrially, hydrogen is obtained by the so-called steam re-forming of methane or light petroleum over a promoted nickel catalyst at about 750 °C. The process is complicated, but the main reaction, illustrated with methane, is given in Reaction 9-1.1.

$$CH_4 + H_2O = CO + 3\ H_2 \qquad (9\text{-}1.1)$$

The mixtures of CO and H_2 that are produced in Reaction 9-1.1 are called synthesis gas, or "syngas." Synthesis gas can now also be produced from trash, sewage, sawdust, scrap wood, newspapers, and so on. The production of syngas from coal is termed "coal gasification."

When desired, the proportion of hydrogen in synthesis gas mixtures can be increased by use of Reaction 9-1.2.

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H = -42\ \text{kJ mol}^{-1} \qquad (9\text{-}1.2)$$

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$$CO + H_2O = CO_2 + H_2 \qquad \Delta H = -42\ \text{kJ mol}^{-1} \qquad (9\text{-}1.2)$$

This is the water–gas shift reaction, which proceeds either at relatively high temperatures (280–350 °C) using an iron–chromate type catalyst, or at lower temperatures using copper-containing catalysts. The carbon dioxide side product is removed by scrubbing with arsenite solution or ethanolamine, from which it is recovered for other uses, such as the manufacturing of dry ice. The remaining small amounts of CO and CO_2 impurities (which may act as unwanted poisons in subsequent chemical uses of the hydrogen) are catalytically converted to methane (which is usually innocuous) according to Reactions 9-1.3 and 9-1.4.

$$CO + 3\ H_2 = CH_4 + H_2O \tag{9-1.3}$$

$$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O \tag{9-1.4}$$

In addition to its use for hydrogen and carbon monoxide production, synthesis gas is used directly in large-scale catalyzed syntheses of methanol (Chapter 30), and of higher alcohols (e.g., ethanol), as shown in Reaction 9-1.5:

$$2\ CO + 4\ H_2 \longrightarrow CH_3CH_2OH + H_2O \tag{9-1.5}$$

or 2-ethylhexanol.

Hydrogen is not an exceptionally reactive element at low temperatures, because the bond dissociation energy of the molecule is considerably endothermic.

$$H_2 = 2\ H \qquad \Delta H = 434.1\ \text{kJ mol}^{-1} \tag{9-1.6}$$

Hydrogen burns in air to form water, and it will react explosively with oxygen and with halogens under certain conditions. At high temperatures, hydrogen gas will reduce many oxides to lower oxides, as in Reaction 9-1.7.

$$2\ MO_2 + H_2 \longrightarrow M_2O_3 + H_2O \tag{9-1.7}$$

It is also useful for the complete reduction of many metal oxides to the metals, as shown in Reactions 9-1.8 through 9-1.10.

$$MO_2 + 2\ H_2 \longrightarrow M + 2\ H_2O \tag{9-1.8}$$

$$M_2O_3 + 3\ H_2 \longrightarrow 2\ M + 3\ H_2O \tag{9-1.9}$$

$$MO + H_2 \longrightarrow M + H_2O \tag{9-1.10}$$

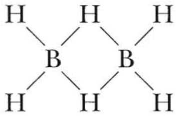
In the presence of iron or ruthenium catalysts at high temperature and pressure, H_2 will react with N_2 to produce NH_3. With electropositive metals and most nonmetals, hydrogen forms hydrides, as we shall discuss in Section 9-6. Hydrogen serves as a reducing or hydrogen-transfer agent for a variety of organic and inorganic substances, but a catalyst is required in most cases. The reduction of alkenes to alkanes by hydrogen over Pt or Ni is a typical example.

9-2 The Bonding of Hydrogen

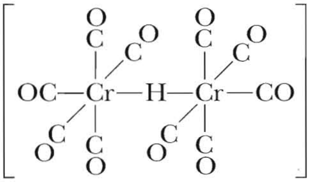
The chemistry of hydrogen depends mainly on the three electronic processes discussed in Chapter 8: (1) loss of a valence electron to give H^+, (2) acquisition of an electron to give H^-, and (3) formation of a single covalent bond, as in CH_4.

However, hydrogen has additional unique bonding features. The nature of the proton and the complete absence of any shielding of the nuclear charge by electron shells allow other forms of chemical activity that are either unique to hydrogen or particularly characteristic of it. Some of these are the following, which we shall discuss in some detail subsequently.

1. The formation of numerous compounds, often nonstoichiometric, with metallic elements. These compounds are generally called hydrides but cannot be regarded as simple saline hydrides (Section 9-6).
2. The formation of hydrogen bridge bonds in electron-deficient compounds (e.g., Structure 9-I) and transition metal complexes (e.g., Structure 9-II).



9-I



9-II

A classic example of bridge bonds is provided by diborane (Structure 9-I) and related compounds (Chapter 12). The electronic nature of such bridge bonds was discussed in Chapter 3.

3. The hydrogen bond is important not only because it is essential to an understanding of much other hydrogen chemistry, but also because it is one of the most intensively studied examples of intermolecular attraction. Hydrogen bonds generally dominate the chemistry of water, aqueous solutions, hydroxylic solvents, and OH-containing species and are of crucial importance in biological systems, since they are responsible for the linking of polypeptide chains in proteins and the base pairs of nucleic acids.

9-3 The Hydrogen Bond

When hydrogen is bonded to another atom X, mainly F, O, N, or Cl, such that the X—H bond is quite polar, with H bearing a partial positive charge, it can interact with another negative or electron-rich atom Y, to form what is called a hydrogen bond (H bond), written as

$$\mathrm{X{-}H{-}{-}{-}Y}$$

Although the details are subject to variation, and controversy, it is generally considered that typical hydrogen bonds are due largely to electrostatic attraction of H and Y. The X—H distance becomes slightly longer, but this bond remains essentially a normal two-electron bond. The H---Y distance is generally much longer than that of a normal covalent H—Y bond.

In the case of the very strongest hydrogen bonds, the X···Y distance becomes quite short and the X—H and Y---H distances come close to being equal. In these cases there are presumably covalent and electrostatic components in both the X—H and Y—H bonds.

Experimental evidence for hydrogen bonding came first from comparisons of the physical properties of hydrogen compounds. The apparently abnormally high boiling points of NH_3, H_2O, and HF (Fig. 9-1) are classic examples which imply association of these molecules in the liquid phase. Other properties such as heats of vaporization provided further evidence for association. Although physical properties reflecting association are still a useful tool in detecting hydrogen bonding, the deeper understanding of H bonds and the determination of their parameters comes from X-ray or neutron diffraction of solids, and from other techniques, notably ion cyclotron resonance, NMR, IR, and Raman spectroscopies, and calorimetry.

Structural evidence for hydrogen bonds is provided by the $X \cdots Y$ distances, which are shorter than the expected van der Waals contact when a hydrogen bond exists. For instance, in crystalline $NaHCO_3$ there are four kinds of $O \cdots O$ distances between HCO_3^- ions with values of 3.12, 3.15, 3.19, and 2.55 Å. The first three are about equal to twice the van der Waals radius of oxygen, but the last one indicates a hydrogen bond, O—H---O. When an X—H group enters into hydrogen bonding, the X—H stretching band in the IR spectrum is lowered in frequency, broadened, and increased in integrated intensity.

The enthalpies of hydrogen bonds are relatively small in most instances: 20–30 kJ mol^{-1}, as compared with covalent bond enthalpies of 200 kJ mol^{-1}, and up. Nevertheless, these weak bonds can have a profound effect on the properties and chemical reactivity of substances in which they occur. This effect is clearly seen from Fig. 9-1, where water would boil at about −100 °C instead of +100 °C if hydrogen bonds did not play their role. Obviously, life itself (as we know it) depends on the existence of such weak hydrogen bonds.

However, there are also strong and very strong hydrogen bonds mainly involving O and F atoms in cations and anions. The enthalpies are in the ranges 50–100 and greater than 100 kJ mol^{-1}, respectively. The best example of a very strong, short bond is that in the FHF^- anion, where the proton is centered between the F atoms that are only 2.26-Å apart. Similar very short bonds are found in $[HOHOH]^-$, HCl_2^-, $H_5O_2^+$, $(CH_3OH)_2H^+$, and $H_3F_2^-$. An unusual example involving nitrogen is the anion $[(OC)_5CrCN—H—NCCr(CO)_5]^-$.

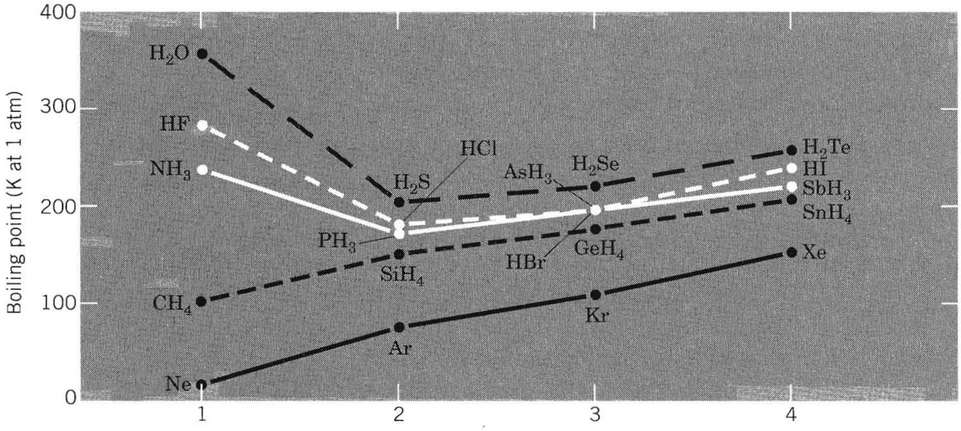


Figure 9-1 Periodic trends in the boiling points of some molecular hydrides, with a comparison to the noble gases.

Finally, we can note a rather similar, though different, type of interaction between hydrogen atoms bound to carbon atoms of ligands (e.g., CH_3 and other alkyl type ligands) and the transition metals to which these ligands are complexed, namely, C—H···M. Such bonds are called agostic, and are identified by a sometimes significant lengthening of the C—H bond. A few additional examples of normal hydrogen bonds involving carbon (C—H···C, C—H···M, and C—H···Cl) and N—H···M have also been characterized.

9-4 Ice and Water

The structure of water is very important since it is the medium in which so much chemistry, including the chemistry of life, takes place. The structure of ice is of interest for clues about the structure of water. There are nine known modifications of ice, the stability of each depending on temperature and pressure. The ice formed in equilibrium with water at 0 °C and 1 atm is called ice I and has the structure shown in Fig. 9-2. There is an infinite array of oxygen atoms, each tetrahedrally surrounded by four others with hydrogen bonds linking each pair.

The structural nature of liquid water is still controversial. The structure is not random, as found in liquids consisting of more-or-less spherical nonpolar molecules; instead, it is highly structured owing to the persistence of hydrogen bonds. Even at 90 °C only a few percent of the water molecules appear not to be hydrogen bonded. Still, there is considerable disorder, or randomness, as befits a liquid.

In an attractive, though not universally accepted, model of liquid water the liquid consists at any instant of an imperfect network, very similar to the network of ice I, but differing in that (a) some interstices contain water molecules that do not belong to the network but, instead, disturb it; (b) the network is patchy and does not extend over long distances without breaks; (c) the short-range ordered regions are constantly disintegrating and re-forming (they are "flickering clus-

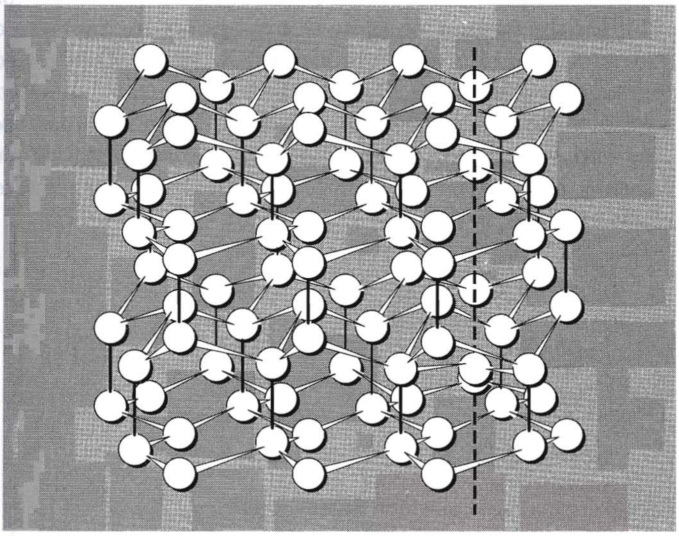


Figure 9-2 The structure of ice I. Only the oxygen atoms are shown. The O···O distances are 2.75 Å.

ters"); and (d) the network is slightly expanded compared with ice I. The fact that water has a slightly higher density than ice I may be attributed to the presence of enough interstitial water molecules to offset the expansion and disordering of the ice I network. This model of water receives support from X-ray scattering studies.

9-5 Hydrates and Water Clathrates

Solids that consist of molecules of a compound together with water molecules are called *hydrates*. The majority contain discrete water molecules either bound to cations through the oxygen atom or bound to anions or other electron-rich atoms through hydrogen bonds, or both, as is shown in Fig. 9-3. In many cases when the hydrate is heated above 100 °C, the water can be driven off leaving the *anhydrous* compound. However, there are many cases where something other than, or in addition to, water is driven off. For example, many hydrated chlorides give off HCl and a basic or oxo chloride is left.

$$ScCl_3 \cdot 6H_2O \xrightarrow{\text{Heat}} ScOCl + 2\ HCl(g) + 5\ H_2O(g) \qquad (9\text{-}5.1)$$

Water also forms materials called *gas hydrates*, which are actually a type of inclusion or clathrate compound. A clathrate (from the Latin clathratus, meaning "enclosed or protected by crossbars or gratings") is a substance in which one component, the host molecule, crystallizes with an open structure that contains holes or channels in which atoms or small molecules of the second component, the guest molecule, can be trapped. Many substances other than water, for example *p*-quinol, $C_6H_4(OH)_2$, urea, and Fe(acac)$_3$, can form inclusion compounds, and a great variety of small molecules can be trapped.

There are two common gas hydrate structures and both are cubic. In one, the unit cell contains 46 molecules of H_2O connected to form six medium-size and two small cages. This structure is adopted when atoms (Ar, Kr, or Xe) or relatively small molecules (e.g., Cl_2, SO_2, or CH_3Cl) are used, generally at pressures greater than 1 atm for the gases. Complete filling of only the medium cages by atoms or molecules (X) would give a composition $X{\cdot}7.67\ H_2O$, while complete filling of all eight cages would lead to $X{\cdot}5.76\ H_2O$. In practice, complete filling of all cages of one or both types is seldom attained. These formulas, therefore, represent limiting rather than observed compositions; for instance, the usual formula for chlorine hydrate is $Cl_2{\cdot}7.30\ H_2O$. The second structure, often

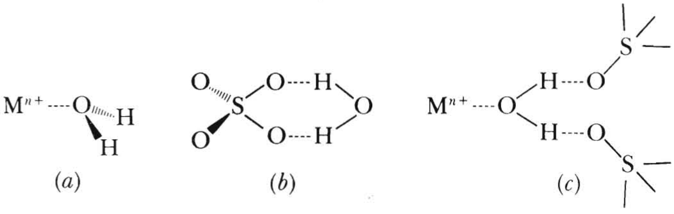


Figure 9-3 Three principal ways in which water molecules are bound in hydrates: (*a*) through oxygen to cations, (*b*) through hydrogen to anions, and (*c*) a combination of the preceding two.

formed in the presence of larger molecules of liquid substances (and thus sometimes called the *liquid hydrate* structure) such as chloroform and ethyl chloride, has a unit cell containing 136 water molecules with 8 large cages and 16 smaller ones. The anesthetic effect of substances such as chloroform may be due to the formation of liquid hydrate crystals in brain tissue. The methane clathrate occurs in vast quantities under arctic permafrost.

A third notable class of clathrate compounds, *salt hydrates*, is formed when tetraalkylammonium or sulfonium salts crystallize from aqueous solution with high water content, for example, $[(C_4H_9)_4N]C_6H_5CO_2{\cdot}39.5H_2O$ or $[(C_4H_9)_3S]F{\cdot}20\ H_2O$. The structures of these substances are very similar to the gas and liquid hydrate structures in a general way, although they are different in detail. These structures consist of frameworks constructed mainly of hydrogen-bonded water molecules, but apparently also include the anions (e.g., F^-) or parts of the anions (e.g., the O atoms of the benzoate ion). The cations and parts of the anions (e.g., the C_6H_5C part of the benzoate ion) occupy cavities in an incomplete and random way.

9-6 Hydrides

Although all compounds of hydrogen could be termed hydrides, not all hydrogen-containing compounds display "hydridic" character. In general, **hydridic substances** are those that either react as hydride ion (H^-) donors or clearly contain anionic hydrogen. Thus it is necessary to distinguish hydridic substances (e.g., NaH) from those that are either neutral (e.g., CH_4) or acidic (e.g., HCl). This distinction between hydrogen-containing substances that are hydridic, neutral, or acidic runs roughly parallel to the bonding considerations mentioned in Section 9-2; that is, hydrogen may be bound in its compounds essentially as (or serve, on reaction, as a source of) H^-, $H\cdot$, or H^+, respectively. It is also, at times, convenient to classify the compounds of hydrogen as being

1. Either ionic or covalent.
2. Either stoichiometric or nonstoichiometric.
3. Either binary or complex.

Among the strictly binary hydrides, Figure 9-4 gives a general idea of the types of compounds formed by hydrogen.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La–Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac			U,Pu												
Saline hydrides				Transition metal hydrides						Borderline hydrides				Covalent hydrides			

Figure 9-4 A classification of the binary hydrides. For the transition elements, in addition to the simple binary hydrides, complex molecules or ions containing M—H bonds are also known.

Covalent Hydrides

The principal covalent hydrides of the nontransition elements will be discussed more completely in the appropriate chapters that remain. Briefly, the covalent hydrides include

1. Neutral, binary XH_4 compounds of Group IVB(14), for example, CH_4.
2. Somewhat basic, binary XH_3 compounds of Group VB(15), for example, NH_3 and PH_3.
3. Weakly acidic or amphoteric, binary XH_2 compounds of Group VIB(16), for example, H_2S and H_2O.
4. Strongly acidic, binary HX compounds of Group VIIB(17), for example, HCl and HI.
5. Numerous covalent hydrides of boron, to be discussed in Chapter 12.
6. Hydridic, complex compounds of hydrogen, two examples of which are $LiAlH_4$ and $NaBH_4$, which serve as powerful reducing agents despite the fact that the Al—H and B—H bonds in these substances are essentially covalent in nature.

The latter two compounds provide an interesting illustration of covalent hydrides that are hydridic. First of all, although the two compounds are ionic (being Li^+ and Na^+ salts), the tetrahedral anions in these salts contain essentially covalent bonds to hydrogen. Furthermore, the tetrahydroaluminate and tetrahydroborate anions are each hydridic, being formed by the action of LiH on Al_2Cl_6 in ether, as in Reaction 9-6.1:

$$8\ LiH + Al_2Cl_6 \longrightarrow 2\ LiAlH_4 + 6\ LiCl \qquad (9\text{-}6.1)$$

and by the action of NaH on diborane, as in Reaction 9-6.2.

$$2\ NaH + B_2H_6 \longrightarrow 2\ NaBH_4 \qquad (9\text{-}6.2)$$

Also, each of the above tetrahydro anions is a powerful hydrogen-transfer agent, as shown in Reactions 9-6.3 and 9-6.4.

$$2\ LiAlH_4 + 2\ SiCl_4 \longrightarrow 2\ SiH_4 + 2\ LiCl + Al_2Cl_6 \qquad (9\text{-}6.3)$$

$$I_2 + 2\ NaBH_4 \longrightarrow B_2H_6 + 2\ NaI + H_2 \qquad (9\text{-}6.4)$$

In Reaction 9-6.3, we have the reduction of $SiCl_4$ by $LiAlH_4$ to give silane (SiH_4), whereas in Reaction 9-6.4 we have the classic synthesis of diborane (B_2H_6) by reduction of I_2 using sodium borohydride.

Saline Hydrides

The most electropositive elements, the alkali metals and the larger of the alkaline earth metals, react directly with dihydrogen to form stoichiometric hydrides having considerable ionic character. These compounds are called the saline (saltlike) hydrides. Those of the heavier metals are truly hydridic substances, since they are properly considered to contain metal cations and H^- ions. However, due to the small size and high charge density of the ions of the smaller metals [Be and Mg in Group IIA(2) and Li in Group IA(1)], their hydrides have more covalent character, and BeH_2 is best described as a covalent polymer having Be—H—Be bridges.

The saline hydrides are ionic substances, as shown by the facts that (a) they conduct electricity when molten, and (b) when dissolved and electrolyzed in molten halides, the saline hydrides evolve dihydrogen at the positive electrode (anode), where oxidation of H^- takes place. The ionic nature of the saline hydrides is further indicated by their structures. The ionic radius of H^- lies between that of F^- and Cl^-, and the alkali metal hydrides, LiH to CsH, all adopt the NaCl structure. The structure of MgH_2 is the same as that of rutile (Chapter 4), whereas CaH_2, SrH_2, and BaH_2 adopt a type of $PbCl_2$ structure having a slightly distorted hcp array.

The saline hydrides are all prepared by direct interaction of the metals with elemental hydrogen at 300–700 °C, as shown in Reactions 9-6.5 and 9-6.6.

$$2\ M(\ell) + H_2(g) \longrightarrow 2\ MH(s) \qquad (9\text{-}6.5)$$

$$M(\ell) + H_2(g) \longrightarrow MH_2(s) \qquad (9\text{-}6.6)$$

The rates for Reaction 9-6.5 are in the order Li > Cs > K > Na. The products of Reactions 9-6.5 and 9-6.6 are white crystalline solids when they are pure, but are usually gray owing to traces of the metals from which they were made.

All of the saline hydrides decompose thermally to give the metal and hydrogen, although lithium hydride alone is stable to its melting point (688 °C). Also, only LiH is unreactive at moderate temperatures towards oxygen or chlorine. Because of its relative unreactivity, LiH finds practical use only in the synthesis of $LiAlH_4$, as in Reaction 9-6.1.

Since they are hydridic, the saline hydrides (except LiH) are quite reactive with water and air, as shown in Reactions 9-6.7 and 9-6.8.

$$MH(s) + H_2O \longrightarrow H_2(g) + MOH(aq) \qquad (9\text{-}6.7)$$

$$MH_2(s) + H_2O \longrightarrow H_2(g) + M(OH)_2(aq) \qquad (9\text{-}6.8)$$

The saline hydrides are powerful reducing or hydrogen-transfer agents, as shown in Reactions 9-6.1 and 9-6.2, as well as by Reactions 9-6.9 through 9-6.11.

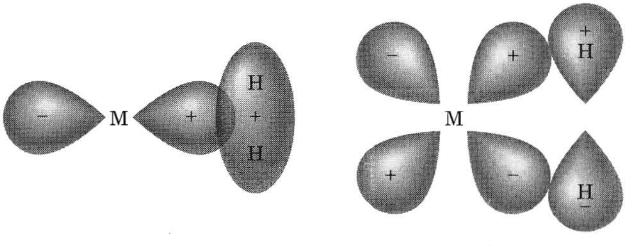
$$NaH + B(OCH_3)_3 \longrightarrow Na[HB(OCH_3)_3] \qquad (9\text{-}6.9)$$

$$4\ NaH + TiCl_4 \longrightarrow Ti^0 + 4\ NaCl + 2\ H_2 \qquad (9\text{-}6.10)$$

$$NaH + ROH \longrightarrow NaOR + H_2 \qquad (9\text{-}6.11)$$

Transition Metal Hydrides

The transition metal hydrides are extremely diverse in their structures and properties. The wide variety of transition metal compounds that contain M—H bonds includes stoichiometric binary anions such as $[ReH_9]^{2-}$ and $[FeH_6]^{4-}$; complex stoichiometric substances with essentially covalent bonds to hydrogen, such as $HMn(CO)_5$ (to be discussed in Chapter 28) and $Re_2H_8(PR_3)_4$; as well as nonstoichiometric compounds formed by the direct reaction of hydrogen with various transition metals, as described below.



(*a*) (*b*)

Figure 9-5 The two components of the metal–dihydrogen bond in so-called "side-on" dihydrogen complexes. (*a*) Donation of electron density from the σ-bonding molecular orbital of dihydrogen into an empty σ orbital of the metal, and (*b*) "back-donation" of π-electron density from a filled *d* orbital of the metal into the σ* antibonding orbital of the H—H linkage. Both components of the M—H_2 bond weaken the H—H linkage.

Hydrogen reacts with many transition metals or their alloys on heating to give exceedingly complicated substances. They are black or grayish-black, nonstoichoimetric solids, typical formulas being $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.7}$, and $ZrH_{1.9}$. Under conditions of excess hydrogen, limiting compositions may be achieved, but in any given preparation, numerous structural phases may be present, each with its own stoichiometric composition.

A satisfactory theoretical understanding of these substances has not yet been developed. Whether the hydrogen is bound in the metal lattice in its hydridic, protonic, or molecular form is not known. The most straightforward view of the compounds is that hydrogen atoms are located in regular interstices between the metal atoms, and these substances are therefore sometimes termed the *interstitial hydrides.* In this fashion, the element palladium (and to a lesser extent Pt) can absorb very large volumes of hydrogen, and thus can be used to purify hydrogen.

Uniquely, uranium forms a well-defined, stoichiometric hydride by the rapid and exothermic reaction of the metal with hydrogen at 250–300 °C to yield a pyrophoric black powder, as in Reaction 9-6.12.

$$U + \tfrac{3}{2} H_2 \longrightarrow UH_3 \qquad (9\text{-}6.12)$$

Uranium hydride (UH_3) is of importance chemically because it is often more suitable for the synthesis of uranium compounds than the metal. For example, with water it yields UO_2, whereas with Cl_2 and H_2S it yields UCl_4 and US_2, respectively.

Dihydrogen (H_2) as a Ligand

Within the past decade, it has been shown that the H_2 molecule can behave as a ligand and occupy a place in the coordination sphere around a metal atom. This happens only under special circumstances, with metals in low oxidation states. The H_2 molecule takes a "side-on" orientation with respect to the metal, and the bonding is accomplished by a combination of (a) weak donation of the bonding electrons of the H_2 molecule to an empty σ orbital of the metal atom and (b) ac-

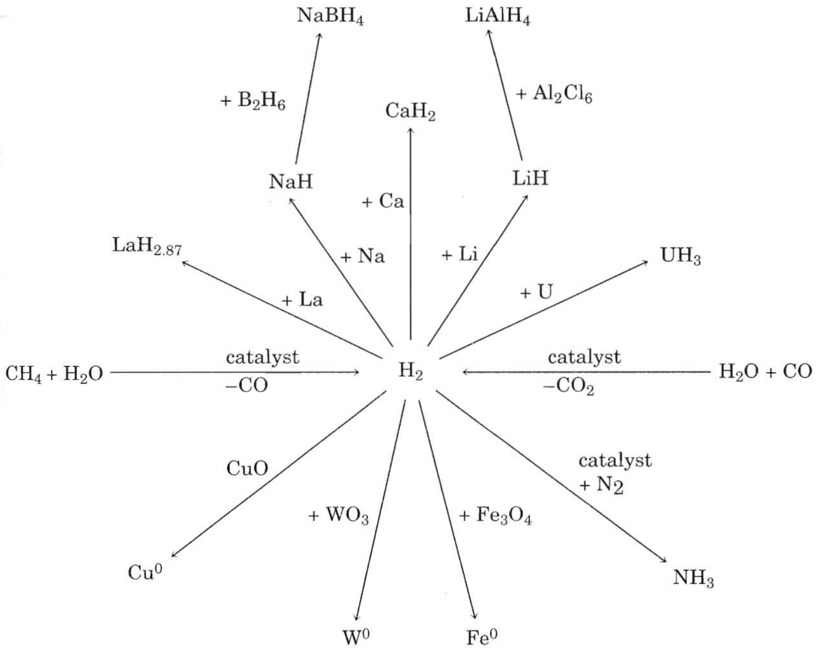
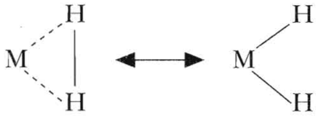


Figure 9-6 Some reactions of hydrogen.

ceptance of electrons from a filled orbital of the metal atom into the σ^* antibonding orbital of H_2, as shown in Fig. 9-5. Clearly, each of these parts of the bonding mechanism weakens and lengthens the H—H bond. Thus, unless conditions are very delicately balanced, the system tends toward a conventional dihydride, as represented by Structure 9-IV.



9-III

9-IV

9-7 Reaction Summary

As a study aid, the various reactions of hydrogen are illustrated in Fig. 9-6 Rather than being a comprehensive list of reactions of hydrogen, Fig. 9-6 is intended only to be an overview of the important types of reactions that hydrogen is capable of undergoing.

STUDY GUIDE

Study Questions

A. Review

1. What are the three isotopes of hydrogen called? What are their approximate natural abundances? Which one is radioactive?
2. What is the chief large-scale use for D_2O?
3. What is one thing that helps to explain the relatively low reactivity of elemental hydrogen?
4. What are the three principal electronic processes that lead to formation of compounds by the hydrogen atom?
5. When a hydrogen bond is symbolized by X—H---Y, what do the solid and dashed lines represent? Which distance is shorter?
6. How does hydrogen-bond formation affect the properties of HF, H_2O, and NH_3? Compared with what?
7. What is the usual range of enthalpies of a hydrogen bond?
8. Describe the main features of the structure of ice I. How is the structure of water believed to differ from that?
9. In what two principal ways is water bound in salt hydrates?
10. Can it safely be assumed that whenever a salt hydrate is heated at 100–120 °C the corresponding anhydrous salt will remain?
11. What is the true nature of so-called chlorine hydrate ($Cl_2 \cdot 7.3\ H_2O$)?
12. What is a saline hydride? What elements form them? Why are they believed to contain cations and H^- ions?
13. Define and cite examples of the different types of hydrogen-containing compounds that are discussed in this chapter, listing the distinguishing electronic, structural, and reactive characteristics of each class.
14. Which are the types of metals that react directly with hydrogen to form (a) ionic and (b) interstitial hydrides?
15. Give an explanation of the structural role of water in each of the following types of compounds, together with an example of a specific chemical substance for each type.
    (a) A hydrated compound.
    (b) A hydrous compound.
    (c) A gas hydrate.
    (d) A liquid hydrate.
    (e) A salt hydrate.
16. How could a nonstoichiometric hydride be made? What metal might one use? How could the hydridic character of the product be demonstrated?

B. Additional Exercises

1. Suggest a means of preparing pure HD.
2. It is believed that the shortest H bonds become symmetrical. How must the conventional description (X—H---Y) be modified to cover this situation?
3. Which H bond would you expect to be stronger, and why?

   S—H---O or O—H---S
4. Prepare a qualitative Born–Haber cycle to explain why only the most electropositive elements form saline hydrides.

5. Complete and balance the following reactions featuring hydrides:
   (a) $CaH_2 + H_2O \rightarrow$
   (b) $B_2H_6 + NaH \rightarrow$
   (c) $SiCl_4 + LiAlH_4$ to give silane, SiH_4
   (d) $Al_2Cl_6 + LiH$ to give $LiAlH_4$
6. The boiling points of the hydrogen halides follow the trend HF(20 °C) > HCl(−85 °C) < HBr(−67 °C) < HI(−36 °C). Explain.
7. The three different aspects of the chemistry of hydrogen can be illustrated by the reactivity of water with NaH, CH_4, and HCl. Explain.
8. Compare the bonding in "BH_3" and BCl_3. Why is BCl_3 monomeric and "BH_3" dimeric?
9. Suggest a synthesis of H_2Se and H_2S; of $NaBH_4$ and $LiAlH_4$; of HCl and HI; of NaH and CaH_2.
10. Prepare an MO description of the linear and symmetrical hydrogen bond in $[F—H—F]^-$ using the 1*s* atomic orbital on the central hydrogen atom and ligand group orbitals (formed from appropriately oriented 2*p* atomic orbitals) on the two fluorine atoms. Prepare the MO energy-level diagram that accompanies these three MO's and add the proper number of electrons to it. What is the bond order in each F—H half?
11. Finish and balance the following equations:
    (a) $CaH_2 + H_2O$
    (b) $K^0 + C_2H_5OH$
    (c) $KH + C_2H_5OH$
    (d) $UH_3 + H_2O$
    (e) $UH_3 + H_2S$
    (f) $UH_3 + HCl$
    (*Hint:* Dihydrogen is a product of all of these reactions.)
12. Suggest a two-step synthesis of lithium aluminum hydride ($LiAlH_4$), using only elements and Al_2Cl_6. Repeat this for $NaBH_4$, using B_2H_6.
13. Write balanced equations for the reaction of dihydrogen with sodium, B_2H_6, calcium, lithium, nitrogen, oxygen, and uranium.
14. Write balanced equations representing the steam re-forming of ethane, reduction of Fe_2O_3 by hydrogen, reaction of CaH_2 with water, and the water–gas shift reaction.
15. Draw the unit cell for NaH. What is the coordination number of Na^+ in this structure?
16. Review the material of Chapter 4 and draw out a Born–Haber cycle for NaH. After considering each step of the cycle, explain what two steps in the cycle give sodium (and the other alkali metal hydrides) an advantage over other metals in the formation of an ionic hydride as opposed to a covalent hydride.
17. The gallium analog of $LiAlH_4$, namely, $LiGaH_4$, is thermally unstable, decomposing to LiH and elements. Write a balanced equation to represent this. Why do you expect that the same reaction for $LiAlH_4$ is not observed?

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