16 Boron Chemistry for Hydrogen Storage

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16.1 INTRODUCTION

As a clean and renewable energy carrier, hydrogen is an important component of most alternative energy portfolios. Hydrogen has a very high energy content by weight and combines with oxygen to produce only water with release of energy. For these reasons, hydrogen is an excellent fuel that can be used to power fuel cells, combustion engines, and turbines, without production of carbon dioxide greenhouse gas at the point of use [1,2]. However, a major drawback for the practical use of hydrogen is its low volumetric density, making pure hydrogen impractical to store and transport [3]. Thus, implementation of hydrogen technologies requires materials that can safely store and release large amounts of hydrogen under practical conditions [4].

In recent years, governmental agencies around the world, including the U.S. Department of Energy (DOE), have sponsored extensive research on hydrogen storage materials, including those based on boron [5,6]. These efforts have resulted in significant advances in hydrogen storage

technologies. Among the many options investigated, boron materials stand out as leading candidates for advanced hydrogen storage. Combining excellent hydrogen densities, release rates, and safety characteristics, some boron materials can hold substantially more hydrogen by weight and volume than even pure liquid hydrogen. Reviews covering various aspects of boron-containing hydrogen storage materials include those by Wang and Kang, Umegaki et al., Hamilton et al., and Orimo et al. [7–10].

Nonmilitary government-funded research on hydrogen storage has focused largely on automotive applications, where metrics were established relating to practical system requirements for fuel cell vehicles (FCVs) [11]. These include volumetric and gravimetric parameters needed to deliver sufficient amounts of hydrogen at appropriate rates to power a vehicle 300 miles without unusual intrusion on the interior space of the vehicle. To meet these requirements, the DOE set challenging targets for onboard hydrogen storage relating to the weight, volume, and cost of hydrogen storage systems [11]. Changes in DOE priorities have led to a suspension of most government-sponsored automotive hydrogen storage programs in the United States in 2010. Nevertheless, considerable interest remains for development of nonautomotive applications of hydrogen storage, including portable and backup power supplies for civilian and military applications, where boron-based hydrogen storage systems can provide considerably more power than conventional high-capacity batteries at equivalent weight and volume. A number of these applications are now either commercialized or in development. Civilian uses include portable electronics, underground mining vehicles, forklifts, airport tows, camping and recreation, hand tools, remote sensors, and emergency and backup power supplies. Military uses include soldier power packs, unmanned aerial vehicles, and backup power supplies [12].
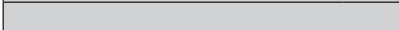
16.2 WHY HYDROGEN STORAGE?

Although hydrogen has excellent attributes as an energy carrier, its practical use in transportation and other applications presents significant challenges. Although hydrogen contains considerably more energy by weight than other conventional fuels, such as natural gas, gasoline, and ethanol, it has low volumetric density. The high gravimetric energy density of hydrogen is illustrated in Table 16.1, showing the energy content of one kilogram of hydrogen (120 MJ/kg on lower heating value [LHV] basis) compared with the same weight of other fuel options: gasoline, natural gas, and ethanol [13].

Unfortunately, hydrogen has very low volumetric energy density. A volume of 1 L of hydrogen gas has an energy content of only 0.011 MJ at normal temperature and pressure, compared with about 32 MJ for a liter of gasoline (on LHV basis). Even when compressed under high pressure or liquified at −253°C, hydrogen still has relatively low energy content compared with the same volume of other fuels. The energy content of hydrogen under different conditions compared with the same volume of gasoline is illustrated in Table 16.2 [13]. When high-pressure or cryogenic containment systems are included, the poor volumetric energy density of hydrogen becomes even more pronounced.

The low volumetric density of hydrogen presents a particular problem for transportation use. For example, consider a vehicle having a 53-L (14 gallon) fuel tank. This tank will hold about 39.2 kg of

TABLE 16.1
Energy Content per kilogram for Hydrogen Compared with Other Fuels (on LHV Basis)

Fuel	MJ/kg	Proportion
Hydrogen	120	
Natural gas	47.2	
Gasoline	43.7	
Ethanol	26.9	

TABLE 16.2

Energy Content of 1.0 L of Hydrogen at 20°C and Various Pressures Compared with the Same Volume of Gasoline (on LHV Basis) [13]

Fuel	MJ/L	Proportion
H$_2$ at 20°C, 1 atm (14.7 psi)	0.01	
H$_2$, 3000 psi	1.82	
H$_2$, 10,000 psi	4.71	
H$_2$, liquid (−253°C)	8.14	
Gasoline at 20°C	32.36	

gasoline with an energy content of about 1713 MJ (LHV basis). The volume of hydrogen compressed at a pressure of 3000 psi needed to supply the same amount of energy is about 941 L, requiring a fuel tank nearly 18 times larger. Yet, the weight of hydrogen in this tank is only about 14.3 kg. If the hydrogen is compressed to a very high pressure of 10,000 psi, the required volume decreases to about 364 L, but this is still almost seven times larger than the gasoline tank. Even if the hydrogen is liquified at −253°C, the equivalent energy volume of liquid hydrogen is 210 L, or about four times larger, not counting the substantial volume of the cryogenic containment system that would be needed. In addition, the amount of energy required to liquefy hydrogen or compress it is substantial [1].

16.3 CHEMICAL HYDRIDES

Although hydrogen has very low volumetric density, many chemical compounds of hydrogen, referred to as chemical hydrides, can pack substantially more hydrogen into a given volume than is found even in pure liquid hydrogen. In order to achieve high hydrogen densities by weight, the elements to which hydrogen are bonded must be of low atomic mass, limiting the range of elements from which to choose. For this reason, hydride compound-based light elements have drawn attention. In this category, boron is unique among the light elements in its ability to form a wide range of stable chemical hydrides, a number of which have suitable properties for use in hydrogen storage applications, as described below.

The use of boron hydride compounds, and particularly sodium borohydride, to generate hydrogen dates back to the 1940s, when early developments of alkali metal borohydrides were carried out in the research group of Hermann I. Schlesinger at the University of Chicago, USA [14,15]. Sodium borohydride, and related boron hydride compounds, later become important reagents for organic synthesis, largely through the extensive work of Schlesinger's PhD student and 1979 Nobel Prize winner Herbert C. Brown and his coworkers. However, the use of boron hydrides for hydrogen storage received less attention until recent times.

In 2003, the DOE issued a "grand challenge" to the scientific community for hydrogen storage research and development. This challenge called for establishment of three hydrogen storage Centers of Excellence, focusing on (1) chemical hydrogen storage, (2) metal hydrides, and (3) carbon-based materials and sorbents. Selected in 2004, these Centers of Excellence, together with existing DOE hydrogen storage efforts and independently funded projects, made up the framework of the U.S. National Hydrogen Storage Project. In order to meet the requirement to deliver sufficient amounts of hydrogen at appropriate rates to power a vehicle 300 miles without unacceptable intrusion on the interior space of the vehicle, the DOE set specific targets for onboard hydrogen storage systems. These include both volumetric and gravimetric parameters for hydrogen storage systems, as well as targets for costs and delivery rates [11]. These targets were revised during the course of this project, with final project objectives calling for development by 2015 of onboard hydrogen storage systems

achieving a gravimetric target of 9 wt% H_2 (equivalent to 90 g/kg or 3 kWh/kg) and a volumetric target of 2.7 kWh/L, with a cost of $2/kWh. An interim target of 6 wt% H_2 (60 g/kg, 2 kWh/kg) with volume and cost goals of 1.5 kWh/L and $4/kWh was set for 2010. It should be noted that the system weight includes not only the hydrogen storage material, but also the weight of all other containment and hydrogen conditioning equipment that might be needed leading up to the fuel cell.

Driven by the challenging automotive storage targets set by the DOE, and consequent need to utilize light elements to achieve them, both the Metal Hydride and Chemical Hydrogen Storage Centers focused significant attention on boron-based materials, including metal borohydride and boron–nitrogen (B–N) systems. In fact, most of the activities within the Chemical Hydrogen Storage Center involved boron compounds. Changes in priorities at the DOE resulted in the discontinuation of the Hydrogen Storage Centers of Excellence in 2010, with the focus of programs shifting away from automotive applications to hydrogen storage for stationary and nonautomotive portable power systems. The Hydrogen Storage Centers, along with other members of the international research community, accomplished major advances in the development of boron-based materials for hydrogen storage and produced numerous scientific publications during this period. The residual momentum of these programs continues with ongoing developments in both the academic and private sectors. A number of companies and academic groups continue to actively pursue the development of these applications, and a number of boron hydride systems are currently in commercial use.

16.4 METAL TETRAHYDROBORATES

The BH_4^- anion is formally called tetrahydroborate, and thus its metal salts and complexes are correctly called metal tetrahydroborates. However, these compounds are often referred to for convenience by the more informal name metal borohydrides, following the nomenclature first given to them by earlier workers in the field [16]. These compounds comprise an extensive class having the general composition $M(BH_4)_n$, where M may be Li, Na, K, Mg, Ca, Sc, Ti, V, Cr, Mn, Zn, Zr, Al, U, and so on, and n is 2–4. Metal borohydrides can contain substantial amounts of hydrolytically or thermally accessible hydrogen on both a weight and volume basis, depending on the atomic number and valence requirements of the metal [17]. The first examples of metal borohydrides were prepared in the research group of A. Stock in Germany [18] and in the groups of H. I. Schlesinger in the United States [19,20] and E. Wiberg in Germany [21]. There is now a vast technical literature associated with these compounds. Some aspects of the more promising metal borohydrides for hydrogen storage applications are discussed briefly here.

Crystal structures of the light metal borohydrides have been reviewed with emphasis on their hydrogen storage properties [22]. These compounds exhibit a wide range of properties, with variations relating to structural differences stemming from the unusual characteristics of the B–H bond and its interactions with metals of different sizes and electronegativities. The BH_4^- anion can form bridging M–H–B bonds with metals, similar to the 3-center/2-electron B–H–B bonds found in diborane. The BH_4^- anion most often acts as a bidentate ligand to metals, but is also known to coordinate in mono and tridentate modes. Metal borohydrides can occur as essentially ionic salts with
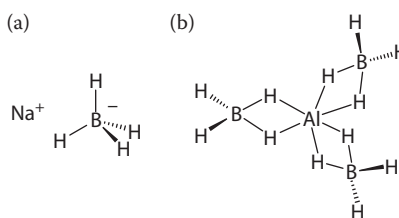
FIGURE 16.1 Sodium borohydride, $Na^+BH_4^-$ (a) is essentially an ionic salt, whereas aluminum borohydride, $Al(BH_2)_3$ (b), is a covalent compound.

TABLE 16.3
Comparison of Liquid Hydrogen with Selected Metal Borohydrides in Terms of Gravimetric and Volumetric Hydrogen Content

Compound	wt% H$_2$	Density^a g/cm^3	g H$_2$/L	MJ H$_2$/L
Liq. H$_2$ (−253°C)	100	0.7099	71	10.1
LiBH$_4$	18.5	0.666	123	17.5
NaBH$_4$	10.7	1.074	115	16.3
Mg(BH$_4$)$_2$	14.9	0.989	147	20.9
Ca(BH$_2$)$_2$	11.6	1.12	130	18.4

^{a} Multiple crystalline phases having different densities exist for most metal borohydrides.

some metal cations, such as Na$^+$ (Figure 16.1a), and primarily as covalent complexes with other metal cations, such as Al^{3+} (Figure 16.1b). It can be noted that NaBH$_4$ is an air-stable solid, whereas Al(BH$_4$)$_3$ is a pyrophoric liquid. However, most of the metal borohydrides are solids at room temperature and exhibit salt-like properties. Table 16.3 lists the more extensively studied lighter metal borohydrides and provides a comparison of their theoretical hydrogen contents with that of pure liquid hydrogen. As discussed below, not all of the theoretical hydrogen content may be accessible for some metal borohydrides under practical release condition, but available hydrogen on a volumetric basis generally exceeds that of liquid hydrogen by a significant amount.

16.4.1 SODIUM BOROHYDRIDE

Sodium borohydride, NaBH$_4$, contains 10.7 wt% H$_2$. It is currently the most commercially important of the boron hydride compounds. Several thousand tons of this material are manufactured annually for use as a reducing agent in various industries applications, including the manufacture of specialty chemicals, pharmaceuticals, paper, and in waste water treatment. Its use in hydrogen storage is also the oldest and most extensively developed among the metal borohydrides.

Sodium borohydride, or correctly sodium tetrahydroborate, is a white crystalline solid that is stable in dry air to ~300°C. It is highly soluble in water and slowly decomposes until the solution becomes alkaline. Decomposition is more rapid in acidic solution, but NaBH$_4$ is kinetically stable in alkaline solutions when the pH is above about 12.9. For this reason, 2%–3% sodium hydroxide is typically added to NaBH$_4$ solutions to provide stability. Although kinetically stable, aqueous solutions of NaBH$_4$ are thermodynamically unstable, and decomposition can be catalyzed by a number of transition metals.

The reaction of sodium borohydride with water, given by Equation 16.1, results in the production of four moles of hydrogen per mole of NaBH$_4$ with the formation of sodium metaborate. This reaction

$$NaBH_4 + 4H_2O \xrightarrow{\text{cat.}} NaB(OH)_4 + 4H_2 \qquad (16.1)$$
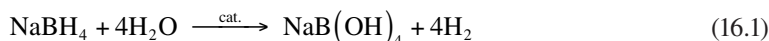
is frequently presented in the literature in the form of Equation 16.2, indicating that the boron-containing product is anhydrous sodium metaborate, NaBO$_2$. However, this common portrayal is

$$NaBH_4 + 2H_2O \xrightarrow{\text{cat.}} NaBO_2 + 4H_2 \qquad (16.2)$$
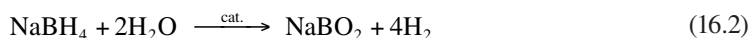
chemically unrealistic, since NaBO$_2$ does not exist in aqueous solution. Instead, it exists as the hydroxy-hydrated borate salt Na[B(OH)$_4$] that contains the tetrahydroxyborate anion, B(OH)$_4^-$.

This borate salt crystallizes without interstitial water above 53.6°C and as the hydrate Na[B(OH)$_4$]·2H$_2$O below this temperature. Both of these forms are well-established commercial products which, as articles of commerce, are referred to by their equivalent formulas, NaBO$_2$·2H$_2$O or Na$_2$O·B$_2$O$_3$·4H$_2$O and NaBO$_2$·4H$_2$O or Na$_2$O·B$_2$O$_3$·8H$_2$O. Based on earlier literature, these compounds in commercial use are commonly called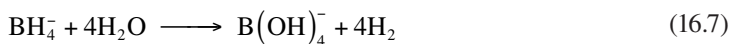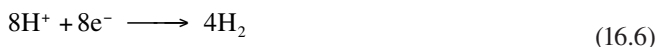 sodium metaborate "4 Mol" and "8 Mol," referring to their oxide formulas (23–25). The full dehydration of these sodium metaborates to NaBO$_2$ requires heating in dry air above 200°C, as given by Equation 16.3.

$$\text{Na}\left[\text{B}\left(\text{OH}\right)_4\right]\cdot x\text{H}_2\text{O} \xrightarrow{>200°C} \text{NaBO}_2 \left(\text{amorphous}\right) + \left(2 + x\right)\text{H}_2\text{O} \tag{16.3}$$
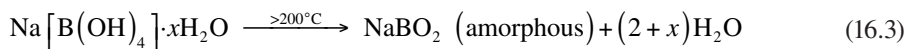
Anhydrous sodium metaborate reacts exothermically with water, rehydrating to Na[B(OH)$_4$]·xH$_2$O, where x is 0 or 2, depending on temperature. Since sodium borohydride–water systems for practical hydrogen generation do not involve conditions where anhydrous sodium metaborate can form, the hydrogen release reaction is more accurately represented by Equation 16.1.

Examination of Equation 16.1 provides important insights into this system. Most important is the recognition that the sodium metaborate product ("spent fuel") contains the same number of hydrogen atoms per mole as the sodium borohydride reactant ("fuel"). This observation emphasizes the fact that borohydride does not act as a source of hydrogen so much as a reducing agent for water. The reduction of water to H$_2$ is a two-electron process, given by Equation 16.4. Since each B–H bond in the borohydride anion, BH$_4^-$, effectively supplies two electrons (Equations 16.5 and 16.6), each molar equivalent of borohydride can reduce four equivalents of water, as expressed by Equation 16.7. Thus, NaBH$_4$ can be considered a source of electrons, or reducing power, rather

$$\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{O}^{2-} + \text{H}_2 \tag{16.4}$$

$$\text{BH}_4^- + 4\text{H}_2\text{O} \longrightarrow \text{B}\left(\text{OH}\right)_4^- + 8\text{H}^+ + 8\text{e}^- \tag{16.5}$$

$$8\text{H}^+ + 8\text{e}^- \longrightarrow 4\text{H}_2 \tag{16.6}$$

$$\text{BH}_4^- + 4\text{H}_2\text{O} \longrightarrow \text{B}\left(\text{OH}\right)_4^- + 4\text{H}_2 \tag{16.7}$$

than hydrogen. Furthermore, using incorrect Equation 16.2 to describe the NaBH$_4$–water system gives the impression that it contains >11 wt% available hydrogen on a stoichiometric basis, which is nearly equivalent to gasoline in energy content by weight. However, correct Equation 16.1 shows that the actual stoichiometric hydrogen content is about 7.3 wt%, or about 88% that of gasoline. Nevertheless, this is still a substantial energy content compared to many other proposed hydrogen storage materials.

Sodium borohydride has been employed as a source of hydrogen gas almost since the compound was first prepared in the 1940s. Indeed, in addition to their classic 1953 paper on the subject [15], the 1950 patent by Schlesinger and Brown titled, "Methods of Preparing Alkali Metal Borohydrides," describes the use of NaBH$_4$ in aqueous solution for hydrogen generation, as well as the use of catalytic accelerators, such as cobalt chloride [14]. Earlier government reports from the Schlesinger group also proposed this application to the military sponsors of this research. Numerous additional patents and publications describing methods to use NaBH$_4$ in hydrogen generation appeared with increasing frequency from the 1950s onwards. Patents specifically describing the use of NaBH$_4$ to provide a regulated flow of hydrogen to proton exchange membrane (PEM) fuel cells were published in the 1960s. For example, a 1968 patent assigned to Mine Safety Appliances Corp. describes

mixtures of $NaBH_4$ with hydrated compounds that release hydrogen on heating [26]. Also, a 1969 patent assigned to Union Carbide Corp describes a portable, self-contained, hydrogen-generating apparatus for fuel cell applications involving release of hydrogen from alkaline aqueous $NaBH_4$ solutions using a Raney nickel catalyst [27]. This patent also describes a method of regulating hydrogen pressure from the device and use of $NaBH_4$ pellets as fuel concentrate. Starting in the late 1990s, the former company Millennium Cell Inc further developed practical systems for hydrogen delivery for automobiles, portable devices, and stationary power systems [28–30]. Devices of this kind are often referred to as HYDROGEN ON DEMAND®, a registered trademark of Millennium Cell Inc.

In general, the concept of HYDROGEN ON DEMAND (HOD), illustrated in Figure 16.2, entails a system allowing an aqueous solution of $NaBH_4$ to be pumped into a catalyst chamber containing selected transition metals (e.g., Co, or Ru) fixed to a porous support material. The evolved hydrogen gas is separated from the resulting sodium metaborate solution, which is returned to a spent fuel tank. The moist hydrogen gas stream, which may be hot due to heat of reaction, is passed through an optional heat exchanger/coolant loop to adjust humidity, and is then supplied to a fuel cell or other hydrogen-using device. The pressure of generated hydrogen gas can be used to control the fuel addition rate to the catalyst chamber, allowing for a constant supply of hydrogen at practical pressures for fuel cell and other applications. Many variations on this general concept have been described.

HOD technology has been commercialized for use in a variety of applications, including military and civilian fuel cell power generators. An advantage of $NaBH_4$ HOD is that it utilizes a safe, energy-dense, water-based fuel. Aqueous solutions of sodium borohydride are not flammable, even when directly exposed to an open flame. Yet, a 30 wt% $NaBH_4$ solution contains 6.7 wt% releasable H_2. Another advantage of $NaBH_4$ is its relatively low heat of reaction with water compared with other metal hydrides and borohydrides, resulting in less waste heat. Furthermore, the reaction of $NaBH_4$ with water does not involve side reactions and formation of volatile by-products other than water. Thus, it can be used to deliver a controllable stream of hydrogen free of unwanted contaminates. The delivered hydrogen contains only water vapor, partly resulting from the heat generated by the hydrolysis reaction.

The lower solubility of sodium metaborate compared with sodium borohydride places a practical limitation on HOD systems. Considering Equation 16.1, it is clear that the need for a liquid discharge from the catalyst chamber of the HOD system requires maintenance of the sodium metaborate
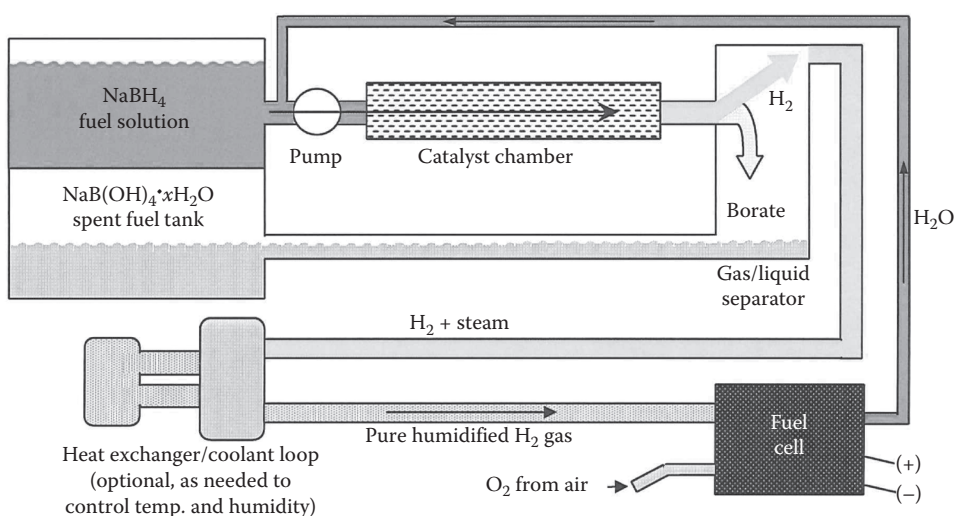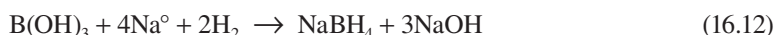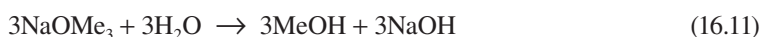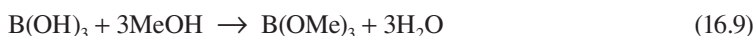

FIGURE 16.2 Schematic of HYDROGEN-ON-DEMAND® system, based on diagrams published by the former company Millennium Cell Inc.

"spent fuel" concentration below its solubility limit. Unfortunately, the lower solubility of sodium metaborate creates an upper limit on the "fuel" concentration, and thus on the total energy density of the system. Although the room-temperature water solubility of $NaBH_4$ is about 35 wt%, the substantially lower solubility of sodium metaborate may require lower practical working concentrations to prevent the metaborate from precipitating in the catalyst chamber. The heat of reaction can assist in maintaining sodium metaborate solubility, but the room-temperature stable phase, $Na[B(OH)_4] \cdot 2H_2O$, will subsequently crystallize in the spent fuel tank, presenting a handling problem. This problem is somewhat alleviated by engineering designs allowing for product water generated by the PEM fuel cell to be recycled back to the catalyst chamber feed, as shown in Figure 16.2. Other proposed solutions involve mechanical handling of sodium borohydride and metaborate as solids, slurries, or gels [27,31–33].

Direct borohydride fuel cells (DBFCs) have also been developed in which $NaBH_4$ is decomposed directly at the fuel cell membrane, avoiding a separate hydrogen generation step [34]. DBFCs are potentially cheaper to manufacture than tradition fuel cells because they do not require platinum catalysts. Instead, nonprecious metals, such as Ni, can be used. They also have low operating temperatures and high power densities, reaching up to 9.3 Wh/g $NaBH_4$. One problem associated with DBFCs is hydrogen evolution at the anode, which leads to lower efficiencies and safety issues. Improvements in electrocatalysts to solve this problem are an active area of research. Hydrogen evolution during the oxidation of borohydride on the fuel cell anode can be prevented by shifting the anode potential to values more positive than the reversible hydrogen electrode (RHE) potential; however, this reduces the advantages of DBFC. Use of new anode catalyst materials has been claimed to allow the complete eight electron oxidation of the BH_4^- anion without hydrogen evolution in an electrode potential region negative to the RHE [35]. Further developments in this area are anticipated.

Sodium borohydride is primarily manufactured by the Schlesinger process, which involves reaction of trimethylborate with sodium hydride at 250–270°C, as given by Equation 16.8 [36]. Trimethylborate is made from boric acid and methanol (Equation 16.9) and sodium hydride is made from sodium metal and hydrogen (Equation 16.10). Thus, sodium borohydride is made from metallic sodium, boric acid, and hydrogen, as expressed by net Equation 16.12.

$$B(OMe)_3 + 4NaH \; \longrightarrow \; NaBH_4 + 3NaOMe \qquad (16.8)$$

$$B(OH)_3 + 3MeOH \; \longrightarrow \; B(OMe)_3 + 3H_2O \qquad (16.9)$$

$$4Na + 2H_2 \; \longrightarrow \; 4NaH \qquad (16.10)$$

$$3NaOMe_3 + 3H_2O \; \longrightarrow \; 3MeOH + 3NaOH \qquad (16.11)$$

$$B(OH)_3 + 4Na° + 2H_2 \; \longrightarrow \; NaBH_4 + 3NaOH \qquad (16.12)$$

Production of 1 mol of $NaBH_4$ requires the consumption of 4 mol of metallic sodium. Although $NaBH_4$ has substantial energy content, the use of reactive metal in its manufacture results in less than optimal efficiency. Schlesinger et al. described in their original reports on $NaBH_4$ an alternate synthesis method involving grinding sodium hydride together with boric oxide, as given by Equation 16.13, where $NaBH_4$ product can be separated by solvent extraction

$$4NaH + B_2O_3 \; \longrightarrow \; NaBH_4 + 3NaBO_2 \qquad (16.13)$$

[11,36]. This method does not eliminate the use of reactive metal, but does avoid the need for distillation of trimethylborate ester, which is another energy-intensive step. It can be noted that the synthesis of metal borohydrides via chemical–mechanical milling methods has gained increasing attention in recent years.

Another process that has been carried out on a commercial scale was developed by Bayer Co. and used for production of $NaBH_4$ for captive use [37]. This process is sometimes called the "Bayer

Process," but should not be confused with more well-known aluminum process of the same name. This $NaBH_4$ process involves reaction of anhydrous borax, sodium metal, and silica at 700°C in a one-pot batch process, as given by Equation 16.14. This process avoids the need to

$$Na_2B_4O_7 + 16Na + 8H_2 + 7SiO_2 \xrightarrow{700°C} 4NaBH_4 + 7Na_2SiO_3 \qquad (16.14)$$
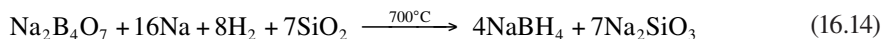
rigorously distill trimethylborate, but still requires consumption of 4 mol sodium metal per mole of $NaBH_4$ produced.

Other advanced methods for the manufacture of $NaBH_4$ have been investigated by Toyota Motor Co and academic researchers in Japan. Most notable is the use of magnesium hydride for direct reduction of boron oxide feedstocks, including anhydrous borax, for initial synthesis of $NaBH_4$ (Equation 16.15) and reduction of anhydrous sodium metaborate for regeneration of spent borohydride (Equation 16.16) [38]. Aluminum metal has also been used instead of magnesium and catalysts employed to improve kinetics.
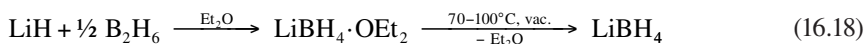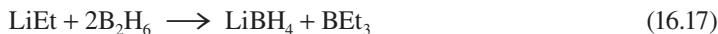
$$Na_2B_4O_7 + Na_2CO_3 + 8MgH_2 \rightarrow 4NaBH_4 + 8MgO + CO_2 \qquad (16.15)$$

$$NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO \qquad (16.16)$$

Wu et al. reviewed and analyzed potentially more efficient manufacturing processes for $NaBH_4$, including methods for the recycle of sodium metaborate back to borohydride [37]. To date, these efforts have not been sufficiently successful to make $NaBH_4$ economically viable for widespread use as an automotive fuel. After extensive analysis concluding that it cannot meet established performance targets, the DOE made a no–go decision in 2007 on $NaBH_4$ as an onboard automotive hydrogen storage system. However, it was acknowledged that $NaBH_4$ may serve as an intermediate in the manufacture of other hydrogen storage materials for initial fill requirements of an automotive fleet, but would not be feasible as an onboard hydrogen carrier. Nevertheless, $NaBH_4$ remains both practical and convenient for many smaller-scale fuel cell applications that may not require the same level of regeneration efficiency necessary for large automotive fleets.

16.4.2 LITHIUM BOROHYDRIDE

Lithium borohydride, $LiBH_4$, has attracted attention because of its high hydrogen content (18.5 wt%) compared with other metal borohydrides [39,40]. It is a hygroscopic white crystalline solid that is decomposed by water. Thus, it is generally handled under inert atmosphere. Lithium borohydride occurs as two phases under ambient pressure. The higher temperature phase forms above ~107°C [41]. Lithium borohydride is currently manufactured in far smaller volumes than sodium borohydride.

Schlesinger and Brown first prepared $LiBH_4$ in the 1930s by reaction of ethyl lithium with diborane under pressure, as given by Equation 16.17 [20]. Schlesinger and coworkers later described the synthesis of $LiBH_4$ by reaction of lithium hydride with diborane in diethyl ether to give the solvate $LiBH_4 \cdot OEt_2$, from which the ether was subsequently removed by heating at 70–100°C under vacuum [42], as in Equation 16.18. These reactions are inconvenient because of the need to handle diborane. In addition, they reported that $LiBH_4$ can be obtained by reaction of lithium hydride with trimethylborate in a manner similar to the process now used for manufacture of $NaBH_4$ [36]. They further described a method using the metathesis reaction of $NaBH_4$ with LiCl in isopropylamine, as given by Equation 16.19 [43]. However, the amine solvent was difficult to remove from the product. Brown and co-workers later described exchange reactions in aprotic solvents in which $LiBH_4$ is soluble, typically ethers, but found that these reactions are slow, requiring energetic mixing and long reaction times, and also the solvents are often difficult to remove from the product [44]. However, they

showed that unsolvated $LiBH_4$ can be obtained in high yield by reaction of lithium hydride with borane-dimethyl sulfide in ethyl ether at 25°C, followed by removal of solvent and dimethyl sulfide by distillation, as given by Equation 16.20. Alternatively, reaction of KBH_4 with LiCl is reported to proceed well in tetrahydrofuran (THF) to give the THF solvate [45]. Another method involves reaction of boron trifluoride with a stoichiometric excess of lithium hydride in an ether solvent, such as THF, as in Equation 16.21 [46], where the BF_3 may be supplied as a more easily handled solvent adduct, such as $BF_3 \cdot THF$.

$$LiEt + 2B_2H_6 \longrightarrow LiBH_4 + BEt_3 \tag{16.17}$$

$$LiH + \tfrac{1}{2} B_2H_6 \xrightarrow[]{Et_2O} LiBH_4 \cdot OEt_2 \xrightarrow[- Et_2O]{70-100°C, \text{ vac.}} LiBH_4 \tag{16.18}$$

$$MBH_4 + LiX \rightarrow LiBH_4 + MX \; (M = Na, K; X = Cl, Br) \tag{16.19}$$

$$LiH + BH_3 \cdot SEt_2 \xrightarrow[-SEt_2]{OEt_2} LiBH_4 \tag{16.20}$$

$$4LiH + BF_3 \xrightarrow{THF} LiBH_4 + 3LiF \tag{16.21}$$

Lithium borohydride liberates very little hydrogen below 380°C. Although $LiBH_4$ has high thermal stability, it is rapidly hydrolyzed by water. This presents a disadvantage compared with $NaBH_4$, which is stable in alkaline solution. As a result, $LiBH_4$, and most other light metal borohydrides, cannot be used in HOD systems of the kind described above, involving catalytic release of hydrogen from aqueous fuel solutions. Hydrogen storage systems have been described involving mechanical mixing of solid lithium borohydride with water [31], but most proposed applications of $LiBH_4$ involve thermal hydrogen release.

On heating, $LiBH_4$ exhibits three thermal events [47]. There is an initial reversible polymorphic phase transition at ~107°C [41]. The compound then fuses at 268–286°C, a process accompanied by loss of ~2 wt% H_2. Major hydrogen gas evolution then commences at ~380°C, with release of ~80% of the H_2 in $LiBH_4$ taking place in the 380–680°C temperature range. The highest rate of hydrogen loss is reported to occur between 483°C and 492°C. Thermal decomposition of $LiBH_4$ occurs with release of three of its four hydrogen atoms in a reaction approximately described by Equation 16.22 [39,48]. This decomposition is complex and involves a

$$2LiBH_4 \xrightarrow{\Delta} LiH + 2B + 3H_2 \quad 13.9 \text{ wt\% } H_2 \tag{16.22}$$
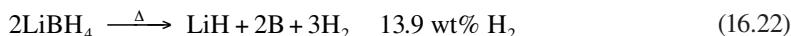
number of intermediates, including $Li_2B_{12}H_{12}$, which contains the kinetically stable [*closo*-$B_{12}H_{12}$]$^{2-}$ anion (48–51). Although $LiBH_4$ contains a total of 18.5 wt% hydrogen, Equation 16.22 shows that not all of this hydrogen is thermally accessible at practical temperatures. The experimentally observed thermally releasable hydrogen content of $LiBH_4$ is ~13.5 wt% [51], which is still considerable compared with many other proposed hydrogen storage materials. Thermal decomposition of $LiBH_4$ is exothermic, with an estimated enthalpy change of 67 kJ/mol of H_2 evolved, indicating that the reverse rehydrogenation reaction is thermodynamically unfavorable [39]. Studies of this rehydrogenation reaction report that it requires extreme conditions such as 600°C under 35 MPa H_2 pressure [52].

The high thermal stability of $LiBH_4$ and need for extreme regeneration conditions reduces its practicality as a hydrogen carrier. Consequently, efforts have been made to find ways to destabilize $LiBH_4$ to enhance hydrogen release rates and facilitate rehydrogenation at lower temperatures. It has been shown that mixing $LiBH_4$ with various other materials can significantly reduce hydrogen release temperatures. These materials include metals (e.g., Mg, Al), metal hydrides (e.g., CaH_2,

MgH_2), metal borohydrides ($NaBH_4$), amides ($LiNH_2$), oxides (e.g., SiO_2, SnO_2, TiO_2), and halides ($TiCl_3$, TiF_3), as well as activated carbon and carbon nanotubes (53–58). Some of these systems rely on the formation of more thermodynamically stable products, and thus do not improve reversibility. However, enhanced reversibility has been claimed in a number of cases. The addition of SiO_2 to $LiBH_4$ is reported to decrease the hydrogen loss temperature to ~200°C [39]. Mechanically milling $LiBH_4$ with 0.5 mol MgH_2 and a small amount of $TiCl_3$ catalyst is reported to form a system that can reversibly store 8–10 wt% H_2 [55]. The modified thermal dehydrogenation reaction for this system can be expressed by Equation 16.23, where formation of MgB_2 improves the thermodynamic pathway for

$$2LiBH_4 + MgH_2 \underset{H_2}{\overset{\Delta}{\rightleftarrows}} 2LiH + MgB_2 + 4H_2 \qquad (16.23)$$

dehydrogenation and regeneration of $LiBH_4$, decreasing in enthalpy change for this process by 25 kJ/mol of H_2 released compared with pure $LiBH_4$.

Ball milling $LiBH_4$ in a 3:1 mole ratio with TiF_3 is reported to result in a reduction in the dehydrogenation onset temperature to ~100°C with a hydrogen capacity reaching 5.0 wt% at 250°C [56]. Hydrogenation/dehydrogenation kinetics were reported to be greatly improved when $LiBH_4$ was incorporated into activated carbon [57]. The $LiBH_4$-activated carbon composite exhibited an onset of hydrogen release at 220°C and a rate of dehydrogenation one order of magnitude faster than that of pure $LiBH_4$ with reduced temperature and hydrogen pressure conditions required for restoring the hydride. It was also reported that milling $LiBH_4$ together with single-walled carbon nanotubes (SWNTs) resulted in a composite material exhibiting dehydrogenation and rehydrogenation reactions at significantly reduced temperature and pressure conditions [58]. A composite of $LiBH_4$ with 30 wt% SWNTs discharged 11.4 wt% H_2 within 50 min at 450°C and more than 6.0 wt% H_2 could be recharged at 400°C under an initial hydrogen pressure of 10 MPa. A high-pressure polymorph of lithium borohydride also has been proposed as a thermally destabilized alternative [59].
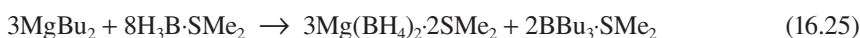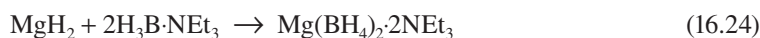
The lithium borohydride–lithium amide system has also attracted attention. Reactant mixtures of composition $(LiNH_2)_x(LiBH_4)_{1-x}$ can be formed by mixing $LiBH_4$ with $LiNH_2$ [60]. This system is dominated by a compound having an ideal stoichiometry of $Li_4BN_3H_{10}$. Within this system, a specific phase of composition $LiB_{0.33}N_{0.67}H_{2.67}$ was reported, having theoretical hydrogen content of 11.9 wt%. This compound releases >10 wt% H_2 when heated. The evolved gas is reported to contain 2–3 mol% NH_3. It was also found that a maximum amount of hydrogen and a minimum amount of ammonia are evolved for compositions $(LiNH_2)_x(LiBH_4)_{1-x}$, where $x = 0.667$ [60]. A crystalline phase of composition $Li_3BN_2H_8$ was reported to form when $LiNH_2$ and $LiBH_4$ are heated or ball milled together in a 2:1 mole ratio [61]. Other phases were also identified in this system.

16.4.3 Magnesium Borohydride

Magnesium borohydride, $Mg(BH_4)_2$, contains 14.9 wt% hydrogen. It is a white crystalline compound that occurs as two phases under ambient pressure. The normal room-temperature phase converts to a high-temperature phase above 184°C. This high-temperature phase persists after cooling back to room temperature [41]. The theoretical hydrogen release capacity of $Mg(BH_4)_2$ is 9.6 wt%. Although this is lower than that of $LiBH_4$ (13.5 wt%), it is still substantial. $Mg(BH_4)_2$ also has a lower decomposition temperature and more favorable enthalpy for hydrogen release than $LiBH_4$. The combination of these properties have prompted considerable interest in $Mg(BH_4)_2$ for hydrogen storage applications [62,63].

First reported by Wiberg and Bauer in 1950, a variety of synthesis methods have since been described for $Mg(BH_4)_2$ [21]. Synthesis routes to unsolvated $Mg(BH_4)_2$ have been reviewed [64]. The diethyl ether solvate of $Mg(BH_4)_2$ can be prepared by reaction of MgH_2 with B_2H_6 in diethyl ether

under pressure, and the ether solvent can be subsequently removed by heating under vacuum at 150–180°C [65]. Exchange reactions of NaBH$_4$ with MgCl$_2$ in various solvents, such as ethanol, dimethylformamide, and THF, also provide Mg(BH$_4$)$_2$ as the corresponding solvates, Mg(BH$_4$)$_2$·nL (n = 1–6; L = solvent), in which the solvent remains even after drying under vacuum [66,67]. Attempts to remove solvent from these compounds typically results in decomposition. However, reaction of NaBH$_4$ with MgCl$_2$ in refluxing diethyl ether gives the Et$_2$O solvate, which can be unsolvated under conditions that provide pure Mg(BH$_4$)$_2$ [64]. Another reported synthesis method for Mg(BH$_4$)$_2$ involves ball milling mixtures of MgCl$_2$ and NaBH$_4$ in diethyl ether [64]. Additional methods for the synthesis of unsolvated Mg(BH$_4$)$_2$ include reaction of MgH$_2$ with the borane-base adduct Et$_3$N·BH$_3$, followed by removal of Et$_3$N [68, Equation 16.24], and reaction of dibutyl magnesium with borane-base adducts such as H$_3$B·SMe$_2$, as shown in Equation 16.25 [69].

$$MgH_2 + 2H_3B \cdot NEt_3 \rightarrow Mg(BH_4)_2 \cdot 2NEt_3 \tag{16.24}$$

$$3MgBu_2 + 8H_3B \cdot SMe_2 \rightarrow 3Mg(BH_4)_2 \cdot 2SMe_2 + 2BBu_3 \cdot SMe_2 \tag{16.25}$$

The enthalpy change for decomposition of Mg(BH$_4$)$_2$ is estimated to be ~40 kJ/mol of H$_2$ released [70,71]. Hydrogen loss occurs in several steps starting at ~290°C. Thermal decomposition of Mg(BH$_4$)$_2$ can be approximated by Equations 16.26 and 16.27 [71]. The tetragonal

$$Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2 \tag{16.26}$$

$$MgH_2 \rightarrow Mg + H_2 \tag{16.27}$$

α-phase of Mg(BH$_4$)$_2$ converts into a cubic β-phase at ~184°C. The compound releases most of its theoretically available hydrogen when heated to ~450°C under vacuum or low hydrogen pressure, and essentially all of it when heated to 500–550°C. The two largest steps have maximum H$_2$ release rates occurring at 295°C (~4.7 wt%) and 325°C (~9.6 wt%). A third smaller step with maximum release rate at 410°C yields an additional 3.3–3.7 wt% H$_2$. A fourth minor step occurs slowly above 500°C under vacuum to provide a final 0.8–1.0 wt% H$_2$. The temperatures associated with these steps vary when dehydrogenation is conducted under hydrogen pressure, but exhibit the same general trend [70,71]. Above 450°C MgB$_2$ is formed from the solid products of these reactions. As with the other metal borohydrides, the actual decomposition pathway is more complex than Equations 16.26 and 16.27 would suggest, and involves formation of kinetically stable polyhedral boranes, including the *closo*-B$_{12}$H$_{12}^{2-}$ anion [72,48].

The amine complex of magnesium borohydride, Mg(BH$_4$)$_2$·2NH$_3$, was prepared by thermal decomposition of Mg(BH$_4$)$_2$·6NH$_3$. The compound was structurally characterized and exhibits N–H···H–B dihydrogen bonds. Mg(BH$_4$)$_2$·2NH$_3$, which contains 16.0 wt% H$_2$, decomposes endothermically starting at 150°C, and exhibits a maximum hydrogen release rate at 205°C, making it an attractive candidate for hydrogen storage [73].

16.4.4 CALCIUM BOROHYDRIDE

Calcium borohydride, Ca(BH$_4$)$_2$, contains 11.6 wt% hydrogen. Although this compound contains less hydrogen by weight than lithium and magnesium borohydride, its accessible hydrogen content is still sufficiently high to make it attractive as a hydrogen storage candidate. Also, Ca(BH$_4$)$_2$ systems appear to have more favorable thermodynamics for reversible hydrogen storage. For these reasons, Ca(BH$_4$)$_2$ has been the object of considerable research interest [74].

In 1954, Kollonitsch and coworkers described syntheses of both Mg(BH$_4$)$_2$ and Ca(BH$_4$)$_2$ by reactions of NaBH$_4$ with the corresponding metal chlorides in alcohol solutions at −50°C to −20°C [75]. A 1965 patent assigned to Callery Chemical Co. describes the synthesis of Ca(BH$_4$)$_2$ by the reaction

of calcium hydride with diborane in THF, followed by removal of solvent from the initially formed solvate by heating at 155°C under vacuum [76]. Notably, this patent also suggests the use of $Ca(BH_4)_2$ as a source of hydrogen. Titov also described in 1964 the synthesis of the THF solvate of $Ca(BH_4)_2$ by reaction of $NaBH_4$ with $CaCl_2$ in THF [77]. Current commercial synthesis of calcium borohydride is primary conducted by modifications of this general method (Equation 16.28), but other solvents and proprietary methods may be used. Calcium borohydride is most commonly available commercially as the THF adduct, $Ca(BH_2)_4 \cdot 2THF$, which is typically unsolvated by heating under vacuum at 200°C.

$$CaCl_2 + 2NaBH_4 \; \underset{-2NaCl}{\overset{THF}{\rightleftarrows}} \; CaBH_4 \cdot 2THF \; \underset{-2\,THF}{\overset{150-200\,°C,\,vac.}{\rightleftarrows}} \; CaBH_4 \qquad (16.28)$$

On heating, $Ca(BH_4)_2$ is reported to undergo a polymorphic transformation at 140–167°C and then decompose in two steps between 347°C and 497°C [74,78], as given by Equation 16.29. Calcium hydride and other intermediates form after the first step, but CaH_2 is the only crystalline phase observed after the second step with a total weight loss of ~9.6 wt% H_2.

$$3Ca(BH_4)_2 \; \rightarrow \; CaB_6 + 2CaH_2 + 10H_2 \quad 9.6\%\ H_2 \qquad (16.29)$$

The enthalpy change for this reaction is estimated to be ca. −53 kJ/mol of H_2 released, which is significantly less exothermic than the corresponding reaction of $LiBH_4$. This should allow the reverse hydrogenation reaction to occur with a maximum theoretical reversible hydrogen storage capacity of ~9.6%. It is reported that ball milling a mixture of CaB_6 and CaH_2 at 400–440°C under 70 MPa H_2 pressure gives $Ca(BH_4)_2$. The kinetics of this reaction are very slow. However, doping with catalysts is reported to enhance the kinetics of this reaction and facilitate regeneration under milder conditions. For example, adding $TiCl_3$ enables rehydrogenation at 350°C under 9 MPa H_2 pressure in a reaction described by Equation 16.30 [79]. The resulting rehydrogenated material was shown to contain ~3.8 wt% H_2, or more than half the amount in the starting sample.

$$7Ca(BH_4)_2 + 4TiCl_3 \; \rightarrow \; 6CaCl_2 + 4TiB_2 + CaB_6 + 28H_2 \qquad (16.30)$$

Thus, it was demonstrated that calcium borohydride can be prepared from its proposed decomposition products, suggesting that it may have potential for use as a reversible hydrogen storage material.

16.4.5 MIXED METAL BOROHYDRIDES

The high thermal stability of the metal borohydrides has prompted an interest in developing new metal borohydride materials having more favorable thermodynamic properties. One approach is the use of mixed cation borohydrides, providing an opportunity to tailor their thermodynamic properties [80,81]. In some cases, this approach is similar to, if not mechanistically the same as, using metals or metal-based additives to facilitate dehydrogenation/rehydrogenation reactions of monometallic borohydrides. However, the synthesis of discrete crystalline mixed metal borohydrides has allowed the design and study of interesting hydrogen storage materials.

Examples can be cited for the mixed alkali metal and alkaline-earth metal borohydrides. It was reported that a Li–Mg borohydride could be formed by mechanical milling and subsequent heating of a mixture of $LiBH_4$ and $Mg(BH_4)_2$ in 1:1 mole ratio. This dual-cation borohydride exhibits a lower dehydrogenation onset temperature [82]. Also, composite materials made by combining $LiBH_4$ and $Ca(BH_4)_2$ are reported to show hydrogen release temperatures lower than for either component alone [83]. Composites of composition $(LiBH_4)_x(1 - x)[Ca(BH_4)_2]$, where H_2 capacity varies with x, were prepared. At intermediate compositions, such as $x = 4$, dehydrogenation was complete below 400°C with release of 10 wt% H_2. Partial reversibility of this system was also reported.

16.5 BORON–NITROGEN SYSTEMS

The desire for materials having high gravimetric hydrogen densities has prompted increasing interest in materials containing only light elements. Meeting this criterion, hydrogen-rich B–N compounds have emerged as particularly promising hydrogen storage materials. These compounds have been the subject of intense study in recent years. The chemistry of B–N compounds in chemical hydrogen storage has been reviewed [8,9].

16.5.1 AMMONIUM BOROHYDRIDE

Ammonium borohydride, $[NH_4]^+[BH_4]^-$, is a white crystalline solid having a remarkably high hydrogen content of 24.5 wt% [84]. This corresponds to 245 g H_2/kg or 155 g H_2/L. Described as having the highest thermodynamically and kinetically accessible hydrogen content of any solid material, ammonium borohydride has attracted considerable attention for its potential use in hydrogen storage [85]. This material releases ~20 wt% H_2 in a complex three-step process when heated from 50°C up to ~160°C, as given by Equation 16.31 [86].

$$\left[NH_4 \right]^+ \left[BH_4 \right]^- \xrightarrow{50-160°C} BNH_x + \left(\frac{8-x}{2} \right) H_2, \ \ x \approx 3.3 \tag{16.31}$$
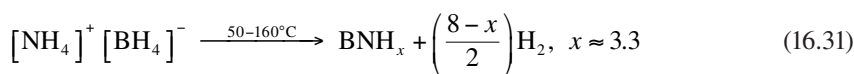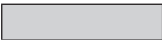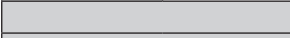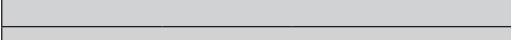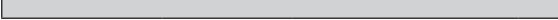
Thermolysis of ammonium borohydride produces nearly pure hydrogen, with only a trace of borazine evolved at higher temperatures. The primary disadvantage of ammonium borohydride for many practical applications is its poor thermal stability. Ammonium borohydride slowly decomposes even at room temperature. Thus, methods to stabilize ammonium borohydride are needed to make this material practical for use in hydrogen storage applications. Ammonium borohydride also serves as a synthetic precursor for ammonia borane (AB), as discussed below.

16.5.2 AMMONIA BORANE

Ammonia borane, H_3NBH_3, also called borazane, is one of the most interesting and extensively studied materials for hydrogen storage. Called AB for short, ammonia borane is a white crystalline solid containing 19.6 wt% hydrogen. It is stable in air and water and has appropriate thermal stability for practical use in a range of hydrogen storage applications [9,87,88].

The amount of hydrogen contained in AB in terms of both weight and volume is impressive, although not quite as high as ammonium borohydride. This volumetric hydrogen density of AB is illustrated in Table 16.4, showing that a 1.0-L volume of AB contains more than twice the weight of hydrogen as found even in liquid hydrogen. These data do not include the volume of any required containment vessel, which can be significant for liquid H_2.

TABLE 16.4
Comparison of the Weights of Hydrogen contained in 1.0 L of Highly Compressed Hydrogen, Liquified Hydrogen, AB, and Ammonium Borohydride

Form of Hydrogen	g H_2/L	Weight Proportion of H_2
Compressed H_2 at 10,000 psi	40	
Liquid H_2 (−253°C)	71	
H_3NBH_3 (AB)	146	
Ammonium borohydride, NH_4BH_4	154	

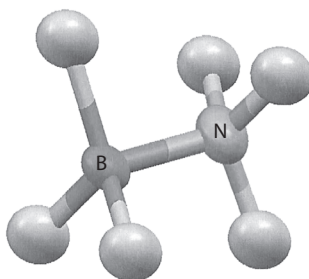**FIGURE 16.3** The structure of H_3NBH_3 (AB).

16.5.2.1 Structure

AB is the Lewis acid–base adduct between NH_3 and BH_3. It is isoelectronic with ethane and has an analogous structure, as shown in Figure 16.3. The fact that it is a solid and not a gas is attributed to intermolecular hydrogen–hydrogen bonding and dipole–dipole interactions, as supported by structural data [89,90].

Single-crystal structures of AB have been published, derived from both x-ray and neutron diffraction data collected at various temperatures [89,90]. The H_3NBH_3 molecule in the solid state has a staggered geometry with a B–N dative bond distance of 1.59 Å. The extended structure exhibits nearly linear N–H···H and bent B–H···H hydrogen–hydrogen bonds, as illustrated in Figure 16.4 [89]. The structure of AB clearly suggests an intermolecular pathway for H_2 formation.

16.5.2.2 Synthesis

AB is the Lewis acid–base adduct that might be anticipated to form in the reaction of ammonia with diborane, B_2H_6. However, early developments in the synthesis of AB were complicated by formation of a higher-molecular-weight compound in this reaction. This compound was identified as a salt referred to as the diammoniate of diborane, $[H_2B(NH_2)_2]^+[BH_4]^-$ (DADB) [91–95]. This product is the result of asymmetric cleavage of diborane, whereas H_3NBH_3 is the product of symmetric cleavage. Details of this chemistry were worked out in careful studies done in the early 1950s in the research group of Robert Parry at the University of Michigan, which are summarized in a more recent review article [96]. The first definitive synthesis of AB was published in 1955, based on the PhD thesis of Sheldon Shore, then a student in Parry's laboratory [97]. This publication described the synthesis of AB from reactions of lithium borohydride with ammonium chloride or sulfate in
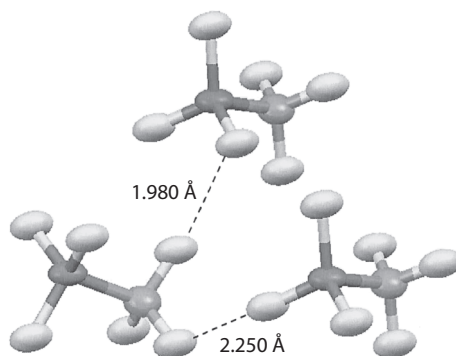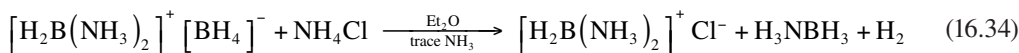

FIGURE 16.4 Hydrogen–hydrogen close approaches in H_3NBH_3 (AB).

diethyl ether, as given by Equations 16.32 and 16.33. This method was reported to give AB in ~45% yield with formation

$$LiBH_4 + NH_4Cl \xrightarrow{\text{Et}_2\text{O}} LiCl + H_3NBH_3 + H_2 \tag{16.32}$$

$$2LiBH_4 + (NH_4)_2 SO_4 \xrightarrow{\text{Et}_2\text{O}} 2H_3NBH_3 + Li_2SO_4 + 2H_2 \tag{16.33}$$

of some DADB coproduct. Since AB is soluble in ether and DADB is not, these products are easily separated. The same publication describes the synthesis of AB by the metathesis reaction of DADB with ammonium chloride, as given by

$$\left[H_2B(NH_3)_2\right]^+ \left[BH_4\right]^- + NH_4Cl \xrightarrow[\text{trace NH}_3]{\text{Et}_2\text{O}} \left[H_2B(NH_3)_2\right]^+ Cl^- + H_3NBH_3 + H_2 \tag{16.34}$$
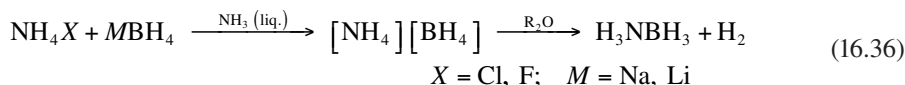
This latter reaction was part of the elegant experimental work to elucidate the identity of DADB and demonstrate that it was not the alternative possible isomeric salt $[H_2N(BH_3)_2]^-[NH_4]^+$ [92,93] Shore and coworkers later published improved synthetic methods for both DADB and AB [98]. Despite having the same empirical formulas, AB does not react readily with water, whereas DADB is immediately hydrolyzed. Upon standing, DADB slowly converts into AB. Thus, AB has more suitable properties for use in hydrogen storage applications.

Another early synthesis of AB described by Schaeffer and Basile in 1954 involves the reaction of diborane with lithium amide [99]. It was found that diborane gas does not react with lithium amide solid. However, when diethyl ether is added to produce a slurry, reaction between these reagents occurs readily according to Equation 16.35, even at −64°C. It was reported that care is required to regulate the reaction to avoid release of large amounts of hydrogen. Polymeric by-products, resulting from dehydrogenation of AB, are formed in reaction.

$$B_2H_6 + LiNH_2 \xrightarrow{\text{Et}_2\text{O}} LiBH_4 + H_3NBH_3 \tag{16.35}$$

More recent work carried out at the Pacific Northwest National Laboratory (PNNL), USA, showed that ammonium borohydride, formed by metathesis reactions of NH_4X (X = Cl, F) and MBH$_4$ (M = Na, Li) in liquid NH$_3$, decomposes in organic ether solvents, such as THF, to give AB in close to quantitative yields, as shown in Equation 16.36 [100]. AB prepared by this one-pot synthetic method

$$NH_4X + M BH_4 \xrightarrow{\text{NH}_3 \text{(liq.)}} \left[NH_4\right]\left[BH_4\right] \xrightarrow{\text{R}_2\text{O}} H_3NBH_3 + H_2 \atop X = \text{Cl, F}; \quad M = \text{Na, Li} \tag{16.36}$$

was shown to have sufficient purity and thermal stability to meet the requirements for onboard automotive hydrogen storage. The kinetics of the reaction of sodium borohydride and ammonium chloride and sulfate in liquid ammonia were described in the 1970s by William Jolly and coworkers at the University of California, Berkeley [101]. These same reactions were described earlier, in then classified government reports from Aerojet Engineering Corp and the Schlesinger research group at the University of Chicago, dating from the 1940s [102,103]. However, pure AB was neither isolated nor definitively characterized in these earlier studies.

Other methods for the synthesis of AB have been described by Shore and coworkers at Ohio State University involving reactions of ammonia with borane adducts of appropriate amines [104].

As discussed above, the direct reaction of diborane with ammonia results in asymmetric cleave of diborane to give DADB. However, if diborane is cleaved prior to reaction with ammonia by a Lewis base, such as an alkyl or aryl amine or dialkylsulfide, then AB can be obtained in a suitable solvent, as given by Equation 16.37 [104]. The ratio of AB to DADB

$$L : BH_3 + NH_3 \xrightarrow{Et_2O} H_3NBH_3 + L \quad \left(L = \text{selected amine}\right) \tag{16.37}$$
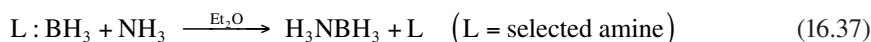
produced in these reactions depends on both the choice of solvent and Lewis base. Shore showed that by using a suitable base, such as dimethylaniline, high-quality AB can be obtained in high yield [104].
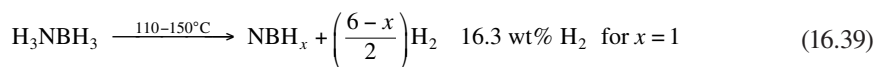
Syntheses of AB via reactions of borate esters with lithium and aluminum hydride reagents have been described. One example of such a method is illustrated by Equation 16.38 [105]. A number of

$$B\left(OMe\right)_3 + LiAlH_4 + NH_4Cl \xrightarrow[30\,h]{THF} H_3NBH_3 + Al\left(OMe\right)_3 + LiCl + H_2 \tag{16.38}$$

other synthetic methods for AB have been reported involving variations on the above general reactions [106].

### 16.5.2.3 Hydrogen Release

The U.S. Army studied B–N compounds, including AB, in the 1980s, as materials to supply hydrogen for gas laser systems [107,108]. On heating, AB releases more than two molar equivalents of hydrogen, as shown in Equation 16.39 where $x = 1 - 2$ [109–114].

$$H_3NBH_3 \xrightarrow{110-150°C} NBH_x + \left(\frac{6-x}{2}\right)H_2 \quad 16.3\text{ wt\% } H_2 \text{ for } x = 1 \tag{16.39}$$

There is some confusion in the literature regarding the dehydrogenation onset temperature of AB [115]. A number of reports describe slow release of hydrogen starting at 70°C. Others describe either dehydrogenation onset or significant H_2 release rates commencing at 80°C. Hydrogen release by thermolysis of AB is a complex process that proceeds in steps. Studies have provided a detailed understanding of this thermal hydrogen release process [9,115]. Once AB is heated above 110°C rapid release of one equivalent of hydrogen occurs. The initial step of hydrogen release, occurring primarily between 110°C and 120°C, involves an intermolecular process resulting in formation of polyaminoborane, $(NH_2BH_2)_n$, as given by Equations 16.40. Thus, AB can release up to one equivalent of hydrogen below 100°C.

$$n\, H_3NBH_3 \xrightarrow{70-120°C} \left(NH_2BH_2\right)_n + nH_2 \quad 6.5\% \text{ } H_2 \tag{16.40}$$
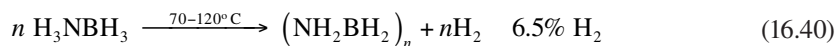
The polyaminoborane product of this first step is a linear polymer that still contains ~14 wt% hydrogen. On further heating this material undergoes more hydrogen loss through both intermolecular and intramolecular processes, leading to formation of polyiminoborane, $(NHBH)_n$, as given by Equation 16.41.

$$\left(NH_2BH_2\right)_n \xrightarrow{120-150°C} \left(NHBH\right)_n + nH_2 \quad 7.0\% \text{ } H_2 \tag{16.41}$$
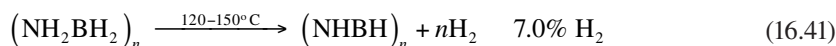
The intermolecular process involves cross-linking between polymer chains. The intramolecular processes involve B–N double bond formation and cyclization reactions within polymer chains. As

a result, the polyiminoborane product may have a complex network structure, the exact nature of which depends on how the thermolysis reaction is carried out. The combination of these steps results in release of ~13.5 wt% hydrogen from AB in the 70–150°C range. At somewhat higher temperatures further cross-linking of polyiminoborane results in release of additional amounts of hydrogen. Heating to much higher temperatures ultimately leads to the formation of boron nitride (BN), as given by Equation 16.42.

$$\left(NHBH\right)_n \xrightarrow{>500°C} BN + H_2 \qquad 7.5\% \ H_2 \qquad (16.42)$$
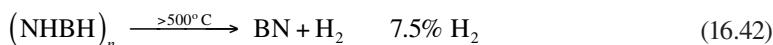
The practical use of AB for hydrogen storage does not involve high-enough temperatures to completely convert AB into BN. In addition, if the spent material is to be recycled, BN may be too stable to allow for practical regeneration of AB. Instead, thermal decomposition of AB is continued to the extent that the spent fuel has a composition of BNH_x, where x is $1 - 2$, as in Equation 16.39. In this way, AB can be used to supply more than 2 mol of hydrogen, or ~15 wt% hydrogen at modest temperatures.

The thermolysis of AB is an overall exothermic process. Once hydrogen release is initiated, sufficient heat may be generated to make the process self-sustaining, depending on reactor design. Initiating the process requires the input of induction energy to start decomposition. The induction energy required to release 2 mol of hydrogen gas is ~16.2 kJ/mol of H_3NBH_3, or 8.1 kJ/mol of H_2. This corresponds to only 3.35% of the chemical energy content of the hydrogen generated [112].

The first step of AB thermal dehydrogenation (Equation 16.39) yields almost entirely H_2 gas. Unfortunately, the subsequent higher temperature steps of AB dehydrogenation produce substantial amounts of volatile by-products, including lower-molecular-weight boranes, ammonia, and borazine, $B_6N_6H_6$, the B–N isoelectronic analogue of benzene. These volatile by-products are particularly undesirable because they can poison PEM fuel cells. The amounts of volatile products generated from AB are observed to be greater when higher temperatures and higher heating rates are used for decomposition. Although nonhydrogen volatiles can be removed using sorbents in a subsequent purification step, this presents an added complication. Thus, methods to facilitate AB decomposition more selectively to generate H_2 of higher purity are needed.

Catalytic hydrogen release from AB is of interest for several reasons. The self-sustaining nature of its thermal decomposition makes AB difficult to use in the regulated generation of hydrogen. Also, the uncontrolled thermolysis of AB produces a number of volatile impurities that poison PEM fuel cells. In addition, it is desirable for fuel cell applications to have relatively fast hydrogen release rates at temperatures below 80°C. In order to address these issues, studies have been made on catalyst systems having potential to direct decomposition pathways and facilitate release of higher-purity hydrogen from AB at or near room temperature [9].

Studies have been done to understand the fundamental aspects of AB catalysis identified a number of homogeneous catalysts for dehydrogenation that operate at lower temperatures in nonaqueous solvents. Aside from enhancing H_2 release rates, this work also showed that the type of catalyst has a strong effect on both total amount of H_2 released and the nature of the dehydrogenated B–N product. For example, the iridium "pincer" complex [(POCOP)Ir(H)$_2$], where POCOP = η^3-1,3-(OP-*tert*-Bu)$_2$C$_6$H$_3$], shown in Figure 16.5a, catalyzes dehydrogenation of AB with excellent rates [116]. However, this catalyst is reported to be highly selective for the formation of a proposed cyclic pentamer product [H$_2$NBH$_2$]$_5$ (Figure 16.5a), leading to release of only 1 mol of hydrogen per mole of AB, as given by Equation 16.43,

$$H_3NBH_3 \xrightarrow[THF, RT]{Ir \ cat.} 1/5\left[H_2NBH_2\right]_5 + H_2 \qquad (16.43)$$
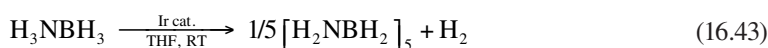
although this is likely an oversimplification of the actual reaction. Alternatively, the nickel carbene complex Ni(NHC)$_2$ (NHC = N-heterocyclic carbene), Figure 16.5b, yields more than 2 mol of H_2 at
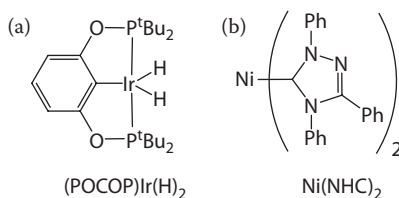
**FIGURE 16.5** Experimental homogeneous catalysts for AB dehydrogenation, (a) $(POCOP)Ir(H)_2$ and (b) $Ni(NHC)_2$, where NHC is a nitrogen heterocyclic carbene.

60°C, but the rate of release is slow. Instead of a cyclic pentamer, this system produces a polymeric material proposed to have the structure, shown in Figure 16.6b, composed of linked borazine moieties [117].

Studies show that AB can be hydrolyzed in water by the action of various chemical reagents or catalysts. Metal salts, including those of Co^{2+}, Ni^{2+}, and Cu^{2+}, can be employed to catalyze hydrolysis [118–121]. Although the practical use of AB for hydrogen storage typically involves solid-state thermolysis, there may be potential for hydrolytic hydrogen generation from AB for some applications. In addition, mechanical mixing of AB with certain metal complexes in the absence of solvent can significantly reduce hydrogen release temperatures. For example, solid-state mechanical mixing of cobalt, nickel, or copper chlorides was reported to result in significant hydrogen evolution even at 60°C. The copper salt was found to be more efficient in this reaction than the other metal salts, releasing 2 mol of hydrogen over 4 h at 60°C with a Cu/H_3NBH_3 mole ratio of 0.15. A significant amount of H_2 is released from this system even at room temperature, albeit slowly [118].

Thermal decomposition of AB in polar, aprotic solvents is slow and results in mixtures of oligomeric products, including cyclic amino- and imino-boranes [122,123]. Dehydrogenation of AB in ionic liquids, such as 1-butyl-3-methylimidazolium chloride (bmimCl) has been investigated [124]. Compared to solid-state dehydrogenation, thermal decomposition of AB in bmimCl shows no induction period, with hydrogen evolution commencing immediately on subjecting the sample to heat. Furthermore, AB was found to release considerably more hydrogen when heated in ionic liquid media at 85–95°C compared with the solid-state reaction, with up to 1.5 equiv. of H_2 released at 95°C over a 22-h period. This system evolved 5.4 wt% H_2 at 95°C, including the weight of the bmimCl solvent. Previous studies of neat AB at 88°C showed that formation of DADB is a critical decomposition step. Consistent with this conclusion, the addition of DADB to AB significantly decreases the induction time for hydrogen release. Studies by NMR spectroscopy of the ionic liquid system suggest that DADB may also be an intermediate in AB dehydrogenation in this media. Since the ionic salt DADB is reported to convert into polyiminoborane with hydrogen release on heating, the activating effect of the ionic liquid may be related to the ability of these solvents to stabilize polar intermediates and transition states.

Researchers at PNNL showed that nanocomposites formed by dispersing AB in mesoporous silica or high-surface-area carbon cryogels exhibit an increase in both the rate and extent of hydrogen release from AB at reduced temperatures [125–127]. For example, composite materials
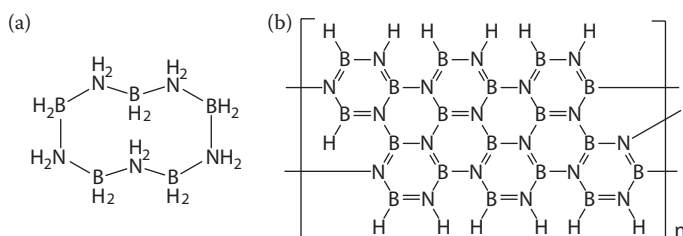
FIGURE 16.6 Cyclic pentamer, $[H_2NBH_2]_5$ (a) and linked borazine structure (b).

composed of intimate mixtures of AB and SBA-15 mesoporous silica in a 1:1 weight ratio showed H_2 release at substantially lower temperatures than observed for neat AB. The H_2 generated from these systems also was higher in purity than that obtained from dehydrogenation of neat AB under the same conditions, being substantially free of the unwanted borazine by-product. Related studies showed that AB encapsulated in a mesoporous carbon framework (CMK-3) exhibited substantially reduced dehydrogenation temperatures with the majority of the H_2 release occurring in the 75–95°C temperature range, compared with 110–145°C for neat AB [128]. This system exhibited a one-step dehydrogenation process, in contrast to the two-step process of neat AB. However, the H_2 generated was found to contain some ammonia impurity. It was further reported that doping the CMK-3 framework with 5 wt% Li^+ completely suppressed the release of volatile by-products, including ammonia and borazine, when heated to 150°C. Lithium doping of the framework further reduced the dehydrogenation onset temperature to ~55°C. The 1:1 weight ratio AB/Li–CMK-3 system was reported to release ~7 wt% H_2 at 60°C, or ~3.5 wt% hydrogen for the entire system.

Dehydrogenation of AB can also be accomplished through acid catalysis using either Lewis or Brønsted acids. Addition of strong acids can initiate hydrogen release from AB even at 25°C, according to Equation 16.44 [129].

$$H_3NBH_3 + H^+ + 3H_2O \longrightarrow NH_4^+ + B(OH)_3 + 3H_2 \qquad (16.44)$$
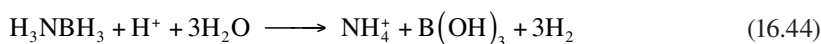
Such acid-catalyzed H_2 release can also be accomplished using immobilized acids, in the form of zeolites or ion exchange resins, providing interesting possibilities for engineered hydrogen delivery devices [130]. The ultimate boron-containing product resulting from AB hydrolysis is typically an ammonium borate. Depending on the reaction stoichiometry, this can be either ammonium pentaborate, $NH_4[B_5O_6(OH)_4]\cdot2H_2O$, forming at lower pH values, or ammonium tetraborate, $NH_4[B_4O_5(OH)_4]\cdot\sim2H_2O$, forming at higher pH values. Both of these ammonium borates are important commercial products that have been manufactured on multiton industrial scale for many decades. Both compounds have well-established crystal structures [131,132]. It can be noted that $NH_4[B_4O_5(OH)_4]\cdot2H_2O$ is often called ammonium biborate as an article of commerce and has a variable amount of interstitial water.

Addition of the strong Lewis acids, such as $B(C_6F_5)_3$, also initiates hydrogen release via the formation of boronium intermediates. These intermediates then further react with AB to form oligomeric or polymer aminoboranes with release of H_2. The relative concentration of Lewis acid needs to be kept low (≤0.5 mol%) to avoid chain termination resulting in aminodiborane, $B_2H_5(\mu\text{-}NH_2)$, and concentrated solutions can also produce large amounts of borazine.

16.5.2.4   Regeneration

A number of strategies have been proposed for regeneration of AB spent fuel [9]. One approach involves regeneration via solvolysis reactions of AB. A transition metal-catalyzed solvolysis system was reported that converts AB into $[NH_4][B(OMe)_4]$ with liberation of hydrogen, as given by Equation 16.45 [133]. The latter could be converted back into AB by treatment with NH_4Cl and $LiAlH_4$ (Equation 16.46). This approach would require reduction of $Al(OMe)_3$ back to $LiAlH_4$. A disadvantage of this method is a requirement for the consumption of a strong reducing agent.

$$H_3NBH_3 + 4MeOH \rightarrow NH_4B(OMe)_4 + 3H_2 \qquad (16.45)$$

$$NH_4B(OMe)_4 + LiAlH_4 + NH_4Cl \rightarrow H_3NBH_3 + Al(OMe_3)_3 + MeOH + H_2 + LiCl + NH_3 \quad (16.46)$$

Another approach to AB regeneration involves digestion of spent material followed by reduction. The dehydrogenation of AB produces a complex mixture of products of general composition BNHx, all of which contain B–N linkages that must be broken. Acidic compounds (HX) can be used to cleave these bonds to release the nitrogen component with the formation of B–X bond-containing
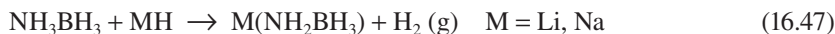
products. These B–X bonds in these digestion products can then be reduced using a reducing agent to form B–H bonds. In order to have an energetically efficient recycle system for AB regeneration, it is necessary to use reactions that are not overly endothermic or exothermic. Various methods of digestion and reduction have been explored in efforts to find practical and thermodynamically favorable regeneration systems.

Efforts made at Los Alamos National Laboratory toward regeneration of BNH_x-spent fuel involved digestion with 1,2-benzenedithiol to form ammonia adducts of dithioboron compounds [134]. The B–S bonds in these compounds were then reduced using a tin hydride, which could be in turn regenerated by efficient methods. Another method proposed by PNNL involves digestion of BNH_x-spent fuel in a suitable alcohol to form a borate ester that can be reduced by a metal hydride catalyst, which can be regenerated by reaction with hydrogen. Although B–O bonds are generally regarded as too strong to allow energy-efficient reduction, calculations indicate that judicious choice of alcohols can provide borate esters having sufficient hydride affinity to undergo facile reduction by a metal hydride. Borate esters produced by digestion with suitably substituted phenols appear to be capable of acting as efficient regeneration intermediates. In addition to hydrides of precious metals, base metal catalysts have also shown promise in for hydride transfer to borate esters in this regeneration cycle.

16.5.3 METAL AMIDOBORANES

Another approach to altering the thermal stability of AB involves chemical modification. The replacement of one N–H hydrogen atom in AB with a metal results in metal amidotrihydroborates, which are commonly called metal amidoboranes (MABs). MABs have the general composition $M(NH_2BH_3)_n$, where M can be a wide variety of elements, including both main group and transition metals [135–137]. Numerous MAB compounds have been prepared [135]. Although the replacement of one hydrogen atom in AB by a metal results in a penalty in terms of gravimetric hydrogen content, these compounds still carry substantial amounts of hydrogen. With H_2 contents in the 10.1–13.7 wt% range, MABs derived from the light alkali and alkaline earth metals, including $LiNH_2BH_3$, $NaNH_2BH_3$, $Mg(NH_2BH_3)_2$, and $Ca(NH_2BH_3)_2$, have been the most intensively studied. However, transition MABs can also contain substantial amounts of hydrogen. For example, $Ti(NH_2BH_3)_4$ contains 12.0 wt% H_2. Mixed MABs have also been prepared, including $LiAl(NH_2BH_3)_4$ (13.1 wt% H_2) and $Li_2[Zn(NH_2BH_3)_4]$ (10.1 wt% H_2) [135].

MABs, such as LiAB and NaAB, can be prepared by reactions of AB with metal hydrides in solution, as given by Equation 16.47. The synthesis of other MABs has been accomplished by exchange reactions with alkali metal MABs, as in the example given by Equation 16.48 [135]. Syntheses of MABs by high-energy ball milling of AB with alkali metal hydrides have also been reported [137].

$$NH_3BH_3 + MH \;\rightarrow\; M(NH_2BH_3) + H_2\,(g) \quad M = Li, Na \qquad (16.47)$$

$$MgCl_2 + 2\,NaNH_2BH_3 \;\rightarrow\; Mg(NH_2BH_3)_2 + 2\,NaCl \qquad (16.48)$$

MABs offer certain advantages over AB. A number of crystal structures have been determined for MABs [136,137]. A feature of the alkali-MABs is the presence of both positively charged (–NH_2) and negatively charged (–BH_3) hydrogen atoms. This provides a relatively low-energy pathway for local combination of $H^{\delta+}$ and $H^{\delta-}$ atoms to more readily produce H_2. Kinetic studies of hydrogen release from MABs have been carried out providing evidence that the metal atom also assists in hydride transfer to the amine group [138–140]. The thermal decomposition of AB generates hydrogen-containing impurities, including low-molecular-weight boron hydrides, borazine, and aminoboranes. It has been demonstrated for several MABs that their thermolysis generates large amounts of hydrogen without these unwanted impurities [135–137], which is a significant advantage

over AB. Ammonia generation during thermolysis of $LiNH_2BH_3$ and $NaNH_2BH_3$ has been reported. For example, lithium amidoborane, $LiNH_2BH_3$, and sodium amidoborane, $NaNH_2BH_3$, are reported to release 7.5 and 10.9 wt% H_2, respectively, when heated to 91°C. Another problem associated with AB is its tendency to foam during thermolysis. At least some of the MABs do not foam during thermolysis. For example, $Ca(NH_2BH_3)_2$ (10.1 wt% H_2) releases hydrogen over a temperature range of 100°C to 170°C without foaming [137].

Other complex MAB derivatives have been reported. For example, reaction of LiH with two equivalents of AB, or the reaction of $LiNH_2BH_3$ with a second equivalent of AB, results in the crystalline complex $LiNH_2BH_3 \cdot H_3NBH_3$. Thermolysis of $Li(NH_2BH_3) \cdot H_3NBH_3$ is reported to produce 14% H_2 in a stepwise manner with maximum release rates occurring at ~80°C and ~140°C, without emission of detectable amounts of borazine or aminoborane [141]. An ammoniate of composition $Ca(NH_2BH_3)_2 \cdot 2NH_3$ has also been described, which releases >8 wt% H_2 when heated to 150°C without emission of borazine [142].

16.5.4 GUANIDINIUM BOROHYDRIDES

Guanidinium borohydride (GBH) is a compound related to both the metal and ammonium borohydrides discussed above [143]. An air-stable white solid having the composition $[C(NH_2)_3]^+[BH_4]^-$, GBH contains 13.5 wt% H_2, of which 10.8 wt% is thermally accessible. This corresponds to four molar equivalents of H_2. With a calculated density of 0.905 g cm^{-3}, GBH can supply 97.7 g H_2/L. Although not as high as AB or most of the metal borohydrides of interest for hydrogen storage, GBH still has a thermally releasable hydrogen density that is nearly one-third greater than pure liquid hydrogen.

GBH is reported to be thermally stable at 55°C and to very slowly lose hydrogen at 60°C. Rapid hydrogen loss occurs when GBH is heated to 110°C, at which point dehydrogenation is exothermic and self-sustaining. Hydrogen yields above 10 wt% are reported for self-sustaining GBH thermolysis, which can reach temperatures as high as 450°C. The hydrogen obtained from GBH thermolysis was reported to be 95–97% pure, but contained 3–5% ammonia. It was further found that addition of ethylenediamine bis(borane), $H_2N(CH_2)_2NH \cdot 2BH_3$, completely suppressed the formation of the ammonia impurity.

The synthesis of GBH in 65%–75% yield was reported from the room-temperature metathesis of guanidinium carbonate or sulfate with sodium borohydride in anhydrous isopropanol solvent. The single-crystal x-ray structure of GBH shows stacks and layers of one-dimensional ribbons of $C(NH_2)_3^+$ and BH_4^- units. Within these ribbons, four of the six protic N–H guanidinium hydrogen atoms form close approaches to the four hydridic B–H hydrogen atoms of adjacent borohydride groups. These dihydrogen interactions provide a low-energy pathway for thermal elimination of four of the five equivalents of H_2 theoretically present in GBH [143].

Other GBHs have been described, mostly resulting from rocket propellant research. Guanidinium hydrotriborate, $[C(NH_2)_3][B_3H_8]$, was prepared by the reaction of guanidinium sulfate with sodium hydrotriborate [144]. This compound decomposes slowly when stored at room temperature and violently when heated to ~100°C with release of 12.3 wt% H_2. The related triaminoguanidinium hydrotriborate, $[C(NHNH_2)_3][B_3H_8]$ was prepared by the reaction of pentaborane with triaminoguanidine, which has a potential hydrogen storage capacity of 11.0 wt%, assuming a loss of eight equivalents of H_2 [145].

16.5.5 B–N SORBENT MATERIALS

Boron nitride nanostructures have drawn attention for their storage potential. Hydrogen storage in various nanoporous sorbent materials has been a subject of considerable interest. A primary advantage of these materials is their ease of reversibility [146]. This also creates a disadvantage because hydrogen is only weakly held within these materials, requiring low temperatures to achieve

acceptable levels of hydrogen uptake. Sorbent materials typically retain hydrogen around the temperature of liquid nitrogen (−196°C). Such materials studied for hydrogen storage applications include zeolitic structures, microporous polymers, metal–organic frameworks, and various forms of carbon, such as activated carbon and carbon nanofibers and nanotubes.

Another class of materials proposed for hydrogen storage is BN nanotubes. These interesting materials, which are isoelectronic and isostructural with carbon nanotubes, were first described by Sheldon Shore and coworkers in 1993 [147]. The use of nanostructured materials having high surface areas for hydrogen adsorption and desorption under practical temperature and pressure conditions depends on the binding energy of the material. Therefore, a key objective in the design of new sorbent materials is the achievement of higher binding energies for hydrogen. BN nanotubes have been estimated to have 40% greater binding energies for hydrogen than analogous carbon nanotubes, in the appropriate range for room-temperature hydrogen storage [148].

16.5.6 ORGANOBORON COMPOUNDS

Organoboron boron compounds show promise for hydrogen storage. Many hydrogen storage systems suffer from thermodynamic imbalance between their hydrogen-containing and hydrogen-depleted states. In order to have an efficient and recyclable hydrogen carrier, it is desirable that the free energy for hydrogen release be close to zero. One approach to designing such thermoneutral systems is through the use of B–N bond-containing heterocycles that can undergo dehydrogenation with $\Delta G \approx 0$ kcal mol^{-1} [149].

The dehydrogenation of C–C bonds is thermodynamically unfavorable. For example, the dehydrogenation of ethane to ethylene ($H_3C–CH_3 \rightarrow H_2C=CH_2 + H_2$) is substantially endergonic, with $\Delta G = +23.9$ kcal mol^{-1}. On the other hand, the analogous dehydrogenation of AB, which is isoelectronic with ethane, ($H_3NBH_3 \rightarrow H_2NBH_2 + H_2$) is exergonic, with $\Delta G = −13.6$ kcal mol^{-1} [149]. On the basis of computational results, the replacement of two methylene groups in cyclohexane with an H_2NBH_2 group results in a material that has 7.1 wt% accessible hydrogen for the loss of three equivalents of H_2 and $\Delta G = 1.9$ kcal mol^{-1}, as shown in Equation 16.49 for R=H [150]. The near thermoneutrality of this 1,2-azaboracyclohexane system for
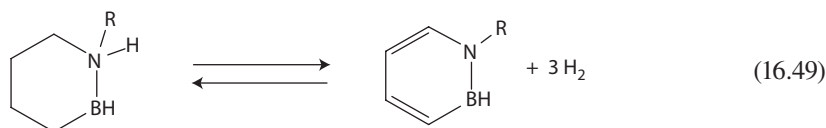
$$ (16.49) $$

dehydrogenation/rehydrogenation makes it highly attractive for reversible hydrogen storage. Compounds of this type have been prepared. As an example, calculations indicate that Equation 16.49, where R = *t*-butyl, has $\Delta G = −0.4$ kcal mol^{-1}, with aspects of this systems demonstrated experimentally [151].

Another strategy for hydrogen storage is through the use of "frustrated Lewis pairs." For example, a phosphonium borate compound has been described that reversibly stores hydrogen in a practical temperature range [152]. The phosphino-borane compound shown on the left-hand side of Equation 16.50 was shown to accept 1 equiv. of hydrogen, at 1 atm and 25°C,

$$ (16.50) $$

Mes = 2,4,6 -trimethylphenyl
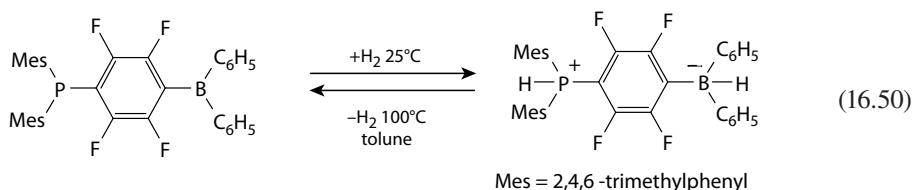
forming the phosphonium borate zwitterion on the right. The latter compound releases hydrogen again on heating to 100°C. Although the hydrogen storage capacity of this compound is only 0.25 wt%, well below the level required for practical use, this system suggests new possibilities for the use of boron compounds.

Other examples involve combinations of sterically hindered *N*-heterocyclic Lewis bases and $B(C_6F_5)_3$ that also form "frustrated" Lewis pair systems capable of activating hydrogen [153,154]. This was demonstrated, for example, for the lutidine-tri(pentafluorophenyl)borane system shown in Scheme 16.1.

The equilibrium between the adduct **1** and free Lewis acid and base allows this system to be exploited for frustrated Lewis pair reactivity. Addition of H_2 to this mixture at a pressure of 1 atm was shown to result in the formation of salt **2** through cleavage of hydrogen [153].

16.6   BORON RESOURCES

The proposed use of boron materials for hydrogen storage in large automotive fleets involving hundreds of millions of vehicles has prompted questions regarding the adequacy of boron resources to meet these enormous demands. For this reason, U.S. Borax Inc. assessed borate reserves in both the United States and the world and compared this assessment with potential initial fill requirements of a recyclable boron-based fuel for a large fleet of FCVs.

Assessment of world boron resources in terms of known borate minerals reserves involves analysis and reconciliation of publicly available information on borate reserves in various parts of the world. Analysis of key sources was used to estimate total borate resources projected out to 2050 adjusted for estimated boron demands from other competing industrial applications. This demand-adjusted assessment of boron resources was then compared with estimated requirements for boron materials needed for hydrogen storage over the period relevant to FCV deployment based on DOE scenarios [155].

The assessment of borate resources concludes that global borate ore reserves are sufficient for foreseen automotive hydrogen storage applications, and that sufficient borate reserves exist in the United States to satisfy the initial fill requirements of an AB fueled U.S. FVC fleet. In this analysis it is assumed that AB will be recycled to a large extent following initial fill of an automotive fleet. These conclusions are based on published data indicating that more than 1 billion B_2O_3 tonnes are
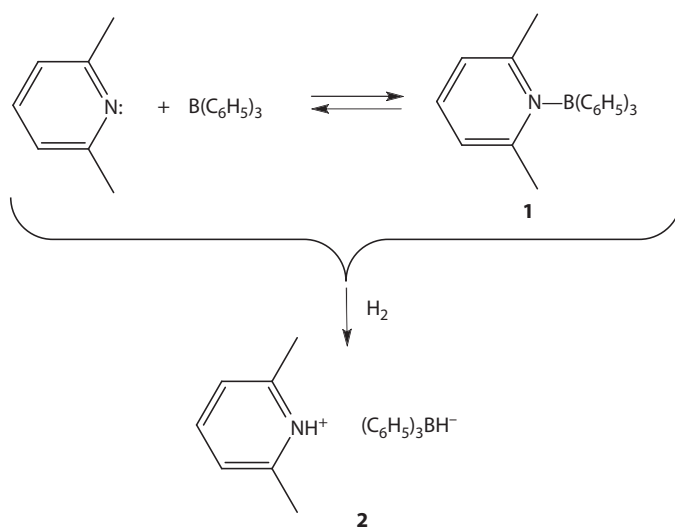
SCHEME 16.1   Hydrogen activation by frustrated Lewis pair.

available worldwide from known borate reserves, of which over 100 million B_2O_3 ton are located in the United States [156,157]. The cumulative boron requirement is estimated at 60 million B_2O_3 ton for a U.S. fleet of 360 million FCVs and 360 million B_2O_3 ton for a global fleet of 2 billion vehicles.

16.7 SUMMARY

Boron-based materials stand out among the many materials studied for hydrogen storage applications. Combining excellent hydrogen densities, release rates, and safety characteristics, a number of boron materials can hold substantially more releasable hydrogen by weight and volume than pure liquid hydrogen.

Hydrogen-on-demand technologies developed for commercially available sodium borohydride offer convenient and compact power for portable devices, underground mining vehicles, and backup power systems. Developing technologies based on other metal borohydrides, AB, and MABs have the potential to provide even higher power densities than the more developed sodium borohydride systems.

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