## Chapter 9 Hydrogen

Diborane,  $B_2H_6$ , is the simplest member of a large class of compounds, the electron-deficient boron hydrides. Like all boron hydrides, it has a positive standard free energy of formation, and so cannot be prepared directly from boron and hydrogen. The bridge B–H bonds are longer and weaker than the terminal B–H bonds (1.32 vs. 1.19 Å).



**S9.1** Reactions of hydrogen compounds? (a)  $Ca(s) + H_2(g) \rightarrow CaH_2(s)$ . This is the reaction of an active s-metal with hydrogen, which is the way that saline metal hydrides are prepared.

(b)  $NH_3(g) + BF_3(g) \rightarrow H_3N-BF_3(g)$ . This is the reaction of a Lewis base and a Lewis acid. The product is a Lewis acid-base complex.

(c)  $LiOH(s) + H_2(g) \rightarrow NR$ . Although dihydrogen can behave as an oxidant (e.g., with Li to form LiH) or as a reductant (e.g., with O<sub>2</sub> to form H<sub>2</sub>O), it does not behave as a Brønsted or Lewis acid or base. It does not react with strong bases, like LiOH, or with strong acids.

S9.2 A procedure for making Et<sub>3</sub>MeSn? A possible procedure is as follows:

 $2Et_3SnH + 2Na \rightarrow 2Na^+Et_3Sn^- + H_2$ 

 $Na^{+}Et_{3}Sn^{-} + CH_{3}Br \rightarrow Et_{3}MeSn + NaBr$ 

9.1 Where does Hydrogen fit in the periodic chart? (a) Hydrogen in group 1? Hydrogen has one valence electron like the group 1 metals and is stable as H<sup>+</sup>, especially in aqueous media. The other group 1 metals have one valence electron and are quite stable as M<sup>+</sup> cations in solution and in the solid state as simple ionic salts. In most periodic charts, hydrogen is generally put with this group, given the above information. However, physically, hydrogen does not fit in this group, it is a diatomic gas, while the group 1 metals are just that, metals. Your text does mention that hydrogen may exit as a solid under extreme pressures.

(b) Hydrogen in group 17? Hydrogen can fill its 1s orbital and make a hydride H<sup>-</sup>. Hydrides are isoelectronic to He, a noble gas configuration, thus are relatively stable. Group 1 and group 2 metals, as well as transition metals, stabilize hydrides. The halogens form stable  $X^-$  anions, obtaining a noble gas configuration, both in solution and in the solid state as simple ionic salts. Some periodic charts put hydrogen both in group 1 and in group 17 for the reasons stated above. The halogens are diatomic gases just like hydrogen, so physically hydrogen fits well in group 17, but chemically it fits well in both group 1 and group 17.

(c) Hydrogen in group 14? There is no reason, chemical or physical, for hydrogen to be placed in this group

- **9.2** Low reactivity of hydrogen? Hydrogen exists as a diatomic molecule (H<sub>2</sub>). It has a high bond enthalpy (see Table 2.5); thus it takes a lot of energy to break the bond. It also only has two electrons shared between two protons, which is energetically very stable, leading to its chemical stability.
- 9.3 Assign oxidation numbers to elements? (a)  $H_2S$ ? When hydrogen is less electronegative than the other element in a binary compound (H is 2.20, S is 2.58; see Table 1.8), its oxidation number is chosen to be +1. Therefore, the oxidation number of sulfur in hydrogen sulfide (sulfane) is -2.

(b) KH? In this case, hydrogen (2.20) is more electronegative than potassium (0.82), so its oxidation number is chosen to be -1. Therefore, the oxidation number of potassium in potassium hydride is +1.

(c)  $[ReH_9]^{2-?}$  The electronegativity of rhenium is not given in Table 1.8. However, since it is a metal, it is reasonable to conclude that it is less electronegative than hydrogen. Therefore, if hydrogen is counted as -1, then the rhenium atom in the  $[ReH_9]^{2-}$  ion has an oxidation number of +7.

(d)  $H_2SO_4$ ? The structure of sulfuric acid is shown below. Since the hydrogen atoms are bound to very electronegative oxygen atoms, their oxidation number is +1. Furthermore, since oxygen is always assigned an oxidation number of -2 (except for O<sub>2</sub> and peroxides), sulfur has an oxidation number of +6.



(e)  $H_2PO(OH)$ ? The structure of hypophosphorous acid (also called phosphinic acid) is shown above. There are two types of hydrogen atoms. The one that is bonded to an oxygen atom has an oxidation number of +1. The two that are bonded to the phosphorus atom present a problem, since phosphorus (2.19) and hydrogen (2.20) have nearly equal electronegativities. If these two hydrogen atoms are assigned an oxidation number of +1, and oxygen, as above, is assigned an oxidation number of -2, then the phosphorus atom in  $H_2PO(OH)$  has an oxidation number of +1.

**9.4 Preparation of hydrogen gas?** As discussed in Section 9.3, *Properties and reactions of dihydrogen*, the three industrial methods of preparing H<sub>2</sub> are (i) steam reforming, (ii) the water-gas reaction, and (iii) the shift reaction (also called the water-gas shift reaction). The balanced equations are:

(i)  $CH_4(g) + H_2O \rightarrow CO(g) + 3H_2(g)$  (1000°C) (ii)  $C(s) + H_2O \rightarrow CO(g) + H_2(g)$  (1000°C) (iii)  $CO(g) + H_2O \rightarrow CO_2(g) + H_2(g)$ 

These reactions are not very convenient for the preparation of small quantities of hydrogen in the laboratory. Instead, (iv) treatment of an acid with an active metal (such as zinc) or (v) treatment of a metal hydride with water would be suitable. The balanced equations are:

(iv)  $Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$ 

(v) NaH(s) + H<sub>2</sub>O  $\rightarrow$  Na<sup>+</sup>(aq) + OH<sup>-</sup>(aq) + H<sub>2</sub>(g)

9.5 Properties of hydrides of the elements? (a) Position in the periodic table? See Figure 9.3.

(b) Trends in  $\Delta_t G^{\circ}$ ? See Table 9.6.

(c) Different molecular hydrides? Molecular hydrides are found in groups 13/III through 17/VII. Those in group 13/III are electron-deficient, those in group 14/IV are electron-precise, and those in group 15/V through 17/VII are electron-rich.

**9.6** What are the physical properties of water without hydrogen bonding? Read Section 9.4 (b) *Hydrogen bonding*. If water did not have hydrogen bonds, it most likely would be a gas at room temperature like its heavier homologues H<sub>2</sub>S, H<sub>2</sub>Se, and H<sub>2</sub>Te; see Figure 9.4. Also, most pure compounds are denser as a solid

than as a liquid. Because of hydrogen bonding, water is actually less dense and has the structure shown in figure 9.5. This is why ice floats. If there were no hydrogen bonds, it would be expected that ice would be denser than water.

- **9.7** Which molecule has the stronger hydrogen bonds? Hydrogen bonds consist of a hydrogen atom bonded to an atom more electronegative than itself, i.e., F, N, and O (See Table 1.8). This renders polarity between the E-H bond (E = a *p*-block nonmetal) and allows donation of a lone pair from another molecule to form the hydrogen bond. Since S is less electronegative than O, the partial positive charge felt by the H in O-H is stronger than that in S-H, therefore, S-H…O has a weaker hydrogen bond than O-H…S.
- 9.8 Name and classify the following? (a) BaH<sub>2</sub>? This compound is named barium hydride. It is a saline hydride.

(b) SiH<sub>4</sub>? This compound is named silane. It is an electron-precise molecular hydride.

(c)  $NH_3$ ? This familiar compound is known by its common name, ammonia, rather than by the systematic names azane or nitrane. Ammonia is an electron-rich molecular hydride.

(d) AsH<sub>3</sub>? This compound is generally known by its common name, arsine, rather than by its systematic name, arsane. It is also an electron-rich molecular hydride.

(e) PdH<sub>0.9</sub>? This compound is named palladium hydride. It is a metallic hydride.

(f) HI? This compound is known by its common name, hydrogen iodide, rather than by its systematic name, iodane. It is an electron-rich molecular hydride.

9.9 Chemical characteristics of hydrides? (a) Hydridic character? Barium hydride is a good example, since it reacts with proton sources such as H<sub>2</sub>O to form H<sub>2</sub>:

 $BaH_2(s) + 2H_2O(1) \rightarrow 2H_2(g) + Ba(OH)_2(s)$ 

## Net reaction: $2H^- + 2H^+ \rightarrow 2H_2$

(b) Bronsted acidity? Hydrogen iodide is a good example, since it transfers its proton to a variety of bases, including pyridine:



(c) Variable composition? The compound PdH<sub>0.9</sub> is a good example.

(d) Lewis basicity? Ammonia is a good example, since it forms acid-base complexes with a variety of Lewis acids, including BMe<sub>3</sub>:

 $NH_3(g) + BMe_3(g) \rightarrow H_3NBMe_3(g)$ 

9.10 Phases of hydrides of the elements? Of the compounds listed in Exercise 9.8, BaH<sub>2</sub> and PdH<sub>0.9</sub> are solids, none is a liquid, and SiH<sub>4</sub>, NH<sub>3</sub>, AsH<sub>3</sub>, and HI are gases (see Figure 9.3). Only PdH<sub>0.9</sub> is likely to be a good electrical conductor.

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## The structures of H<sub>2</sub>Se, P<sub>2</sub>H<sub>4</sub>, and H<sub>30</sub><sup>+</sup>? The Lewis structures of these three species are: H H H + H + H



According to the VSEPR model (see Section 2.3),  $H_2$ Se should be bent, and so it belongs to the  $C_{2v}$  point group;  $H_3O^+$  should be trigonal pyramidal (like NH<sub>3</sub>), and so it belongs to the  $C_{3v}$  point group; each phosphorus atom of  $P_2H_4$  should have local pyramidal structure. If the molecule adopts the skew conformation (see the Newman diagram below), then it belongs to the  $C_2$  point group (the  $C_2$  axis bisects the P–P bond).

A drawing of the structure of  $P_2H_4$ . The P–P and P–H bond distances are 2.22 and 1.42 Å, respectively, and the P–P–H bond angles are all about 94° (cf. PH<sub>3</sub>, in which the H–P–H bond angles are 93.8° (see Table 9.3)).

A Newman projection of the skew, or gauche, conformation of  $P_2H_4$ . The only element of symmetry that this structure possesses is a  $C_2$  axis that bisects the P–P bond. Therefore, it has  $C_2$  symmetry.



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**9.12** The reaction that will give the highest proportion of HD? Reactions (a) and (c) both involve the production of both H and D atoms at the surface of a metal. The recombination of these atoms will give a statistical distribution of H<sub>2</sub> (25%), HD (50%), and D<sub>2</sub> (25%). However, reaction (b) involves a source of protons that is  $100\%^{2}H^{+}$  (i.e., D<sup>+</sup>) and a source of hydride ions that is  $100\%^{1}H^{-}$ :

$$D_2O$$
 + NaH(s)  $\rightarrow$  HD(g) + NaOD(s)

Net reaction: 
$$D^+ + H^- \rightarrow HD$$

Thus, reaction (b) will produce 100% HD and no  $H_2$  or  $D_2$ .

**9.13** Most likely to undergo radical reactions? Of the compounds H<sub>2</sub>O, NH<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>SiH, and (CH<sub>3</sub>)<sub>3</sub>SnH, the tin compound is the most likely to undergo radical reactions with alkyl halides. This is because the Sn-H bond in (CH<sub>3</sub>)<sub>3</sub>SnH is less polar *and* weaker than either O-H, N-H, or Si-H bonds. The formation of radicals involves the homolytic cleavage of the bond between the central element and hydrogen, and a weak nonpolar bond undergoes homolysis most readily.

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Arrange H2O, H2S, and H2Se in order? (a) Increasing acidity? As discussed in Section 4.3, Periodic trends in aqua acid strength, acidities of EH, increase down a group in the p block, mostly because the decrease in E-H bond enthalpy lowers the proton affinity of  $[EH_{n-1}]^-$  (E is a generic p-block element) Therefore, the order of increasing acidity is  $H_2O < H_2S < H_2Se$ .

(b) Increasing basicity toward a hard acid? In general, soft character increases down a group, so the hardest base of these three compounds is H2O. The order of increasing basicity toward a hard acid is H2Se <  $H_2S < H_2O_1$ 

9.15

The synthesis of binary hydrogen compounds? The three main methods of synthesis of binary hydrogen compounds are (i) direct combination of the elements, (ii) protonation of a Brønsted base, and (iii) metathesis using a compound such as LiH, NaBH4, or LiAlH4. The first method is limited to those binary hydrogen compounds that are exoergic. An example is:

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## (i) $2Li(s) + H_2(g) \rightarrow 2LiH(s)$

The second method can be used for the preparation of  $EH_n$  compounds when a source of the  $E^{n-}$  anion is available. An example is:

(ii) 
$$CaF_2(s) + H_2SO_4(l) \rightarrow 2HF(g) + CaSO_4(s)$$

Almost all of the hydrogen fluoride that is prepared industrially is made this way. The third method can be used to convert the chlorides of many elements E to the corresponding hydrides, as in the following example:

$$PCl_3(l) + 3LiH(s) \rightarrow PH_3(g) + 3LiCl(s)$$

Compare BH<sub>4</sub>, AlH<sub>4</sub>, and GaH<sub>4</sub>? Since Al has the lowest electronegativity of the three elements B 9.16 (2.04), Al (1.61), and Ga (1.81, see Table 1.8), the Al-H bonds of  $AlH_4^-$  are more hydridic than the B-H bonds of BH4 or the Ga-H bonds of GaH4. Therefore, since AlH4 is more "hydride-like," it is the strongest reducing agent. The reaction of GaH<sub>4</sub> with aqueous HCl is as follows:

$$GaH_4^{-}(aq) + 4HCl(aq) \rightarrow GaCl_4^{-}(aq) + 4H_2(g)$$

- Compare period 2 and period 3 hydrogen compounds? One important difference between period 2 and 9.17 period 3 hydrogen compounds is their relative stabilities. The period 2 compounds, except for B<sub>2</sub>H<sub>6</sub>, are all exoergic (see Table 9.6). Their period 3 homologues either are much less exoergic or are endoergic (cf. HF and HCl, for which  $\Delta_f G^\circ = -273.2$  and -95.3 kJ mol<sup>-1</sup>, and NH<sub>3</sub> and PH<sub>3</sub>, for which  $\Delta_f G^\circ = -16.5$  and +13.4 kJ mol<sup>-1</sup>). Another important chemical difference is that period 2 compounds tend to be weaker Brønsted acids and stronger Brønsted bases than their period 3 homologues. Diborane, B<sub>2</sub>H<sub>6</sub>, is a gas while AlH<sub>3</sub> is a solid. Methane, CH4, is inert to oxygen and water, while silane, SiH4, reacts vigorously with both. The bond angles in period 2 hydrogen compounds reflect a greater degree of  $sp^3$  hybridization than the homologous period 3 compounds (compare the H-O-H and H-N-H bond angles of water and ammonia, which are 104.5° and 106.6°, respectively, with the H-S-H and H-P-H bond angles of hydrogen sulfide and phosphane, which are 92° and 93.8°, respectively). Several period 2 compounds exhibit strong hydrogen bonding, namely, HF, H<sub>2</sub>O, and NH<sub>3</sub>, while their period 3 homologues do not (see Figure 9.4). As a consequence of hydrogen bonding, the boiling points of HF, H<sub>2</sub>O, and NH<sub>3</sub> are all higher than their respective period 3 homologues.
- 9.18 Describe the compound formed between water and Kr? This compound is called a clathrate hydrate (see Section 9.4(b)). It consists of cages of water molecules, all hydrogen bonded together, each surrounding a single krypton atom (cf. the structure of the clathrate hydrate of molecular chlorine, shown in Figure 8.8). Strong dipole-dipole forces hold the cages together, while weaker van der Waals forces hold the krypton atoms in the centers of their respective cages.
- 9.19 Potential energy surfaces for hydrogen bonds? (See Figure 9.7) There are two important differences between the potential energy surfaces for the hydrogen bond between H<sub>2</sub>O and Cl<sup>-</sup> ion and for the hydrogen bond in bifluoride ion, HF2. The first difference is that the surface for the H2O, Cl system has a double