HYDRIDES

1. Introduction

Hydrogen is a versatile element that forms compounds with most of the other elements in the periodic table. Strictly speaking, a hydride is a compound in which hydrogen is present as a negative ion, H-. Only the most electropositive metals, the alkalis and alkaline earths, form the simple hydrides which conform to this strict ionic definition. The complex hydrides containing the borohydride and aluminohydride ions are also generally considered as hydrides. These two classes of hydrides are used primarily as reducing agents in the metals processing, pharmaceutical and other fine chemical industries.

The term hydride is also frequently applied to the hydrogen compounds with transition and rare-earth elements. These compounds, known as metallic hydrides, are of great interest because of their unique capability to store large quantities of hydrogen safely. Although not yet fully commercial, wide-spread use and applications in the transportation and utility industries are envisioned.

2. Simple Hydrides

2.1. Ionic Hydrides. The ionic or saline hydrides contain metal cations and negatively charged hydrogen ions. These crystallize in the cubic lattice similar to that of the corresponding metal halide, and when pure, are white solids. When dissolved in molten salts or hydroxides and electrolyzed, hydrogen gas is liberated at the anode. The densities are greater than those of the parent metal, and formation is exothermic. All are strong bases.

Alkali Metal Hydrides. Physical properties of the alkali metal hydrides are given in Table 1.

Lithium Hydride. Lithium hydride [7580-67-8], LiH, is very stable thermally and melts without decomposition. It is prepared by the addition of hydrogen,

$$2\mathrm{Li} + H_2 \rightarrow 2\mathrm{LiH} \tag{1}$$

to molten lithium at 680–900°C at about 100 kPa (ca 1 atm) of hydrogen pressure.

Lithium hydride reacts vigorously with silicates above 180°C. Therefore, glass, quartz, and porcelain containers cannot be used in preparative processes. That only traces dissolve in polar solvents such as ether reflects its significant (60–75%) covalent bond character. It is completely soluble in, and forms eutectic melting compositions with, a number of fused salts.

Normally, lithium hydride ignites in air only at high temperatures. When heated it reacts vigorously with CO_2 and nitrogen. With the former, lithium formate is obtained. Reaction at high temperature with nitrogen produces lithium nitride. Therefore, dry limestone or NaCl powders are used to extinguish LiH fires. Lithium hydride reacts exothermically with moist air and violently with water.

$$\mathrm{LiH} + \mathrm{H_2O} \longrightarrow \mathrm{LiOH} + \mathrm{H_2(g)} \qquad \Delta H_{298} = -132\ \mathrm{kJ/mol}\ (-31.5\ \mathrm{kcal/mol}) \tag{2}$$

Reaction with $AlCl_3$ gives lithium aluminum hydride, which is the main application of lithium hydride. Reaction with ammonia yields lithium amide (eq. 3).

$$\mathrm{LiH} + \mathrm{NH_3} \xrightarrow{430^\circ\mathrm{C}} \mathrm{LiNH_2} + \mathrm{H_2(g)} \tag{3}$$

Table 1. **Physical Properties of Alkali Metal Hydrides**

Hydride	CAS Registry number	Mp, °C	$\Delta H_{(298)}$, kJ/mol[a]	$\Delta F_{(298)}$, kJ/mol[a]	S, J/(mol·K)[a]	Lattice energy, kJ/mol[a]	Density, g/cm^3	Ref.
LiH	[7580-67-8]	688	−90.7	−70	25	916	0.77	1
NaH	[7646-69-7]	420 dec	−56.5	−37.7	48	791	1.36	2
KH	[7693-26-7]	dec	−57.9	−37.3	61	720	1.43	
RbH	[13446-75-8]	300 dec					2.60	
CsH	[13772-47-9]	dec					3.4	

[a] To convert J to cal, divide by 4.184.

An industrially important use of lithium and sodium hydride is in the generation of silane for semiconductor uses (see SILICON COMPOUNDS, SILANES; SEMICONDUCTORS, SILICON-BASED SEMICONDUCTORS). The exceptionally large amount of hydrogen available from the hydrolysis of lithium hydride (1 g LiH yields 2.82 L H_2) has led to use as an easily portable source of hydrogen for inflation of weather balloons and the like. However, calcium hydride is cheaper and therefore preferred. Lithium hydride is employed as a lightweight nuclear shielding material because of its high hydrogen content. Castings of up to 1 metric ton have been made (3).

In organic chemistry, LiH serves as a condensation agent. In the presence of trialkyl boranes very powerful reducing agents, $LiBHR_3$, which are soluble in THF, are obtained. These materials reduce aliphatic halides and in some cases highly stereospecific reductions can be accomplished.

Annual U.S. production is less than 100 t; the 1992 price was ca $72/kg. *Chemical Market Reporter* published a price of $29.15/lb ($64.13/kg) without variation between 1994 to 2000 for bulk quantities. Commercial producers include Chemetall, FMC (Lithium Corporation of America) and Rohm and Haas (Morton/Ventron).

Sodium Hydride. Sodium hydride [7646-69-7], NaH, decomposes to its elements without melting, starting at ca 300°C. Decomposition is rapid at 420°C. Sodium hydride is insoluble in organic solvents but soluble in fused salt mixtures and fused hydroxides such as NaOH. It oxidizes in dry air and hydrolyzes rapidly in moist air. The pure material reacts violently with water:

$$\mathrm{NaH} + \mathrm{H_2O} \longrightarrow \mathrm{NaOH} + \mathrm{H_2(g)} \qquad (4)$$

and with carbon dioxide under mild conditions to form sodium formate:

$$\mathrm{NaH} + \mathrm{CO_2} \longrightarrow \mathrm{HCOONa} \qquad (5)$$

Sodium hydride is manufactured by the reaction of hydrogen and molten sodium metal dispersed by vigorous agitation in mineral oil (4).

$$2\,\mathrm{Na} + \mathrm{H_2} \xrightarrow[1\ \mathrm{MPa}\ (10\ \mathrm{atm})]{250-265^\circ\mathrm{C}} 2\,\mathrm{NaH} \qquad (6)$$

A 25% dispersion of NaH crystals in oil is obtained. The commercial product, after filtration, is a 60% dispersion of NaH crystals (5–50 μm). The oil dispersions can be handled quite safely because the oil phase provides a barrier to air and moisture, whereas the unprotected crystals react vigorously. Traces of unreacted sodium metal give the product a gray color.

An important industrial use of NaH involves its *in situ* formation in molten-NaOH or in fused eutectic salt baths. At concentrations of 1–2% NaH, these compositions are powerful reducing systems for metal salts and oxides (5). They have been used industrially for descaling metals such as high alloy steels, titanium, zirconium, etc.

In organic synthesis, NaH acts as a powerful base without substantial reducing activity. Because it is insoluble in organic solvents, its reactions are heterogeneous. Hence finely divided, high surface area NaH in oil is the preferred reagent, unless the mineral oil interferes with the isolation of the product.

Table 2. **Physical Properties of Alkaline-Earth Metal Hydrides**

Hydride	CAS Registry number	$\Delta H_{(298)}$, kJ/mol[a]	$\Delta F_{(298)}$, kJ/mol[a]	S, J/(mol · K)[a]	Density, g/cm^3
CaH_2	[7789-78-8]	−186.3	−147.4	42	1.90
SrH_2	[13598-33-9]	−180.5	−138.6	54	3.27
BaH_2	[13477-09-3]	−171.2	−132.3	67	4.16

[a] To convert J to cal, divide by 4.184.

Sodium hydride has significant advantages over other bases such as sodium alcoholates, sodium amide, and metallic sodium. Sodium hydride is a stronger base and its high reactivity leads to clean reactions without byproduct formation and side reactions, usually at lower temperatures than are required with competitive bases. Reactions are easily monitored by measuring the hydrogen evolution which accompanies the reaction of NaH and organics. Important industrial inorganic reactions of NaH include addition reactions using Lewis acids and reductions of inorganic halides. Industrial organic reactions include alkylations and acylations (see ALKYLATION), reactions with acidic organic compounds (metallations), a wide variety (aldol, Claisen, Diekmann, Darzens, and Stobbe) of addition/condensation reactions, and polymerizations, especially of caprolactam (qv).

Annual U.S. noncaptive production of the 60% NaH in oil dispersion is less than 200 t; the 1992 price was ca $15/kg. *Chemical Market Reporter* published a price of $6.15/lb ($13.53/kg) without variation between 1994 to 2000 for 220 lb drum quantities. Commercial producers include Chemetall, Degussa and Rohm and Haas (Morton/Ventron).

Alkaline-Earth Metal Hydrides. Table 2 gives thermochemical data of alkaline-earth metal hydride.

Calcium Hydride. Calcium hydride [7789-78-8], CaH_2, dissociates into calcium and hydrogen at 990°C without melting. It is highly ionic and is insoluble in all common inert solvents. It can be handled in dry air at low temperatures without difficulty. When heated to about 500°C, it reacts with air to form both calcium oxide and nitride. Calcium hydride reacts vigorously with water in either liquid or vapor states at room temperature. The reaction with water provides 1.06 liters of hydrogen per gram CaH_2.

$$CaH_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + 2\,H_2(g) \qquad (7)$$

At elevated temperatures, CaH_2 reacts with halogens, sulfur, phosphorus, alcohols, and ammonia. At high temperatures, it reacts with refractory metal oxides and halides. Calcium hydride is substantially inert to organic compounds that do not contain acidic hydrogens.

Calcium hydride is prepared on a commercial scale by heating calcium metal to about 300°C in a high alloy steel, covered crucible under 101 kPa (1 atm) of hydrogen gas. Hydrogen is rapidly absorbed at this temperature and the reaction is exothermic.

The principal industrial applications for calcium hydride include (*1*) reduction at 600−1000°C of refractory oxides of metals such as titanium, zirconium, vanadium, niobium, uranium, thorium, chromium, and mixtures of these to

Table 3. **Properties of Covalent Hydrides**

Hydride	CAS Registry number	Formula	Mp, °C	Bp, °C	Density[a]	
					g/cm^3	g/L
beryllium hydride[b]	[13597-97-2]	BeH_2	125 dec	220[c]		
magnesium hydride	[7693-27-8]	MgH_2	280 dec		1.45	
aluminum hydride	[7784-21-6]	AlH_3				
silane[d]	[7803-62-5]	SiH_4	−185[e]	−119.9	0.68[f] (−185)	1.44[g] (20)
germane	[7782-65-2]	GeH_4	−165	−90	1.523[f] (−142)	3.43[g] (0)
stannane	[2406-52-2]	SnH_4	−150	52		
arsine	[7784-42-1]	AsH_3	−116.9[e]	−62	1.604[f] (64)	2.695[g]

[a] Temperature in °C is given in parentheses.

[b] $\Delta H_{298} = 19.3$ kJ/mol (4.6 kcal/mol).

[c] Begins to dissociate.

[d] $\Delta H_{298} = 30.55$ kJ/mol (7.30 kcal/mol).

[e] Freezing point.

[f] Liquid.

[g] Gas at atmospheric pressure.

produce metal and alloy powders (6); (*2*) use as a portable source of hydrogen. The military has used hydrogen generators based on the reaction of water and calcium hydride to inflate weather balloons for many years. A variety of generator sizes are available commercially; and (*3*) drying of liquids and gases (see DESICCANTS). Because of its low reactivity with most organic liquids and its high reactivity with water, calcium hydride is widely used as a superdrying agent of esters, ketones, halides, electrical insulator oils, silicones, solvents for Ziegler-Natta polymerization systems, monomers, and air and other gases. It is also used as an analytical reagent to determine water in organic liquids.

Annual U.S. production is less than 25 t; the 1992 price was ca $55/kg. *Chemical Market Reporter* published a price range of $10.50–13.25 per lb ($23.10–13.22/kg) without variation between 1994 to 1999 for 25–1000 lb-lots (11.3–453 kg lots). Commercial producers include Chemetall. It is available as a powder, granule, or irregular lumps.

2.2. Covalent Hydrides. In all hydrides, hydrogen is bound to an atom of lower electronegativity ($X_H = 2.1$) than itself. In covalent hydrides, the hydrogen–metal bond is effected through a common electron pair. Beryllium and magnesium hydrides are included in this group and are polymeric materials, as is aluminum hydride. The simple hydrides of silicon, germanium, tin, and arsenic are gaseous or easily volatile compounds. Table 3 gives some properties of these compounds.

Main Group Metal Hydrides. Beryllium Hydride. Beryllium hydride [13597-97-2] is an amorphous, colorless, highly toxic polymeric solid ($H = 18.3\%$) that is stable to water but hydrolyzed by acid (49). It is insoluble in organic solvents but reacts with tertiary amines at 160°C to form stable adducts, eg,$(R_3N \cdot BeH_2)_2$ (7). It is prepared by continuous thermal decomposition of a di-*t*-butylberyllium-ethyl ether complex in a boiling hydrocarbon (8).

$$\left[(CH_3)_3C\right]_2Be \cdot O(C_2H_5)_2 \longrightarrow BeH_2 + 2(CH_3)_2C{=}CH_2 + (C_2H_5)_2O \qquad (8)$$

Beryllium hydride was formerly of interest as a rocket fuel and as a moderator for nuclear reactors. Toxicity has been a serious barrier to its commercialization.

Magnesium Hydride. Magnesium hydride [7693-27-8], MgH_2, is a gray powder of about 97% purity which is insoluble in inert organic solvents. It is easily oxidized, and when heated to about 280°C, dissociates without melting. When prepared by direct reaction of the elements, magnesium hydride is stable in air and only mildly reactive with water.

$$\mathrm{Mg} + \mathrm{H_2} \xrightarrow[10-15\,\mathrm{MPa}\,(100-150\,\mathrm{atm})]{300-400^{\circ}\mathrm{C}} \mathrm{MgH_2} \tag{9}$$

However, when it is obtained by pyrolysis of diethylmagnesium or by reaction of diethylmagnesium and $LiAlH_4$ (9), it is very reactive with both air and water. This difference in reactivity mainly results from the much finer particle size of the product obtained by the pyrolysis route. This high reactivity allows reaction with 1-alkenes to form dialkyl magnesium compounds used in the production of Ziegler catalysts. Other uses for magnesium hydride include hydrogen storage and as a drying agent.

Aluminum Hydride. Aluminum hydride is a relatively unstable polymeric covalent hydride that received considerable attention in the mid-1960s because of its potential as a high energy additive to solid rocket propellants. The projected uses, including aluminum plating, never materialized, and in spite of intense research and development, commercial manufacture has not been undertaken. The synthetic methods developed were costly, eg,

$$3\,\mathrm{LiAlH_4} + \mathrm{AlCl_3} \xrightarrow{(\mathrm{C_2H_5})_2\mathrm{O}} 4\,\mathrm{AlH_3}\cdot x(\mathrm{C_2H_5})_2\mathrm{O} + 3\,\mathrm{LiCl} \tag{10}$$

Silane. Silane is a colorless gas that is spontaneously flammable in air and slowly decomposed by water; in the presence of aqueous alkali it is completely hydrolyzed to form hydrogen and silicates. It is manufactured on a commercial scale and sold as a compressed gas in cylinders. It is prepared by the reaction

$$4\,\mathrm{LiH} + \mathrm{SiCl_4} \longrightarrow \mathrm{SiH_4(g)} + 4\,\mathrm{LiCl} \tag{11}$$

Silane, pure or doped, is used to prepare semiconducting silicon by thermal decomposition at >600°C. Gaseous dopants such as germane, arsine, or diborane may be added to the silane at very low concentrations in the epitaxial growing of semiconducting silicon for the electronics industry. Higher silanes, eg, Si_2H_6 and Si_3H_8, are known but are less stable than SiH_4. These are analogues of lower saturated hydrocarbons.

Germane. Germane is a colorless gas, spontaneously flammable in air. It is manufactured in small amounts and is available as a compressed gas in cylinders.

$$\mathrm{GeCl_4} + 4\,\mathrm{NaBH_4} + 12\,\mathrm{H_2O} \longrightarrow \mathrm{GeH_4} + 4\,\mathrm{NaCl} + 4\,\mathrm{B(OH)_3} + 12\,\mathrm{H_2(g)} \tag{12}$$

Germane is used primarily to produce high purity germanium metal or epitaxial deposits of germanium on substrates for electronics by thermal decomposition at about 350°C (see GERMANIUM AND GERMANIUM COMPOUNDS).

Stannane. Stannane is a colorless poisonous gas that decomposes rapidly at room temperature. A large number of organostannanes, eg, R_3SnH and R_2SnH_2, are known, and their properties as organic reducing agents have been extensively investigated. Tributyltin hydride [688-73-3] is used frequently to dehalogenate organic compounds (10).

Arsine. Arsine is a highly toxic colorless gas, made in small amounts as a dopant for silicon in the electronics industry by the reaction

$$4\,H_3AsO_3 + 3BH_4^- + 3\,H^+ \longrightarrow 4\,AsH_3 + 3\,H_3BO_3 + 3\,H_2O \qquad (13)$$

Other Simple Hydrides. Potassium hydride is commercially available. It is a stronger base than NaH and is used to make the strong reducing agent $KBH(C_2H_5)_3$ and super bases RNHK and ROK. Strontium and barium hydrides resemble calcium hydride in properties and reactivity. They have no significant commercial applications.

3. Complex Hydrides

The complex hydrides are a large group of compounds in which hydrogen is combined in fixed proportions with two other constituents, generally metallic elements. These compounds have the general formula $M(M'H_4)_n$, where n is the valence of M, and M′ is a trivalent Group 3 (IIIA) element such as boron, aluminum, or gallium. In the BH_4^- and AlH_4^- anions, the hydrogen atoms are arranged tetrahedrally around the boron or aluminum and retain significant hydride or electron-rich character. For this reason, the complex hydrides have achieved significant and broad use as reducing agents in many different areas of chemistry. Lithium, sodium, and potassium borohydrides, lithium aluminum hydride, and sodium dihydrobis(2-methoxyethoxy)aluminate are commercially available, but many others are known, such as the corresponding alkaline-earth and other metal, as well as quaternary ammonium and phosphonium complex hydrides. Sodium borohydride in particular and lithium aluminum hydride are the most important commercially. In addition, compounds have been prepared in which from one to three hydrogen atoms have been replaced by other groups. The most important complex hydrides are listed in Table 4.

Although the IUPAC has recommended the names tetrahydroborate, tetrahydroaluminate, etc, this nomenclature is not yet in general use.

3.1. Borohydrides.

The alkali metal borohydrides are the most important complex hydrides. They are ionic, white, crystalline, high melting solids that are sensitive to moisture but not to oxygen. Group 3 (IIIA) and transition-metal borohydrides, on the other hand, are covalently bonded and are either liquids or sublimable solids. The alkaline-earth borohydrides are intermediate between these two extremes, and display some covalent character.

Modification of the BH_4^- anion has provided derivatives of widely differing reducing properties. Alkoxyborohydrides, such as sodium trimethyoxyborohydride [16940-17-3], $NaBH(OCH_3)_3$, exhibit enhanced reducing power but are less selective and more sensitive to decomposition by water. Sodium cyanoborohydride [25895-60-7], $NaBH_3CN$, on the other hand, shows weakened reducing

Table 4. **Complex Hydrides**

Formula	CAS Registry number	Density, g/cm^3	Mp, °C
$LiBH_4$	[16949-15-8]	0.66	278
$NaBH_4$	[16940-66-2]	1.074	505
KBH_4	[13762-51-1]	1.177	585
$Be(BH_4)_2$	[17440-85-6]	0.702	123 dec
$Mg(BH_4)_2$	[16903-37-0]		320 dec
$Ca(BH_4)_2$	[17068-95-0]		260 dec
$Zn(BH_4)_2$	[17611-70-0]		>50 dec
$Al(BH_4)_3$	[16962-07-5]	0.549	−64.5[a]
$Zr(BH_4)_4$	[23840-95-1]	1.13	28.7
$Th(BH_4)_4$	[33725-13-2]	2.59	204 dec
$U(BH_4)_4$	[33725-14-3]	2.67	100 dec
$(CH_3)_4NBH_4$	[16883-45-7]	0.84	>310
$(C_2H_5)_4NBH_4$	[17083-85-1]	0.926	225 dec
$(C_4H_9)_4NBH_4$	[33725-74-5]		>300
$(C_8H_{17})_3CH_3NBH_4$	[17083-38-4]	0.9	ca 30
$C_{16}H_{33}(CH_3)_3NBH_4$		0.9	ca 160
$NaBH_3CN$	[25895-60-7]	1.20	240 dec
$NaBH(OCH_3)_3$	[16940-17-3]	1.24	230 dec
$LiAlH_4$	[16853-85-3]	0.917	190 dec
$NaAlH_4$	[13770-96-2]	1.28	178
$Mg(AlH_4)_2$	[17300-62-8]		140 dec
$Ca(AlH_4)_2$	[16941-10-9]		
>230 dec			
$LiAlH(OCH_3)_3$	[12706-93-6]		
$LiAlH(OC_2H_5)_3$	[17250-30-5]		
$LiAlH(OC_4H_9)_3$	[38884-28-5]	1.03	>400
$NaAlH_2(OC_2H_4OCH_3)_2$	[22722-98-1]	1.122	205 dec
$NaAlH_2(C_2H_5)_2$	[17836-88-3]		85

[a] Bp, 44.5°C.

properties and is unique among the complex hydrides because it is stable in acidic aqueous solutions to a pH of about 3. Typical behavior of a number of borohydride derivatives toward organic functional groups are summarized in Table 5.

Unusual reducing properties can be obtained with borohydride derivatives formed*in situ*. A variety of reductions have been reported, including hydrogenolysis of carbonyls and alkylation of amines with sodium borohydride in carboxylic acids such as acetic and trifluoroacetic (11), in which the acyloxyborohydride is the reducing agent.

Sodium or tetramethylammonium triacetoxyborohydride has become the reagent of choice for diastereoselective reduction of β-hydroxyketones to anti-diols. Trialkylborohydrides, eg, alkali metal tri-*sec*-butylborohydrides, show outstanding stereoselectivity in ketone reductions (12).

Sodium Borohydride. Sodium borohydride [16940-66-2], $NaBH_4$, is a thermally stable, white crystalline solid that decomposes *in vacuo* above 400°C. The heat of formation is −192 kJ/mol (−45.9 kcal/mol). $NaBH_4$ is hygroscopic and absorbs water rapidly from moist air to form a dihydrate that decomposes slowly to sodium metaborate and hydrogen. It is soluble in many solvents including water, alcohols, liquid ammonia and amines, glycol ethers, and dimethyl sulfoxide.

Table 5. **Behavior of Various Functional Groups Toward Hydride Reagents**[a]

Hydride reagents	Aldehyde	Ketone	Acid chloride	Ester	Carboxylic acid	Carboxylic salt	Amide
$NaBH_4$	+	+	+	±[b]	−	−	−
$LiBH_4$	+	+	+	+	−	−	−
$Zn(BH_4)_2$	+	+	+	−			
$NaBH_4/AlCl_3$	+	+	+	+	+	−	+
$NaBH_3CN$	+[c]	+[c]		−			−
$NaBH_2S_3$	+	+	−	−			+
$LiBH(R)_3$	+	+	+	+			
$NaBH(OOCCH_3)_3$	+	±[d]					
$NaBH_3(OOCCH_3)$				−			+
$NaBH(OOCCF_3)_3$							
$NaBH_3(OOCCF_3)$				−			+
$NaBH(OR)_3$	+	+	+	+[f]			
$NaBH_3(OH)$		+		+			
$NaBH_3$ (anilide)	+	+	+	+			−
$NaBH_2$ (ethanedithiolate)							
$THF{\cdot}BH_3$	+	+	−	+[b]	+	−	+
$(3\text{-}CH_3\text{-}2\text{-}C_4H_9)_2BH$	+	+	−	−	−		
$(CF_3COO)_2BH$							
$LiAlH_4$	+	+	+	+	+	+	+
$LiAlH(OCH_3)_3$	+	+	+	+	+		
$LiAlH(O\text{-}t\text{-}C_4H_9)_3$	+	+	+[i]	−	−	−	−
$NaAlH_2(OC_2H_4^-OCH_{32})$	+	+	+	+	+	+	
AlH_3	+	+	+	+	+	+	+

[a] +, Reduction;−, no reduction;±, reduction of some, but not all members of this class.
[b] Moderate reaction over long time period.
[c] At pH 3–4.
[d] < 10% reduction in refluxing benzene.
[e] In enamines, quinolines, and indoles.
[f] At elevated temperature.
[g] Reaction in 1:1 ratio.
[h] Indole to indoline.
[i] Reverse addition yields aldehyde.

Sodium borohydride is manufactured from sodium hydride and trimethyl borate in a mineral oil medium at about 275°C (14),

$$4\,NaH + (CH_3O)_3B \longrightarrow NaBH_4 + 3\,NaOCH_3 \qquad (14)$$

The process is shown schematically in Figure 1 which also shows the conversion to potassium borohydride. Commercial $NaBH_4$ is 97 + % pure; yields are better than 90%. Other processes for manufacturing $NaBH_4$ have been described (15,16), but are not commercially important. Sodium borohydride and potassium borohydride [13762-51-1] are unique among the complex hydrides because they are stable in alkaline solution. Decomposition by hydrolysis is slow in water, but is accelerated by increasing acidity or temperature.

$$BH_4^- + 2\,H_2O \longrightarrow BO_2^- + 4\,H_2 \qquad (15)$$

The decomposition rate of $NaBH_4$ solutions in water is conveniently estimated from equation 11 which expresses half-life in terms of the two most

Table 5. (*Continued*)

Imide	Epoxide	Lactone	Carbinol	Imine	Nitrile	Nitro	Unsat. quat.	Halide	Tosylhydrazone	Olefin
−	±	±		+	−	−	+	−		−
	+	+			−	−		−		−
	−	−								−
	+	+			+	−				+
+				+	−	−	+	+	+	+
		+			+	+				−
	+	+								
							+		+	$+^{e}$
					+	−				
			+							$+^{e}$
					+	−				
					$+^{f}$					
					+	+				
					-	+				
+						+				
	+	+			+	−				+
		$+^{g}$			+	+				+
										$+^{h}$
+	+	+		+	+	+	+	+	+	−
		+			+					−
	−	−			−					−
	+	+			−			+		−
	+	+			+	−		−		−

important variables, pH and temperature when $t_{1/2}$ is in minutes and T is in K (50).

$$\log_{10} t_{1/2} = \text{pH} - (0.034T - 1.92) \tag{16}$$

Solutions of $NaBH_4$ in methanol, and to a lesser degree ethanol, are subject to a similar decomposition reaction that evolves hydrogen; these solutions can be stabilized by alkali. The solubility of $NaBH_4$ in lower aliphatic alcohols decreases as the carbon chain length increases, but the stability increases. Solutions in 2-propanol and *t*-butanol are stable without alkali (18,19).

Reactions. Complete hydrolysis of $NaBH_4$ produces 2.37 L hydrogen (STP) per gram of borohydride; similarly, addition of acid to a cold aqueous solution liberates the theoretical amount of hydrogen. Rapid, controlled complete generation of hydrogen can be accomplished by adding an acidic compound or an appropriate metal salt such as nickel or cobalt chloride. These salts are effective catalytic accelerators. In the absence of acid, the hydrogen evolution slows down after a short time owing to the increase in pH caused by the formation of the basic metaborate ion. Conversely, dissolving the borohydride in a basic solution prevents initial hydrolysis and permits the reagent to be used in an aqueous solution.

The inorganic reductions with $NaBH_4$ are numerous and varied (Table 6). Comparatively few anions are reduced, yet the reduction of bisulfite to dithionite (hydrosulfite) (20), which is used in thepulp (qv) andpaper (qv), clay and vat dyeing industries, is an important inorganic application of $NaBH_4$.

$$8\ HSO_3^- + BH_4^- \longrightarrow 4\ S_2O_4^{2-} + BO_2^- + 6\ H_2O \tag{17}$$

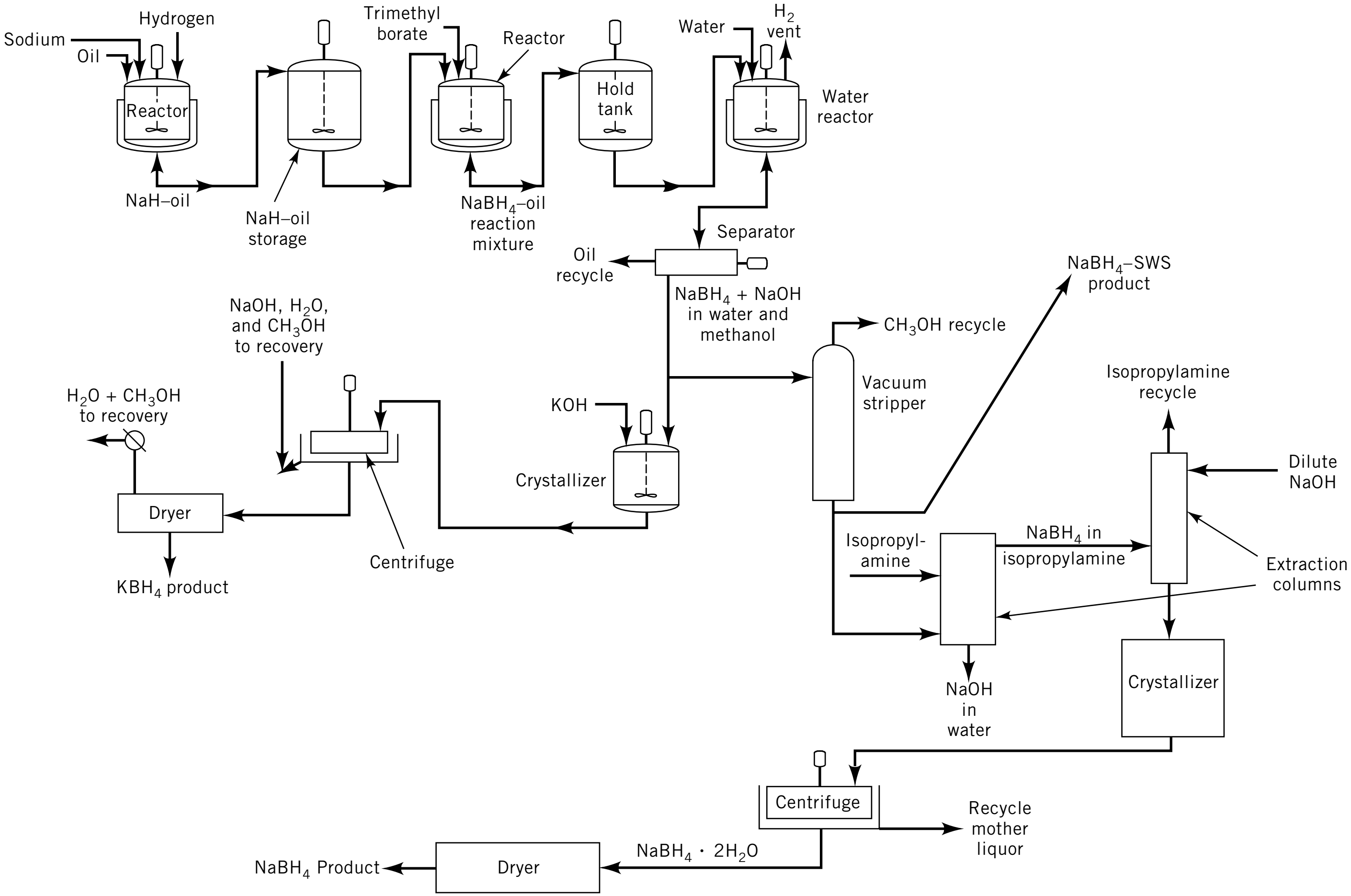


Fig. 1. Sodium and potassium borohydride production process.

Table 6. **Summary of Inorganic Reductions by Sodium Borohydride**[a]

1 (IA)	2 (IIA)	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8	9 (VIIIB)
H1+ ⟶0								
Li	Be							
Na	Mg							
K	Ca	Sc	Ti	V5+⟶4+5+⟶3+	Cr6+⟶3+3+⟶CrB_2	Mn7+⟶2+⟶4+⟶6+	Fe3+⟶2+	Co2+⟶Co_2B
Rb	Sr	Y	Zr	Nb	Mo6+⟶3+6+⟶5+	Tc	Ru3+⟶0	Rh3+⟶0
Cs	Ba	La-Lu	Hf	Ta	W6+⟶W Blue	Re	Os8+⟶0	Ir4+⟶0
Fr	Ra	Ac						

[a] Reducible by $NaBH_4$;reduction known to be quantitative.

Iodate, chlorate, and hypochlorite are reduced quantitatively; permanganate and perrhenate are also reduced. Cation reductions in aqueous solution occur by one of four possible paths: reduction to a stable and soluble lower valence state, eg, Ce (+4 to +3), V(+5 to +4 to +3), Fe(+3 to +2), Cr(+6 to +3); reduction to the free metal, eg, Ag, As, Sb, Bi, Pb, Hg, and the noble metals; precipitation of a metal boride, eg, Ni, Co, and Cu; or formation of a volatile hydride, eg, B, Ge, Sn, As, Sb, and Bi. The borides and noble metals have been used as hydrogenation catalysts and to generate hydrogen quantitatively from aqueous $NaBH_4$.

Sodium borohydride reacts with boron halides to form diborane [19287-45-7], B_2H_6, which is more conveniently handled as the monomer BH_3 complexed with an ether, sulfide, or amine (see BORON COMPOUNDS). Sodium borohydride is used extensively for the reduction of organic compounds. Its broad synthetic utility is based not only on its ability to reducealdehydes andketones selectively and efficiently in the presence of other functional groups, but also to reduce other functional groups, eg, esters, di- and polysulfides, imines and quaternary iminium compounds, under special conditions or with added catalysts or coreagents.

Storage and Handling. Sodium borohydride is classified as a flammable solid. It is available as powder, caplets, and granules and as a 12% solution in caustic soda. The dry powder, caplets, and granules should be stored and handled in the same manner as other flammable hygroscopic material. In dry air or in sealed containers they are stable indefinitely. Fire extinguishers should be of the dry chemical type; carbon dioxide or halocarbon extinguishers must not be used. Accepted storage and handling procedures for the 12% solution are the same as for 50% liquid caustic soda. $NaBH_4$ solutions may decompose with hydrogen evolution when heated, subjected to acid conditions, or in the presence of the metal salts or finely divided metallic precipitates of nickel, cobalt, copper, or iron. Under normal storage conditions, the 12% solution loses less than 0.1% $NaBH_4$ per year by decomposition. Storage and reaction vessels should be provided with adequate venting. $NaBH_4$ has been widely used in chemical processes for many years and is considered safe to handle and use, with normal industrial safety precautions.

Economic Aspects. Global annual consumption is ca 3000 t. Sodium borohydride is sold mainly as a powder or a stabilized caustic + water solution. Commercial quantities of powder sell for ca \$55/kg (1992 price); the 12% solution in caustic soda is priced at ca \$47/kg of contained $NaBH_4$. *Chemical Market Reporter* published a price of \$23.25/lb (\$51.15/kg) for the powder and \$19.10/lb (42.02/kg) for the solution without variation between 1994 to 2000 for bulk quantities. Commercial producers include Chemetall, Bayer and Rohm and Haas (Morton/Ventron).

Uses. The principal uses of $NaBH_4$ are in synthesis of pharmaceuticals and fine organic chemicals; removal of trace impurities from bulk organic chemicals; wood-pulp bleaching, clay leaching, and vat-dye reductions; and removal and recovery of trace metals from plant effluents.

In pharmaceutical applications, the selectivity of sodium borohydride is ideally suited for conversion of high value intermediates, such as steroids, in multistep syntheses. It is used in the manufacture of a broad spectrum of products such as analgesics, antiarthritics, antibiotics, prostaglandins, and central nervous system suppressants. Typical examples of commercial aldehyde reductions are found in the manufacture of vitamin A (21) (see VITAMINS) and dihydrostreptomycin (22). An acyl azide is reduced in the synthesis of the antibiotic chloramphenicol (23) and a carbon–carbon double bond is reduced in an intermediate in the manufacture of the analgesic Talwin (24).

A particularly useful reaction has been the selective 1,2-reduction of α, β-unsaturated carbonyl compounds to allylic alcohols, accomplished by $NaBH_4$ in the presence of lanthanide halides, especially cerium chloride. Initially applied to ketones (25), it has been broadened to aldehydes (26) and acid chlorides (27). $NaBH_4$ by itself gives mixtures of the saturated and unsaturated alcohols.

Sodium borohydride is used for the removal of trace impurities, such as carbonyls or peroxides, from bulk organic chemicals (alcohols or glycols). This is called process-stream purification, and greatly improves stability in products sensitive to deterioration and development of undesirable colors and odors in, for example, plasticizer alcohols. Sodium borohydride is used widely to generate sodium hydrosulfite (eq. 17) for reductive bleaching of mechanical pulps for manufacture of several grades of paper, especially newsprint. This technology is also being applied in clay leaching and in vat dye reductions. Sodium borohydride provides a simple, efficient means of removing dissolved trace metals from manufacturing-plant effluents, eg, by precipitating mercury from chloralkali plant effluents, lead from wastewater streams of tetraethyllead producers, and copper and other metals from printed circuit board manufacturing operations. This precipitation method allows recovery and recycle of valuable metals, such as silver, gold, and noble metals from spent photographic fixer solutions, film manufacturing effluents, and used x-ray and photographic films, plating solutions, etc. There is also extensive use of $NaBH_4$ in the analytical determination of metals which form volatile hydrides (As, Sb, Bi, Sn, Pb, etc).

Potassium borohydride. Potassium borohydride [13762-51-1], KBH_4, is used in lesser amounts as a selective reducing agent. *Chemical Market Reporter* published a price of $27.10–29.55/lb ($59.62–65.01/kg) for the powder in 100-1000 lb lots (45–453 kg lots).

Lithium Borohydride. Lithium borohydride [16949-15-8], $LiBH_4$, is made by metathesis between sodium borohydride and lithium chloride (28) in isopropylamine.

$$LiCl + NaBH_4 \longrightarrow LiBH_4 + NaCl \tag{18}$$

After the amine is removed, a single extraction with ethyl ether is sufficient to provide a 98% pure product in ca 75% yield. Lithium borohydride is a hygroscopic, white powder that decomposes slowly at its melting point, evolving hydrogen. The heat of formation is −190 kJ/mol (−45.4 kcal/mol).

Unlike many other borohydrides, lithium borohydride is highly soluble in ethers including aliphatic ethers, THF, and polyglycol ethers. It is also very soluble in amines and ammonia. Dissolution in water and lower aliphatic alcohols leads to extensive decomposition and hydrogen evolution.

Lithium borohydride contains 18.5% hydrogen by weight and, on complete hydrolysis, liberates 4.1 L (STP) hydrogen per gram.

$$LiBH_4 + 4\ H_2O \longrightarrow LiOH + H_3BO_3 + 4\ H_2 \tag{19}$$

Lithium borohydride is a more powerful reducing agent than sodium borohydride, but not as powerful as lithium aluminum hydride (Table 5). In contrast to sodium borohydride, the lithium salt, in general, reduces esters to the corresponding primary alcohol in refluxing ethers. An equimolar mixture of sodium or potassium borohydride and a lithium halide can also be used for this purpose (17,18).

Sodium Cyanoborohydride. Sodium cyanoborohydride [25895-60-7] $NaBH_3CN$, is a hygroscopic white solid that is remarkably stable, both thermally and hydrolytically. It is prepared by reaction of $NaBH_4$ and HCN in THF (29),

$$NaBH_4 + HCN \underset{THF}{\overrightarrow{}} NaBH_3CN + H_2 \qquad (20)$$

or by the reaction of borane and sodium cyanide in THF (30),

$$THF \cdot BH_3 + NaCN \longrightarrow NaBH_3CN + THF \qquad (21)$$

which avoids handling toxic, hazardous hydrogen cyanide. Sodium cyanoborohydride and its solutions in THF are very toxic and must be handled with great care. Ingestion and skin contact must be avoided.

Sodium cyanoborohydride is remarkably chemoselective. Reduction of aldehydes and ketones are, unlike those with $NaBH_4$, pH-dependent, and practical reduction rates are achieved at pH 3 to 4. At pH 5–7, imines ($>C{=}N{-}$) are reduced more rapidly than carbonyls. This reactivity permits reductive amination of aldehydes and ketones under very mild conditions (31).

$$R_2C{=}O + HNR'_2 \xrightarrow{H^+} R_2C{=}NR'_2 \xrightarrow{NaBH_3CN} R_2CHNR'_2 \qquad (22)$$

In addition, sodium cyanoborohydride reduces a wide variety of substrates (32) (see Table 5).

Sodium cyanoborohydride has become important in biochemical applications that require hydrolytic stability of the reducing agent and chemoselectivity, in sensitive molecules. It is also a preferred reagent for oxime reductions.

4. Aluminohydrides

Complex hydrides of aluminum have been known since the late 1940s, when lithium aluminum hydride was first made (13). In the ensuing decades, it was commercialized as a reducing agent in the synthesis of pharmaceuticals and other specialty organics. Sodium aluminum hydride [13770-96-2] (Table 4) was marketed in the 1960s and early 1970s, and has become available again in quantity in the 1990s, but as of this writing this less costly aluminohydride has not become widely used. A dialkoxy derivative of $NaAlH_4$, sodium dihydrobis(2-methoxyethoxy)aluminate [22722-98-1], $NaAlH_2(OC_2H_4OCH_3)_2$, is another aluminohydride which is commercially available. Other aluminohydrides have been prepared only on a laboratory scale.

In general, the aluminohydrides are more active and powerful reducing agents than the corresponding borohydrides. They decompose vigorously with water. Reaction also occurs with alcohols, although more moderately, providing a route to substituted derivatives.

Lithium Aluminum Hydride. Freshly prepared lithium aluminum hydride [16853-85-3] is a white crystalline solid that tends to become gray during storage, although very little loss in purity occurs. The solid hydride is stable in dry air at room temperature, but decomposes above 125°C. Its heat of formation is −117 kJ/mol(−28.0 kcal/mol).

$$2\ LiAlH_4 \longrightarrow 2\ LiH + 2\ Al + 3\ H_2 \qquad (23)$$

Lithium aluminum hydride is hygroscopic. In moist air it decomposes slowly, but it reacts vigorously with water. Because of this potential for simultaneous evolution of significant amounts of heat and hydrogen gas(2.36 L/g 2.36 at STP), careful storage and handling of $LiAlH_4$ are required. It is classified as a flammable solid. Complete protection from moisture, such as excessive humidity or condensate drip from cold water lines, is mandatory. Equipment in which the hydride is to be used must also be dry and purged with dry nitrogen, adequately vented, and fully grounded to eliminate static electricity hazards. Suitable explosion-resistant electrical services must also be provided.

$LiAlH_4$ is soluble in ethers, 35 – 40 g/100 g diethyl ether at 25°C. Solubility in THF, the other common solvent for $LiAlH_4$, is 13 g/100 g at 25°C. Polyethylene glycol dialkyl ethers are also good solvents.

Reactions. Although lithium aluminum hydride is best known as a nucleophilic reagent for organic reductions, it converts many metal halides to the corresponding hydride, eg, Ge, As, Sn, Sb, and Si (33).

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3 \qquad (24)$$

Organohalides of silicon can also be used to make organosilanes. Group 1 and 2 halides generally undergo metathesis, but the products are unstable, with few exceptions.

$$MX_n + n LiAlH_4 \longrightarrow M(AlH_4)_n + n LiX \qquad (25)$$

Aluminum hydride, formed from $AlCl_3$ (13), is a polymeric solid that is difficult to obtain completely free of the ether solvent used.

$$3\ LiAlH_4 + AlCl_3 \longrightarrow 4\ AlH_3 + 3\ LiCl \qquad (26)$$

Lithium aluminum hydride is a powerful reducing agent for organic functional groups, a property that has led to its extensive use especially in pharmaceutical synthesis. The voluminous literature describing its uses has resulted in several excellent reviews on the subject (see General References). Nearly all of the usual functional groups are reduced by $LiAlH_4$, olefinic bonds being the notable exception. These reductions are generally rapid and take place under mild conditions. Although isolated carbon−carbon multiple bonds are not reducible by $LiAlH_4$, reduction is possible when conjugation or suitable substituents are present.

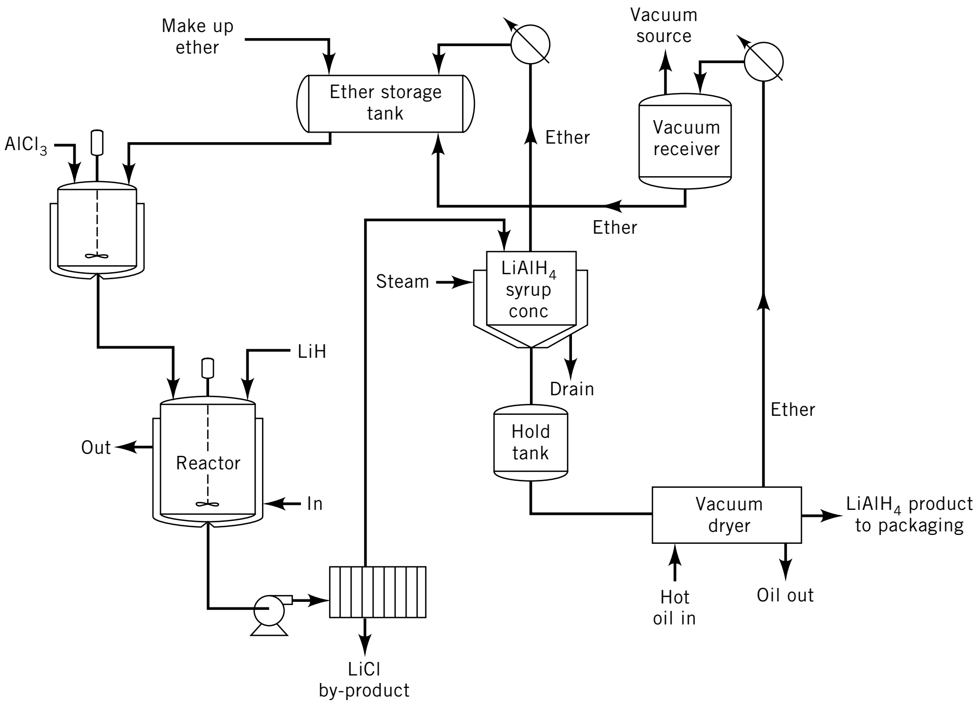


Fig. 2. Commercial manufacture of lithium aluminum hydride.

Preparation. Commercial manufacture of $LiAlH_4$ uses the original synthetic method (13), ie, addition of a diethyl ether solution of aluminum chloride to a slurry of lithium hydride (Fig.2).

$$4\,LiH + AlCl_3 \longrightarrow LiAlH_4 + 3\,LiCl \tag{27}$$

The stoichiometry (4 mol lithium hydride to 1 mol $LiAlH_4$) makes this an inherently expensive process, even though high yields of pure product are obtained. For large-scale production, metathesis from $NaAlH_4$ is economically preferred.

$$NaAlH_4 + LiCl \longrightarrow LiAlH_4 + NaCl \tag{28}$$

Sodium Aluminum Hydride. Sodium aluminum hydride can be prepared from NaH,

$$4\,NaH + AlCl_3 \longrightarrow NaAlH_4 + 3\,NaCl \tag{29}$$

but direct synthesis from the elements is more economical (34,35),

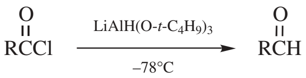
$$Na + Al + 2\,H_2 \xrightarrow[13.8\,MPa\,(138\,atm)]{150^\circ C} NaAlH_4 \tag{30}$$

The direct synthesis in an aromatic hydrocarbon medium is patented, using a triethylaluminum catalyst (36); in this case, crystallization of the product from a solvent is not needed.

The reactions of $NaAlH_4$ are the same as those of $LiAlH_4$. However, it is much less soluble; THF is the only good solvent. Heterogeneous reductions in good yield with $NaAlH_4$ in hydrocarbon media have been reported (37).

5. Aluminohydride Derivatives

The few known derivatives of the aluminohydrides are principally alkoxy substitutions, including the trimethoxy, $LiAlH(OCH_3)_3$, triethoxy, $LiAlH(OC_2H_5)_3$, and tri-*t*-butoxy aluminohydrides, $LiAlH(O\text{-}t\text{-}C_4H_9)_3$. The alkoxyaluminohydrides are milder reducing agents than $LiAlH_4$. Steric and electronic effects in lithium tri-*t*-butoxyaluminohydride [38884-28-5] make this compound very chemoselective, resembling $NaBH_4$ more closely than $LiAlH_4$ in this regard. A key reaction of $LiAlH(O\text{-}t\text{-}C_4H_9)_3$ is the partial reduction of acid chlorides to the aldehyde, rather than to the alcohol, which can be carried out in the presence of a variety of other functional groups (51).



$$R\overset{O}{\overset{\|}{C}}Cl \xrightarrow[-78^\circ C]{LiAlH(O\text{-}t\text{-}C_4H_9)_3} R\overset{O}{\overset{\|}{C}}H \qquad (31)$$

Sodium dihydrobis(2-methoxyethoxy)aluminate [22722-98-1], $NaAlH_2(OC_2H_4OCH_3)_2$, has the largest commercial use among the aluminohydride derivatives. The pure compound is a slightly yellow, glassy solid, soluble in ethers and aromatic hydrocarbons. It is supplied as a 70% solution in benzene or toluene. Like $LiAlH_4$, it reduces a wide range of organic compounds, including aldehydes, ketones, acid chlorides, carboxylic acids and anhydrides, esters, lactones and lactams, amides, oximes, nitriles, and nitro compounds (38). Both aliphatic and aromatic halides are dehalogenated by the reagent. Convenience in handling and solubility in aromatic hydrocarbons are the principal advantages of this compound.

6. Metallic Hydrides

A number of metal alloys are very useful for safely storing large volumes of hydrogen because these easily dissolve hydrogen at relatively low temperatures and pressures, forming interstitial hydrides. The hydrogen is subsequently released by applying heat and lowering the pressure. Many metals and binary and ternary alloys have been thoroughly studied for this application. Reference (39) contains an exhaustive compilation of alloys screened for hydrogen storage. An on-line version is available at http://hydpark. ca.sandia.gov.

The storage of hydrogen in the form of a metal hydride is described by the reversible reaction

$$M + x/2H_2 \longleftrightarrow MHx \qquad (32)$$

where the metal M can be an element, intermetallic compound, solid solution alloy, multiphase alloy, amorphous alloy, etc.

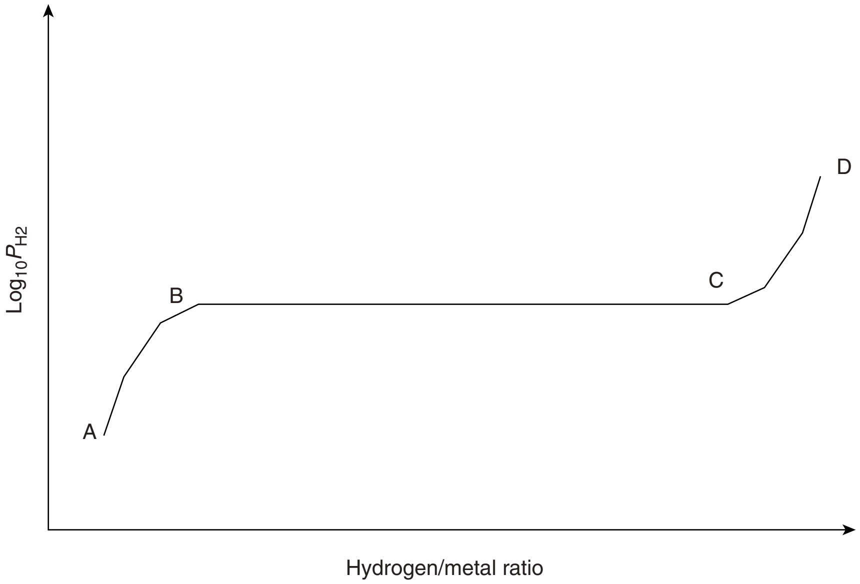


Fig. 3. Representative isotherm for metallic hydride used for hydrogen storage. See text for explanation of symbols.

Figure 3 is a representative isotherm which shows the relationship between the equilibrium pressure of hydrogen in the gas phase and the hydrogen/metal ratio in the solid at a given temperature. The metal initially takes up hydrogen by dissolving it, as represented by region AB on Figure 3. At point B hydride formation begins and the pressure remains constant. The plateau region, shown as the region BC in Figure 3, represents the reversible hydrogen storage capacity for the material at the isotherm temperature. Further increases in hydrogen pressure (region CD) lead to little additional capacity since the hydrogen is merely being dissolved in the completely hydrided solid.

The pressure-temperature relationship for the location of the dissociation plateau is often correlated using an equation of the form

$$\log_{10} P_{\mathrm{H2}} = -A/T + B \tag{33}$$

where A and B are constants for the particular compound.

The most important alloys appear to be

$$\mathrm{FeTi} \underset{-\mathrm{H_2}}{\overset{\mathrm{H_2}}{\longleftrightarrow}} \mathrm{FeTiH_{1-2}} \tag{34}$$

FeTi can also be modified with rare-earth metals, Ni, or Mn (40). AB_5 alloys where A is a rare-earth metal or mischmetal, Ca, or Th, and B is Co or Ni have also been used. $LaNi_5$ has shown special promise (41).

$$\mathrm{LaNi_5} \xrightarrow{\mathrm{H_2}} \mathrm{LaNi_5H_{6.7}} \tag{35}$$

Magnesium titanium alloys form the hydrides Mg_2TiH_6 [74811-18-0] and $MgTi_2H_6$ [58244-88-5] (42). Traces of a third metal are often added to adjust dissociation pressures and/or temperatures to convenient ranges.

Hydrogen-storage alloys (43,44) are commercially available from several companies in the United States, Japan, and Europe. A commercial use has been developed in rechargeable nickel–metal hydride batteries which are superior to nickel–cadmium batteries by virtue of improved capacity and elimination of the toxic metal cadmium (see BATTERIES, SECONDARY CELLS-ALKALINE). Other uses are expected to develop in nonpolluting internal combustion engines andfuel cells (qv), heat pumps and refrigerators, and electric utility peak-load shaving (45).

Transition-metal hydrides of titanium and zirconium have commercial use besides those related to hydrogen storage. The following paragraphs describe these two hydrides in more detail.

Titanium Hydride. Titanium hydride [7704-98-5], TiH_2, is a brittle, metallic-gray solid, density 3.8 g/cm^3, which produces 448 mL H_2 at STP per gram TiH_2. Titanium hydride powder is stable at room temperature and inert to water and most chemical reagents. At elevated temperatures TiH_2 is attacked by oxidizing agents and acids and by cold acid fluoride solutions. TiH_2 powder burns quietly when ignited but reacts violently when burned in the presence of oxidizers. Dissociation of TiH_2 begins at 300°C in vacuum and is nearly complete at 600°C at 1 mPa (7.5×10^{-3} μm Hg).

TiH_2 is prepared on an industrial scale by direct combination of hydrogen and the metal (sponge, ingot, scrap, etc) at 200–650°C, followed by cooling in an H_2 atmosphere. An alternative method is the reduction of the oxide using calcium hydride under hydrogen:

$$TiO_2 + 2\,CaH_2 \xrightarrow[H_2]{950-1000^\circ C} TiH_2 + 2\,CaO + H_2(g) \qquad (36)$$

The calcium oxide is leached out with acid (HCl), leaving a finely divided TiH_2 powder.

Titanium hydride is used as a source for Ti powder, alloys, and coatings; as a getter in vacuum systems and electronic tubes; as a sealer of metals; and as a hydrogen source.

Chemical Market Report published a price range from \$25.50–26.00/lb (\$56.10–57.20/kg) between 1994 to 1999 for the electronics grade material. More recent prices have jumped to \$66.00/lb (\$145.20/kg). Commercial producers include Chemetall.

Zirconium Hydride. Zirconium hydride [7704-99-6], ZrH_2, is a brittle, metallic-gray solid that is stable in air and water, and has a density of 5.6 g/cm^3. The chemical properties of ZrH_2 closely resemble those of titanium hydride. Thermal decomposition in vacuum (1 mPa (7.5×10^{-3} μmHg)) begins at 300°C and is nearly complete at 500–700°C. It is prepared in the same manner as TiH_2.

Commercial uses are as a getter in the manufacture of vacuum tubes and other systems; as a hydrogen source for foaming metals; as a hydrogen reservoir; for the introduction of zirconium into powdered alloys; for metal–ceramic and

Table 7. **Group 5 (VB) Hydrides**

Compound	CAS Registry number	Formula	Density, g/cm^3
vanadium hydride	[13761-67-6]	VH	5.4
niobium hydride	[13981-86-7]	NbH	6.6
niobium dihydride[a]	[13981-96-7]	NbH_2	
tantalum hydride	[13981-95-8]	TaH	15.1

[a] Decomposes slowly.

metal–metal bonding; as a moderator in nuclear reactors; and as a source of Zr metal powder and alloys. Several organometallic compounds containing a zirconium hydrogen bond are known. Both TiH_2 and ZrH_2 have moderate fibrogenic and toxic action when inhaled (47).

Rare-Earth Hydrides. Activated rare-earth metals react directly with hydrogen even at room temperature. These metals are activated by heating to 300°C in H_2, followed by cooling under H_2. Lanthanum dihydride [13823-36-4], and lathanum trihydride [13864-01-2] are both known compositions (see LANTHANIDES). Cerium hydride [13569-50-1], CeH_2, and hydrides of higher hydrogen content ($CeH_{<3}$) have been made and studied (see CERIUM AND CERIUM COMPOUNDS) (46). Both cerium and lanthanum hydrides are black pyrophoric solids. Hydrogen content can be varied with hydrogen pressure and temperature over the metal hydride. Cerium and lanthanum hydrides are very reactive chemically and ignite spontaneously in air. They react with N_2 at 20°C and with water at 0°C. The most important uses of cerium and lanthanum hydrides are in the hydrogen-storage alloys $LaNi_5$ and $CeMg_2$. There is some interest in these materials as hydrogenation catalysts. The other rare earth metals (praseodymium, samarium, europium, gadolinium, and yttrium) react with hydrogen to form hydrides of varying composition.

Group 5 (VB) Hydrides. These hydrides (Table 7) are formed from the metals, preferably by heating the metals in powder form in a hydrogen atmosphere up to 1000°C. Trace impurities (oxides, nitrides) in the metal prevent complete hydriding. The hydrides are brittle powders that can be handled in air. Heating to above 400°C initiates hydrogen evolution; complete hydrogen removal is usually obtained at 700°C under vacuum. Tantalum and niobium hydrides are superconductors at <10 K. These hydrides are manufactured in small amounts mainly for research and development work in powder metallurgy (see METALLURGY, POWDER METALLURGY).

7. Health and Safety Factors

Generalizations on the toxicity of hydrides as a class of compounds are difficult to make because of variations in their chemical reactivity. Furthermore, there is little published toxicological information available.

Qualitative insight can, however, be obtained by focusing on the reactions with water, the extent and vigor of which can vary widely. In general, however, hydrides react exothermically with water, resulting in the generation of hydrogen.

$$MH_n + nH_2O \longrightarrow M(OH)_n + nH_2 \qquad (37)$$

This hydrolysis reaction is accelerated by acids or heat and, in some instances, by catalysts. Because the flammable gas hydrogen is formed, a potential fire hazard may result unless adequate ventilation is provided. Ingestion of hydrides must be avoided because hydrolysis to form hydrogen could result in gas embolism.

Another aspect of the hydrolysis of hydrides is the alkalinity that results, especially from alkali metal and alkaline-earth hydrides. This alkalinity can cause chemical burns in skin and other tissues. Affected skin areas should be flooded with copious amounts of water.

The importance of hydrolysis potential, ie, whether moisture or water is present, is illustrated by the following example. In the normal dermal toxicity test, namely dry product on dry animal skin, sodium borohydride was found to be nontoxic under the classification of the Federal Hazardous Substances Act. Furthermore, it was not a skin sensitizer. But on moist skin, severe irritation and burns resulted.

Hydrolysis considerations obviously demand that hydrides be kept away from contact with acids.

Although there is little toxicity information published on hydrides, a threshold limit value (TLV) for lithium hydride in air of 25 μg/m^3 has been established (48). More extensive data are available for sodium borohydride in the powder and solution forms. The acute oral LD_{50} of $NaBH_4$ is 50 – 100 mg/kg for $NaBH_4$ and 50 – 1000 mg/kg for the solution. The acute dermal LD_{50} (on dry skin) is 4 – 8 g/kg for $NaBH_4$ and 100 – 500 mg/kg for the solution. The reaction or decomposition by-product sodium metaborate is slightly toxic orally (LD_{50} is 2000 – 4000 mg/kg) and nontoxic dermally.

BIBLIOGRAPHY

"Hydrides" in *ECT* 1st ed., Vol. 7, pp. 595–598, by C. R. Hough, Polytechnic Institute of Brooklyn; in *ECT* 2nd ed., Vol. 11, pp. 200–224, by A. A. Hinckley, Ventron Corp.; in *ECT* 2nd ed., Suppl., pp. 499–509, by E. A. Sullivan, Ventron Corp.; in *ECT* 3rd ed., Vol. 12, pp. 772–792, by E. A. Sullivan and R. C. Wade, Thiokol/Ventron Div.; "Hydrides" in *ECT* 4th ed., Vol. 13, pp. 606–629, by E. A. Sullivan, Morton International; "Hydrides" in *ECT* (online), Posting date: December 4, 2000, by Tim Eggeman, Neoterics International.

CITED PUBLICATIONS

1. C. E. Messer, *A Survey Report on Lithium Hydride,* Tufts University, Medford, Mass., 1960.
2. J. Plesek and S. Hermanek, *Sodium Hydride: Its Use in the Laboratory and in Technology*, trans. by G. Jones, Academic, Prague, 1968.
3. F. H. Welch, *Nucl. Eng. Des.* **26**, 444 (1974).

4. M. D. Banus and A. A. Hinckley, *Adv. Chem. Ser.* **19**, 106 (1957).
5. H. L. Alexander, *Iron Steel Eng.* **24**(5), 44 (1947); M. Sittig, *Iron Age* **172**(25), 137 (1953); U.S. Pat. 3,721,626 (Mar. 20, 1973), V. Lhoty and J. Mostecky (to Valcovny Plechu, Narodni Podnik); Jpn. Pat. Appl. 83 84,984 (May 21, 1983) (to Mitsubishi Heavy Industries, Ltd).
6. Jpn. Pat. Appl. 87,262,407 (Nov. 14, 1987), K. Uchida and M. Tokunaga (to Hitachi Metals, Ltd.); Jpn. Pat. Appl. 89,110,705 (Apr. 27, 1989), H. Shibusawa (to Hitachi Metals, Ltd.).
7. L. H. Shepherd, G. L. Ter Haar, and E. M. Martlett, *Inorg. Chem.* **8**, 976 (1969); U.S. Pat. 3,577,414 (May 4, 1971), L. H. Shepherd (to Ethyl Corp.); U.S. Pat. 3,806,520 (Apr. 23, 1974), G. Ter Haar (to Ethyl Corp.).
8. U.S. Pat. 3,816,608 (June 11, 1974), R. W. Baker, C. R. Bergeron, and A. Nugent (to Ethyl Corp.); U.S. Pats. 3,830,906 (Aug. 20, 1974) and 3,832,456 (Aug. 27, 1974), R. J. Larans, P. Kobetz, and R. W. Johnson (to Ethyl Corp.); U.S. Pat. 3,883,645 (May 13, 1975), C. R. Bergeron and R. W. Baker (to Ethyl Corp.).
9. E. C. Ashby and R. G. Beach, *Inorg. Chem.* **9**, 2300 (1970).
10. J. T. Groves and S. Kittisopikul, *Tetrahedron Lett.*, 4291 (1977); B. A. San Miguel, B. Maillard, and B. Delmond, *Tetrahedron Lett.* **28**, 2127 (1987); H. Oelschlager and co-workers, *Sci. Pharm.* **57**, 367 (1989).
11. G. W. Gribble and co-workers, *J. Am. Chem. Soc.* **96**, 7812 (1974); M. Soucek, J. Urban, and D. Saman, *Collect. Czech. Chem. Commun.* **55**, 761 (1990); A. F. Abdel-Magid, C. A. Maryannoff, and K. G. Carson, *Tetrahedron Lett.* **31**, 5595 (1990); G. W. Gribble and C. F. Nutaitis, *Org. Prep. Proced. Int.* **17**, 317 (1985); C. F. Nutaitis, *J. Chem. Ed.* **66**, 673 (1978); C. K. McClure and K-Y. Jung, *J. Org. Chem.* **56**, 2326 (1991); D. A. Evans and W. C. Black, *J. Am. Chem. Soc.* **114**, 2260 (1992).
12. H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.* **94**, 7159 (1972); H. C. Brown, S. C. Kim, and S. Krishnamurthy, *J. Org. Chem.* **45**, 1 (1980).
13. A. E. Finholt, A. C. Bond and H. I. Schlesinger, *J. Am. Chem. Soc.* **69**, 1199 (1947).
14. H. I. Schlesinger, H. C. Brown, and A. E. Finholt, *J. Am. Chem. Soc.* **75**, 205 (1953).
15. T. P. Forbath, *Chem. Eng.* **68**, 92 (June 12, 1961).
16. U.S. Pat. 3,515,522 (June 2, 1970), V. Pecak, J. Vit, and V. Prochazka (to Czechoslovakia Academy of Sciences); Jpn. Pat. Appl. 90,217,304 (Aug. 30, 1990), T. Iwao and and co-workers (to Mitsui Toatsu Chemicals, Inc.); Jpn. Pat. Appl. 91,275,502 (Dec. 6, 1991), T. Iwao and co-workers (to Nippon Aluminum Alkyls, Ltd.).
17. R. Paul and N. Joseph, *Bull. Soc. Chim. Fr.* **19**, 550 (1952).
18. H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.* **77**, 6209 (1955). H. C. Brown, S. Narasimhan, and Y. M. Choi, *J. Org. Chem.* **47**, 4702 (1982); K. Higashiura and K. Ienaga, *J. Org. Chem.* **57**, 764 (1992).
19. H. C. Brown and K. Ichekawa, *J. Am. Chem. Soc.* **83**, 4372 (1961).
20. G. S. Panson and C. E. Weill, *J. Inorg. Nucl. Chem.* **15**, 184 (1960).
21. Brit. Pat. 778,753 (July 10, 1957), O. D. Hawks (to Eastman Kodak Co.).
22. U.S. Pat. 2,790,792 (Apr. 30, 1957), M. A. Kaplan (to Bristol Labs, Inc.); U.S. Pat. 3,397,197 (Aug. 13, 1968), E. H. Makepeace (to Charls. Pfizer and Co., Inc.).
23. G. Ehrhart, W. Siedel, and H. Nahm, *Chem. Ber.* **90**, 2088 (1957).
24. U.S. Pat. 3,250,678 (May 10, 1966), S. Archer (to Sterling Drug Inc.).
25. J. L. Luche, *J. Am. Chem. Soc.* **100**, 2226 (1978); A. L. Gemal and J. L. Luche, *J. Am. Chem. Soc.* **103**, 5459 (1981); A. S. Lee, A. W. Norman, and W. H. Okamura, *J. Org. Chem.* **57**, 3846 (1992); L. A. Sandareses and J. L. Luche, *J. Org. Chem.* **57**, 2757 (1992).
26. J. D. White and co-workers, *J. Org. Chem.* **57**, 2270 (1992); C. J. Moody and co-workers, *J. Org. Chem.* **57**, 2105 (1992); G. Mehta, N. Krishnamurthy, and S. P. Karra, *J. Am. Chem. Soc.* **113**, 5765 (1991).

27. K. V. Lakshmy and co-workers, *Org. Prep. Proced. Int.* **17**, 251 (1985).
28. H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.* **75**, 186 (1953).
29. R. C. Wade and co-workers, *Inorg. Chem.* **9**, 2146 (1970).
30. U.S. Pat. 4,301,129 (Nov. 17, 1981), R. C. Wade and B. C. Hui (to Thiokol Corp.).
31. R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Am. Chem. Soc.* **93**, 2897 (1971).
32. R. O. Hutchins and N. R. Natale, *Org. Prep. Proced. Int.* **11**, 201 (1979).
33. A. E. Finholt and co-workers, *J. Am. Chem. Soc.* **69**, 2692 (1947).
34. E. C. Ashby, G. J. Brendel, and H. E. Redman, *Inorg. Chem.* **2**, 499 (1963).
35. U.S. Pat. 3,556,740 (Jan. 19, 1971), J. H. Murib (to National Distillers and Chemicals Corp.).
36. U.S. Pat. 4,045,545 (Aug. 30, 1977), E. C. Ashby (to Ethyl Corp.).
37. L. I. Zakharkin, D. N. Maslin, and V. V. Gavrilenko, *Izv. Akad. Nauk SSSR Ser. Khim.*, 561 (1964).
38. V. Bazant and co-workers, *Tetrahedron Lett.*, 3303 (1968).
39. G. Sandrock and G. Thomas, *Compilation of IEA/DOE/SNL Hydride Databases*, IEA Technical Report IEA/H2/A12-97, Sept. 1997.
40. J. J. Reilly and J. R. Johnson, *Report 1976, BNL-22062;* J. J. Reilly, *Report 1977, BNL-23047,* Brookhaven National Laboratory, Upton, NY.
41. J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Rep.* **25**, 133 (1970).
42. Jpn. Pat. 75,116,308 (Sept. 11, 1975), M. Kitada (to Hitachi Ltd.).
43. "Hydrogen Energy," *Proceedings of Hydrogen Economy, Miami Energy Conference, 1974*, Plenum Press, New York, 1975.
44. D. M. Cavagnaro, *Hydrogen Storage, Pt. 2: Hydrogen as a Hydride*, NTIS, Springfield, Va., 1978. a bibliography with abstracts.
45. M. V. C. Sastri, B. Viswanathan, S. Srinivasa Murthy (ed.), *Metal Hydrides: Fundamentals and Applications*, Springer-Verlag/Narosa, New York, 1998.
46. A. C. Switendick, in R. Bau, *Adv. Chem. Ser.* **167**, 265 (1978).
47. G. A. Shkurko, *Gig. Tr.* **9**, 74 (1973).
48. E. J. Fairchild, ed., *Registry of Toxic Effects of Chemical Substances*, U.S. Dept. of Health, Education and Welfare, Washington, D.C., 1977.
49. G. E. Coats and F. Glocking, *J. Chem. Soc.*, 2526 (1954).
50. K. N. Mochalor, V. S. Khain, and G. G. Gilmanshin, *Kinet. Katal.* **6**, 541 (1965).
51. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.* **80**, 5377 (1958).

GENERAL REFERENCES

T. E. Dergazarian and co-workers, *JANAF Thermochemical Data*, Dow Chemical Co., Midland, Mich., 1961. Thermochemical data from these tables were used whenever possible.

R. Bau, "Transition Metal Hydrides," *Advances in Chemistry Series*, Vol. **167**, American Chemical Society, Washington, D.C., 1978.

G. D. James, *Rec. Chem. Prog.* **31**, 199 (1970). Inorganic chemistry of complex hydrides.

E. R. H. Walker, *Chem. Soc. Rev.* **5**, 23 (1976). Functional group selectivity of complex hydrides.

A. P. Scanzillo, *Encyclopedia Industrial Chemical Analysis*, Vol. **2**, John Wiley & Sons, Inc., New York, 1971 242–260. Analysis of hydrides.

R. M. Adams and A. R. Siedle, *Boron, Metallo-Boron Compounds and Boranes*, Wiley-Interscience, New York, 1964, "Chapt. 6", 373–506. Borohydrides.

W. M. Mueller, J. P. Blackledge, and G. G. Libovitz, *Metal Hydrides*, Academic Press, Inc., New York, 1968, especially “Chapt. 12”, 546–674.

B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, Vol. **11**, Wiley-Interscience, New York, 1970, 99–231. Borohydrides.

J. S. Pizey, *Synthetic Reagents*, Vol. **1**, Ellis Harwood, Ltd., Chichester, U.K., 1974, “Chapt. 2”, 101–294. Lithium aluminum hydride.

E. C. Ashby, *Adv. Inorg. Chem. Radiochem.* **8**, 283 (1966). Aluminohydrides.

N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, New York, 1956.

M. Hudlicky, *Reductions in Organic Chemistry*, Halstead Press (div. of John Wiley & Sons, Inc.), New York, 1984.

A. Pelter, K. Smith, and H. C. Brown, *Borane Reagents*, Academic Press, Inc., London, 1988.

A. Hajos, *Complex Hydrides*, Elsevier/North-Holland, Inc., New York, 1979.

D. T. Hurd, *An Introduction to the Chemistry of the Hydrides*, John Wiley & Sons, New York, 1952.

G. G. Libowitz, *The Solid-State Chemistry of Binary Metal Hydrides*, W. A. Benjamin, Inc., New York, 1965.

W. N. Lipscomb, *Boron Hydrides*, W. A. Benjamin, Inc., New York, 1963.

E. L. Muetterties, ed., *Boron Hydride Chemistry*, Academic Press, New York, 1975.

Sodium Borohydride Digest, 3rd ed., Morton International, 1995.

Chemical Market Reporter, Schnell Publishing, a weekly periodical with prices for chemicals.

TIM EGGEMAN
Neoterics International